PHYSICAL REVIEW VOLUME 103, NUMBER 3 AUGUST 1, 1956

Redetermination of the Hyperfine Splitting in the Ground State of Atomic Hydrogen*

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(Received April 19, 1956)

A redetermination has been made of the zero-field hyperfine splitting of the ground state of atomic hydrogen. A microwave absorption technique was used employing a resonance line with a width of about 3 kc/sec. This width (occasionally as narrow as $\frac{1}{10}$ of the normal Doppler breadth) was obtained through the mechanism of collision reduction of the Doppler effect. The primary relaxation mechanism was electron exchange between hydrogen atoms. The measured result for the hyperfine splitting is $\Delta\nu = 1420.40580 \pm 0.00006$ Mc/sec.

INTRODUCTION

THE hyperfine splitting (hfs) in the ground state of atomic hydrogen has been determined using a microwave absorption technique. The measurement of the hfs in hydrogen is important in that, in conjunction with other experiments,[1] it provides an experimental measure of proton structure and recoil effects in the hydrogen atom.[2] At present these are not amenable to accurate calculation.

As the frequency of a microwave transition can be reliably determined only to the order of a few thousandths of the observed frequency width of the transition, it is of prime importance to reduce this width as far as is experimentally feasible. Other recent measurements[3,4] of the hfs have been made with an atomic beam technique, where transit-time effects prevented resonances narrower than 20 kc/sec. from being observed. By means of a special technique[5] to eliminate Doppler broadening effects without introducing collision broadening, resonances under 2 kc/sec in width were observed in the present experiment.

The work to be reported was previously summarized in a Letter to the Editor.[6]

CAUSES OF LINE BREADTH

The importance of a narrow spectroscopic line has already been emphasized. It is proposed to discuss here the various factors affecting the line breadth. Although the traditional classification of line broadening as natural, Doppler, collision, field, or saturation broadening is incomplete and otherwise imperfect, it does constitute a useful classification and the various effects encountered will be discussed in this order.

Natural Line Breadth

An atom or molecule has a remarkably long radiation lifetime at microwave frequencies when isolated in free space. For the hydrogen hyperfine transition under discussion this lifetime is about 10^7 years. This could be ignored completely as a cause of line breadth if it were not for two factors which greatly increase the radiation rate of the gas. First, the atoms are not in free space but in an enclosure, the cavity, which causes the atom to couple more strongly to the radiation field at the resonance frequency. This increases the radiation rate by a factor of about 80 in the present experiment. Of much greater importance is the effect of coherence.[7,8] The gaseous atoms are excited coherently by the electromagnetic field, and their reradiation is coherent. This decreases the radiation lifetime by a factor equal to the difference in the numbers of atoms in the two energy levels in question at thermal equilibrium. This population difference can be taken to be about 2×10^{11}, giving a radiation lifetime of 20 sec. Compared to other effects to be discussed later, this is still negligible.

Doppler Breadth

A normal Doppler effect[9] is obtained only for a freely moving atom continuously exposed to the radiation field. In this case the Doppler effect has a simple explanation in terms of the conservation of momentum[9] at the time of emission or absorption of radiation and the line breadth is simply given by the Maxwellian distribution of velocities. It has been shown[5] that this is no longer the case when the gas atoms suffer collisions, either with container walls[10,11] or with other gas molecules. In fact, for a gas confined to a vessel having all dimensions sufficiently small compared with a radiation wavelength so that the microwave field strength is substantially constant over the container, there is negligible Doppler effect of any kind. The Doppler effect is then usually replaced

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* This research was supported by the Signal Corps of the Army.

† This work is the basis for a Ph.D. dissertation accepted by Princeton University. Now associated with R.C.A. Laboratories, Princeton, New Jersey.

[1] E.g., Dayhoff, Triebwasser, and Lamb, Phys. Rev. **89**, 106 (1953).

[2] Moellering, Zemach, Klein, and Low, Phys. Rev. **100**, 441 (1955).

[3] A. G. Prodell and P. Kusch, Phys. Rev. **88**, 184 (1952).

[4] P. Kusch, Phys. Rev. **100**, 1188 (1955).

[5] R. H. Dicke, Phys. Rev. **89**, 472 (1953).

[6] J. P. Wittke and R. H. Dicke, Phys. Rev. **96**, 530 (1954).

[7] R. H. Dicke, Phys. Rev. **93**, 99 (1954).

[8] N. Bloembergen and R. V. Pound, Phys. Rev. **95**, 8 (1954).

[9] E. Fermi, Revs. Modern Phys. **4**, 87 (1932).

[10] R. H. Johnson and M. W. P. Strandberg, Phys. Rev. **86**, 811 (1952).

[11] R. H. Romer and R. H. Dicke, Phys. Rev. **99**, 532 (1955).

by a line broadening resulting from collision damping produced by wall collisions.

In the present experiment the gas container is fairly large but the atomic hydrogen is present in a buffer atmosphere of molecular hydrogen. The collisions with the molecular hydrogen greatly modify the Doppler effect, changing the line contour from Gaussian to essentially Lorentz shape and reducing the line width at half-maximum to the value[5]

$$\Delta\nu = 2.8(L/\lambda)\times\text{normal Doppler width.}^{12}$$

Here L is the kinetic mean free path of the hydrogen atoms in the gas. For the molecular hydrogen pressures (0.1 mm Hg) employed in this experiment, the calculated collision quenched Doppler breadth is 200 sec^{-1} as compared with a normal Doppler width of 17400 sec^{-1}. The observed line breadths of about 3 kc/sec indicate that the Doppler effect is negligible and that the breadth is caused by other effects.

Collision Effects

The spectroscopic line may be broadened by several different gas collision effects. In a collision between a hydrogen atom and a hydrogen molecule, a disturbance of the hyperfine spin state results from magnetic interaction between the electron moment of the atom and magnetic fields produced by the molecule. The sources of these fields are the proton magnetic dipole moments of the molecular protons, the rotational moment of the molecule, and motional magnetic fields resulting from motion through the molecular electric fields. These three effects produce magnetic field strengths at the atom of roughly the same value ($\sim$200 gauss at distance of closest approach). The resulting energy level transition probability per collision is about 10^{-9} and leads to a relaxation time at 0.1-mm pressure of the order of 600 seconds. A detailed calculation has not been carried out as these effects are negligible compared with the electron exchange effect to be discussed in detail.

In a collision between two hydrogen atoms there are two new effects which appear. First because both atoms have unpaired electrons there is a dipole-dipole interaction between the two electrons leading to a transition probability per collision of about 10^{-4}. This, though large, is negligible compared with the second effect, that of electron exchange.

Electron Exchange Effects[13]

If two hydrogen atoms with oppositely directed electron spins pass each other with a closest distance of approach of less than about 3.8×10^{-8} cm, there is a probability of $\frac{1}{2}$ that the two electrons interchange spin coordinates. The physical reason for this interchange is to be found in the same mechanism that produces the "exchange forces" that hold the hydrogen molecule together. As the two atoms come together the splitting of the energy levels, symmetric and antisymmetric under interchange of electron space coordinates, leads to this spin interchange. The result is equivalent for antiparallel electron spins to a spin inversion for each of the electrons and leads to the relaxation effects to be discussed.

In a discussion of the electron relaxation mechanism, it is necessary to make a distinction between effects which tend to restore equilibrium population balance between the various hyperfine states and effects which tend to reduce an oscillating dipole moment of the gas to zero. The latter effect is the only one affecting the line width and shape but the first effect is also of great importance for the question of signal strength.

In a treatment of the electron exchange effect, it is convenient to divide the problem into two parts. First to be discussed is a calculation of the cross section for electron exchange; second, the effect of the electron spin exchange on the atomic hyperfine spin state must be discussed.

The two hydrogen atoms taking part in a collision are assumed to both be initially in definite hyperfine spin states. The wave function must be made antisymmetric with respect to electron exchange, but for simplicity the proton coordinates are left unsymmetrized. The effect on the results of thus regarding the protons as distinguishable will be discussed later. The usual adiabatic approximation which treats the two centers of mass as particles interacting under the influence of the molecular force field is used. Because of the electron exchange effect this interaction potential is different for electron-spin symmetric and antisymmetric states. The original atomic spin states are in general neither electron-spin-exchange symmetric nor antisymmetric. In a partial wave treatment of the scattering problem, the two outgoing waves (electron spin symmetric and antisymmetric) of a given l differ in phase because of the difference in scattering potential. A phase shift difference of π results in an exchange of the two electron spin coordinates. The electron exchange probability is proportional to $\sin^2$ of $\frac{1}{2}$ of this phase difference. A sufficiently large phase shift that varies rapidly as a function of the energy of the relative motion of the atoms can be treated as random, giving a probability of $\frac{1}{2}$ that an electron is left on its original proton.

For partial waves of large l, the centrifugal force barrier keeps the two atoms sufficiently far apart that the short range exchange forces are without effect. For a critical value of the orbital quantum number l, ($l\sim11$, center-of-mass coordinate system, for thermal energy) the centrifugal repulsive barrier is reduced to

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[12] This result is derived in Appendix I.

[13] The importance of the electron exchange effect seems to have been first indicated by N. F. Ramsey and V. Weisskopf. Some of the work in this section was carried out in collaboration with E. M. Purcell of Harvard University who contributed several of the basic ideas.

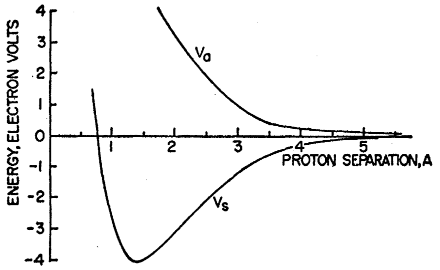

FIG. 1. Energy levels of (space-) symmetric and antisymmetric S states of two hydrogen atoms as a function of proton separation.

such a low height by the short range molecular binding forces that the barrier is no longer sufficiently high to reflect atoms of thermal kinetic energy in the electronic spin singlet state. The exchange forces in the electronic triplet state always are repulsive (see Fig. 1). Thus for partial waves with $l \leqslant l_{\mathrm{crit}}$, atoms in electron-spin singlet states are pulled together for a close encounter, whereas the triplet spin collisions continue to occur at large distance. This results in a large and essentially random difference in the phases of the outgoing waves of same l. Because of the random phase shift for $l \leqslant l_{\mathrm{crit}}$, the cross section for electron exchange is $\frac{1}{2}$ of the maximum reaction cross section of $(\pi/k^2)(2l+1)$. For $l > l_{\mathrm{crit}}$, the phase shift is found by a perturbation calculation to be small and the resulting contribution to scattering cross section is negligible. Consequently the total cross section for electron exchange may be written

$$\sigma_{\mathrm{exch}} = \frac{\pi}{2k^2} \sum_{l=0}^{l_{\mathrm{crit}}} (2lR+1) = \frac{\pi}{2k^2}(l_{\mathrm{crit}}+1)^2.$$

Both k and l_{crit} are energy dependent but in such a way as to largely mutually compensate and the resulting cross section is quite temperature independent:

$$\sigma_{\mathrm{exch}} \approx 2.3 \times 10^{-15}\ \mathrm{cm}^2.$$

It should be noted that this is a large cross section—about an order of magnitude larger than the usual cross sections from kinetic theory.

In the above calculation the protons were regarded as distinguishable. Because of the large value of l_{crit} this should cause no trouble. The difference in statistical weight of the proton singlet and triplet states should have only a minor effect on the sum over all the partial waves up to l_{crit}.

The second problem to be considered is the effect of electron exchange on the atomic spin states. Actually detailed information concerning the effect of electron exchange on the spin states of two atoms, each initially in a completely defined spin state, is not needed. A rather large amount of labor can be saved by using statistical techniques and the density matrix formalism. Here one must choose a Gibbsian ensemble which correctly represents the statistical character of the gas.

A question arises concerning the extent to which two individual hydrogen atoms are statistically independent before an electron exchange takes place. Two atoms would be strongly correlated by the previous electron exchange if it occurred between the same two atoms. However, the probability of this happening is negligibly small. The correlation which results from interaction with a common electromagnetic field causes no trouble statistically as the field is treated as a known and given interaction common to both atoms. Thus the gas may be regarded as an ensemble of statistically independent hydrogen atoms with the effect of the electromagnetic field appearing as an explicit time dependence of the density matrix of the ensemble.

In order to compute the effect of electron exchange, an ensemble of atom pairs is formed by pairing atoms at random. The effect of electron exchange on this new ensemble is computed. The atom pairs are then separated to form a modified ensemble of single-atom systems. These computations are sketched in Appendix II.

Inasmuch as the effect of the atomic spin states on the probability of electron exchange was neglected, the results will be valid only for a hyperfine energy small compared with kT. This "high-temperature" treatment will of course fail to give the proper Boltzmann difference in populations for the case of thermal equilibrium. However, the relaxation rates computed will be quite accurate.

The results of the straightforward, but laborious, calculation outlined in Appendix II can be obtained by a simple, direct argument on physical grounds. Consider the problem of the restoration of the populations to a condition of thermal equilibrium when the populations have been initially disturbed. In the present experiment the microwave transitions were between the two hyperfine states with $M_F = 0$. Consequently the initial ensemble is assumed to be one with the two populations $M_F = \pm 1$ equal. It is further assumed for the moment that there are no oscillating or static magnetic moments. This ensemble is characterized by unpolarized electron and proton distributions. Because of the internal correlations between the electron and proton spins of a given atom the ensemble is not uniform, states of different quantum numbers F, M_F having different populations. The effect of electron exchange between two such atoms is to replace an atom's electron by one which is both unpolarized and uncorrelated with the proton's spin. Hence after exchange the atom is in a completely random spin state with both proton and electron spins unpolarized and uncorrelated. This complete randomness in the atomic spin state is characterized by a uniform ensemble for which all four spin states are equally populated. This is the condition of thermal equilibrium under the infinite temperature approximation used here.

As electron exchanges are randomly distributed in time, the population relaxation effect can be described by a single relaxation time T_1 equal to the mean time between electron exchanges for a given atom. It is interesting that there is but one relaxation time of this type. With four energy levels one might have expected three relaxation times associated with the three normal exponential solutions of the general diffusion equations. One of the normal solutions, which incidently in the present approximation has an infinite relaxation time, disappears because of the assumption of initially equal populations for $M_F=\pm 1$. The other two normal solutions have relaxation times equal to T_1.

Although the argument was carried out only for an assumption of vanishing dipole moment for the gas, it is for all practical purposes correct also when the gas contains an oscillating dipole moment induced by the applied electromagnetic field. Populations are redistributed with a relaxation time T_1. The only remaining problem is one of computing the effect of electron exchange on such an oscillating dipole moment.

To assist in the discussion of the case of an oscillating dipole moment we introduce the notion of an "ensemble model." This is a peculiar concept without a classical analog. Two different ensembles which have the same density matrix cannot be distinguished by any physical measurement. However, the same ensemble may be constructed in various ways and a given construction is here called a "model." For example, one way of constructing a "model" of hydrogen gas with a weak oscillating dipole moment in the z direction is to mix together atoms in several superposition energy states so selected that the expectation value of the oscillating dipole moment is small and the same for all. Another way is to mix together atoms with states of definite F and M_F, and hence without oscillating dipole moments, with a small quantity of strongly oscillating atoms each of which is in a superposition state of equal amounts of the two $M_F=0$ states. It is strange that these two different models which are distinctly different before the mixing become indistinguishable after the identities of the atoms are lost.

The importance of this for the present problem is that a great deal of computing can be avoided by using physical arguments based on the proper model. From a mathematical point of view this is equivalent to decomposing the original density matrix into several parts for each of which the effect of the electron exchange is obtained more easily.

As the gas contains an oscillating dipole moment, the effect of an electron exchange on the ensemble will depend on the phase of the oscillation and must be averaged over all values of this phase. This is most easily done by averaging the effect of an electron exchange for the two cases of the oscillating magnetization instantaneously zero and a maximum. The case of an instantaneously zero magnetization has already been discussed and been shown to produce a uniform ensemble (no oscillating moment). To discuss the case of maximum magnetization, we use the second model discussed above. The hydrogen atoms are assumed to fall into two classes, A and B. Class A atoms, N_A in number, have no polarization. Class B atoms (N_B) are in states for which, at the time of maximum magnetization, the electrons are completely polarized along the direction of the static magnetic field with the proton spin oppositely directed. In an electron exchange between atom pairs chosen at random, the exchange between Class A atoms occurs with a frequency of $N_A^2/2(N_A+N_B)$ and leads to unpolarized atoms. A pairing of a Class A and a Class B atom has a frequency of $N_AN_B/(N_A+N_B)$. It has the following effect. The polarized electron from the Class B atom is combined with the unpolarized proton of the Class A atom. However, the unpolarized protons may be divided into two classes oppositely directed along the Z-axis, in which case there is a probability of $\frac{1}{2}$ that the proton has the same orientation as the original Class B atom. Thus there is a probability of $\frac{1}{2}$ that the original Class B atom remains Class B. In the pairing of Class B atoms with themselves, $N_B^2/2(N_A+N_B)$ Class B atoms pairs are formed and are left unchanged by the exchange process. Thus the total number of Class B electrons is, after the exchange,

$$2\times\frac{N_B^2}{2(N_A+N_B)}+2\times\tfrac{1}{2}\frac{N_AN_B}{(N_A+N_B)}=N_B,$$

and is left unchanged. The averaging of this with the result zero obtained for the case of instantaneous zero magnetization results in the mean magnetization being reduced to $\frac{1}{2}$ its value before exchange. This is a surprising result as the relaxation time for the reduction of an oscillating moment, which by analogy with nuclear magnetic resonance terminology we call T_2, is greater than the relaxation time T_1 discussed above. In fact, $T_2=2T_1$. In nuclear magnetic relaxation, except for pathological cases, $T_1>T_2$. To summarize: the relaxation time for the restoration of the state populations of thermal equilibrium is T_1, equal to the mean time between electron exchanges suffered by some given atom. $T_2=2T_1$ is the relaxation time for the decay of an oscillating magnetization. Assuming room temperature and the electron exchange cross section given earlier,

$$T_2=2T_1=\frac{2}{\sqrt{2}N\bar{v}\sigma_{\text{exch}}}=\frac{2.0\times10^9}{N}\text{ sec},$$

where N is the atomic hydrogen concentration. The effect of these relaxation times on the question of line breadth will be continued in a later section on saturation effects.

Field Broadening

The effect of static fields on the line breadth can be easily discussed. Inasmuch as the transition is magnetic dipole in type, the Stark effect is negligible and the Zeeman effect is quadratic and very small. The Zeeman fractional shift is $\Delta\nu/\nu=1.94\times10^{-6}\ H^2$. For the weak fields employed (under 0.1 gauss) the effect of field inhomogenities was negligible, and the Zeeman correction under 10 sec^{-1}.

Saturation

It appears that the electron exchange effect is the only line broadening effect discussed of any great importance. In any microwave spectroscopy experiment, power saturation can be an important effect and it must be discussed in relation to the relaxation mechanism. While saturation broadening can always be eliminated by reducing the exciting power to a sufficiently low value, this also reduces the signal power. The rate at which information concerning the line center is obtained is maximized by allowing some line broadening by saturation. Because of the difference in the two relaxation times T_1 and T_2, the well-known calculation[14] of the saturation effect on line shape is inapplicable but is easily modified to give the absorbed energy per hydrogen atom as

$$P_{\text{abs}}=\frac{(\hbar\omega)^2}{8kT}\,\frac{\left(\frac{\mu H}{\hbar}\right)^2\frac{1}{T_2}\times N}{(\Delta\omega)^2+\left(\frac{1}{T_2}\right)^2+\frac{T_1}{T_2}\left(\frac{\mu H}{\hbar}\right)^2}.$$

Here N is the total number of hydrogen atoms (including those in the $M_F=\pm1$ states), T is the absolute temperature, μ is the effective dipole moment of the transition ($\mu=\langle F=1,\ M_F=0|\mu_z|F=0,\ M_F=0\rangle$), H is the amplitude of the rf magnetic field, and $\Delta\omega=\omega-\omega_0$, where ω_0 is the (circular) frequency of the line center. This is identical to the usual expression with the exception of the T_1/T_2 factor in the "saturation" term in the denominator. This formula was obtained from a simple physical argument but was verified by calculating the time rate of change of the density matrix describing the statistical character of the atomic spin state under the influence of the radiofrequency field and the relaxation effect.

Pressure Shift

Although collisions with hydrogen molecules do not contribute in an important way to the breadth of the hyperfine transition resonance, they introduce a very small shift in resonance frequency which needs discussion. Physically this shift has its origin in the fact that during a collision the hydrogen atom orbital wave function is disturbed by the presence of the hydrogen molecule. In this disturbed state, the probability of the electron being found at the position of the proton is reduced and this results in a smaller hyperfine interaction energy. Although this occurs only during the collision, the net effect is one of decreasing the average interaction energy measured in the experiment.

In a collision between a hydrogen atom and molecule, the mutual polarization effects cause the hydrogen molecule to produce an electric field at the atom. Such a field serves to mix predominantly P-state wave function into the ground state. It might naively be expected that as a result of the admixed P-wave the electron spin would be disturbed through the spin-orbit coupling term in the Hamiltonian. However, this effect is nonexistent in the approximation considered. The only important effect of the collision is one of reducing the spin-spin interaction for the duration of the collisions.

In the approximation considered, the hyperfine splitting of the atomic hydrogen excited states is neglected in relation to optical energy differences. We consider first a somewhat simplified picture in which the hydrogen atom is acted upon by a uniform static electric field. Neglecting nuclear spin, it is evident from symmetry that the ground states with electron spin parallel and antiparallel to the electric field are both lowered in energy by the same amount. If now the hyperfine splitting of the ground state is included, but neglected in the excited states, because of the smaller energy denominators there results a somewhat greater downward shift for the upper ($F=1$) ground hyperfine state. This reduces the ground state hyperfine splitting to a value equal to the normal value multiplied by the original ground state contribution in the perturbed state.

In a better approximation, the interaction between the atom and molecule which leads to the Van der Waals forces is treated as a mutual polarization of the atomic and molecular systems. Only the dominant electronic contribution to the polarization is included, and nuclear spin interactions are again neglected. A reflection of the electron wave function including spin function in the plane determined by the positions of the three protons leaves the energy invariant. Consequently, in this approximation both hydrogen atom spin states have the same energy and the spin degeneracy of the ground state is unsplit by this interaction. Once again the hyperfine splitting can be included in the ground state if it is neglected in the excited state. This leads to the same conclusion as above, namely, that the splitting is reduced to the normal value multiplied by the probability of the atom being in the normal ground state. Consequently the time-averaged ground state splitting is proportional to the time-averaged probability for the atom being found in the normal ground state. The only significant contribution to the line breadth results from the statistical fluctuation in the collision rate and strength. This effect is completely negligible in the present experiment.

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[14] R. Karplus and J. Schwinger, Phys. Rev. **73**, 1020 (1948).

In order to obtain a rough estimate of the time-averaged ground state probability, an estimated Van der Waals interaction can be used to compute the amount of admixed excited state during a collision. Assuming a dipole-dipole Van der Waals interaction energy of $-A(e^2/a_0)(a_0/R)^6$ and a "collision diameter" of $R=D$, the pressure correction to the frequency is approximately $\Delta\nu/\nu \sim -A(a_0/D)^6(D/L)$, where L is the mean free path. Assuming reasonable values of $A \sim 5$ and $D=2\times 10^{-8}$ cm, the pressure correction becomes roughly equal in cycles per second to the pressure in millimeters of mercury.

This displacement is small and one is tempted to neglect this effect. On the other hand, the result is very sensitive to the assumed collision radius. Also, being a very complex system, the $H-H_2$ system cannot be said to be well understood. In view of these uncertainties, it is believed that the conservative way to treat the data is to assume a linear pressure dependence and determine the slope experimentally.

APPARATUS

Gas Handling

The atomic hydrogen was produced by the dissociation of pure molecular hydrogen gas in a Wood's discharge tube 1 meter long and 0.6 cm in diameter. The molecular hydrogen was commercial-grade electrolytic hydrogen, purified by filtering through the wall of an electrically heated palladium tube. A continuous-flow system was used, hydrogen being admitted to the U-shaped discharge tube near one of the electrodes, and the partially dissociated gas diffusing and being pumped down a Pyrex tube into a spherical bottle, 10 cm in diameter, at the center of the resonant cavity. The gas was pumped from the bottle via another tube and was exhausted into the room.

The discharge was maintained by a dc supply, currents of 0.1 ma to 3.0 ma, at 3000 volts, being used. A small blower air-cooled the electrodes. Series resistance of 750 kilo-ohms or larger was used to stabilize the discharge. Thermocouple gauges, located at the glass tubes just before they entered and after they left spherical bottle in the cavity, were used to determine the pressure in the bottle in the cavity. These were calibrated for molecular hydrogen against a McLeod gauge. Under conditions of data taking, the total pressure in the bottle was between 0.070 and 0.120 mm Hg, of which, as inferred from the breadth of the observed resonance, typically 0.2% was atomic hydrogen, the remainder being molecular hydrogen. Pressure was controlled by varying the temperature of the palladium leak.

As the atomic hydrogen had to travel down about 30 cm of rather small-bore Pyrex tubing before reaching the bottle in the resonant cavity, it was important to find some means of wall "poisoning" to prevent the recombination of the atomic hydrogen on the walls. The poisoning material should not introduce products that would broaden the resonance. A material was found that satisfied this requirement; it was a mixture of dimethyldichlorosilane and methyltrichlorosilane, sold by General Electric under the name Dri-Film SC77. Applied as a vapor to the glass surfaces, it formed a film that was heat-stable, resistant to common solvents, and that had an extremely low vapor pressure at room temperatures. Crude quantitative tests indicated that this film was substantially more effective than any of the other treatments tried (water vapor, concentrated H_2SO_4) in preventing recombination of the atomic hydrogen at glass surfaces.

As there was a fair amount of glassware inside the resonant cavity, Corning No. 707 glass, with a low loss tangent (0.0013) at the microwave frequency, was used for all glassware inside the cavity.

Frequency Stabilization and Measurement

The 1420-Mc/sec microwave power was supplied by the transmitter section of a T-85/APT-5, grounded-grid coaxial line triode oscillator. This was powered by a well-regulated 500-volt supply. The output of the oscillator was phase-locked to the sum frequency of the 14 200th harmonic of a very stable 100-kc/sec crystal-controlled oscillator (Western Electric 0-76/U) and a stable 400-kc/sec tunable signal from a General Radio Model 271 heterodyne frequency meter. The stabilization circuit is shown in Fig. 2. The output frequency of the oscillator could be varied by tuning the frequency meter.

To secure a stability of $1:10^9$ over a period of minutes with this stabilization system, the crystal oscillator driving the multiplier chain must have equal or greater stability. The W.E. 0-76/U oscillator used had better stability than $1:10^9$ over hours, and so was satisfactory. The stability requirement on the variable frequency oscillator (G.R. frequency meter) was not nearly as stringent. As it supplied an additive frequency that was 0.03% of the total, its stability had to be only $3:10^5$ over a period of minutes. With continuous monitoring, it was possible to keep its frequency constant to within $1:10^5$ indefinitely.

The frequency of the frequency meter was continuously monitored with a Hewlett-Packard Model 524B electronic counter accurate to better than $1:10^5$. The frequency of the crystal-controlled 0-76/U oscillator was measured by multiplying the frequency up to 5 Mc/sec and beating the 5-Mc/sec harmonic with the 5-Mc/sec signal from radio station WWV. The difference frequency of about 96 cycles per second was fed into a phase-sensitive detector, whose reference voltage frequency was measured with an electronic counter. The output frequency from the phase detector at about $\frac{1}{2}$ cycle per second was recorded directly on a chart recorder.

Measurements of the 100-kc/sec crystal frequency were made 15–20 times a day, generally six days a

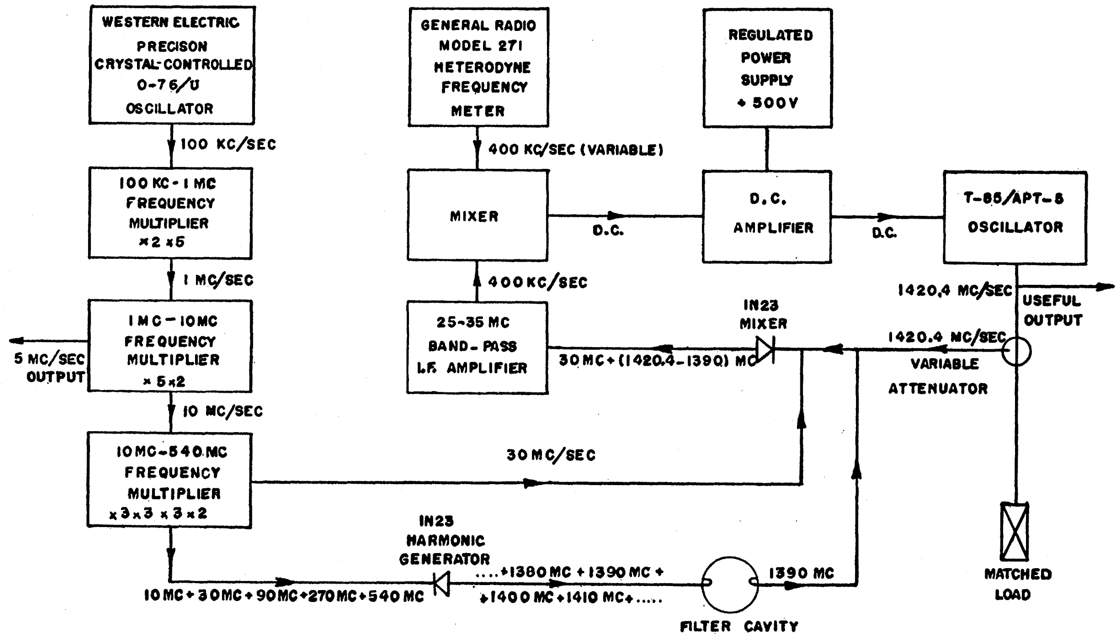

FIG. 2. Phase-lock stabilization system for T-85/APT-5 oscillator.

week during daylight hours, from June, 1954 to August, 1954. It was found that measurements made during a day would scatter roughly $\pm 1.5\times 10^{-8}$ from the daily mean, with measurements made within 5 minutes of each other as apt to differ as much as measurements made several hours apart. This was interpreted as due to virtual Doppler shifts in the ionosphere changing the effective length of the propagation path, as the crystal oscillator was known to be much more stable than this. This was consistent with the observation that on days of electrical storms and poor radio reception due to other atmospheric conditions, the scatter of frequency measurements was apt to be somewhat *greater* than on days of excellent reception. It is known[15] that somewhat after sunrise and before sunset the virtual height of the ionospheric layers changes markedly, the layers approaching the earth as the first rays of the sun increase atmospheric ionization, and leaving the earth as the sun sets. Such shifts should produce very noticeable changes in the observed frequency at such times, and in fact very large frequency deviations (of the order of $1:10^7$) from the daily average were frequently, but not invariably, observed at such times.

There is a question as to whether such virtual Doppler shifts introduced a bias in the frequency measurements. Presumably, the frequency should be monitored continuously to insure that such shifts are averaged out. To investigate whether the frequency as received showed a regular diurnal variation, measurements were made at roughly half-hour intervals for over 30 hours on two occasions. These measurements indicated that there was no systematic diurnal effect detectable (other than the sunrise-sunset effect mentioned above), and especially that the average of frequency measurements made at night agreed with the daytime average. Another possible source of bias could be a correlation between "good observation times" and a virtual Doppler shift. At certain (infrequent) times, it was impossible to measure the WWV frequency due to poor reception conditions (static, fading, etc). If such conditions were always associated with Doppler-shifts in one direction, the "averaging out" of the shifts would be incomplete, and the frequency determinations therefore biased. However, times of bad reception when no measurements could be made were uncommon, and occurred at random times of the day; they therefore were unrelated to the sunrise-sunset effect. Also a correlation analysis of a numerical measure of "quality of observation" with frequency showed no significant correlation. Therefore, it is believed that the frequency measurements reported in this paper are free from such bias.

Detection System

The detection system used is shown in Fig. 3. Power from the frequency-stabilized oscillator was coupled into the bolometers through a ring circuit, the coaxial equivalent of the wave-guide "magic tee." The bolometers were matched to the line so that none of this power, which acted as local oscillator power for the frequency heterodyning in the bolometer, reached the cavity. One bolometer was then slightly mismatched, sending a reflected wave to the (matched) cavity.

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[15] F. R. Terman, *Radio Engineers' Handbook* (McGraw-Hill Book Company, Inc., New York, 1943), first edition, p. 721.

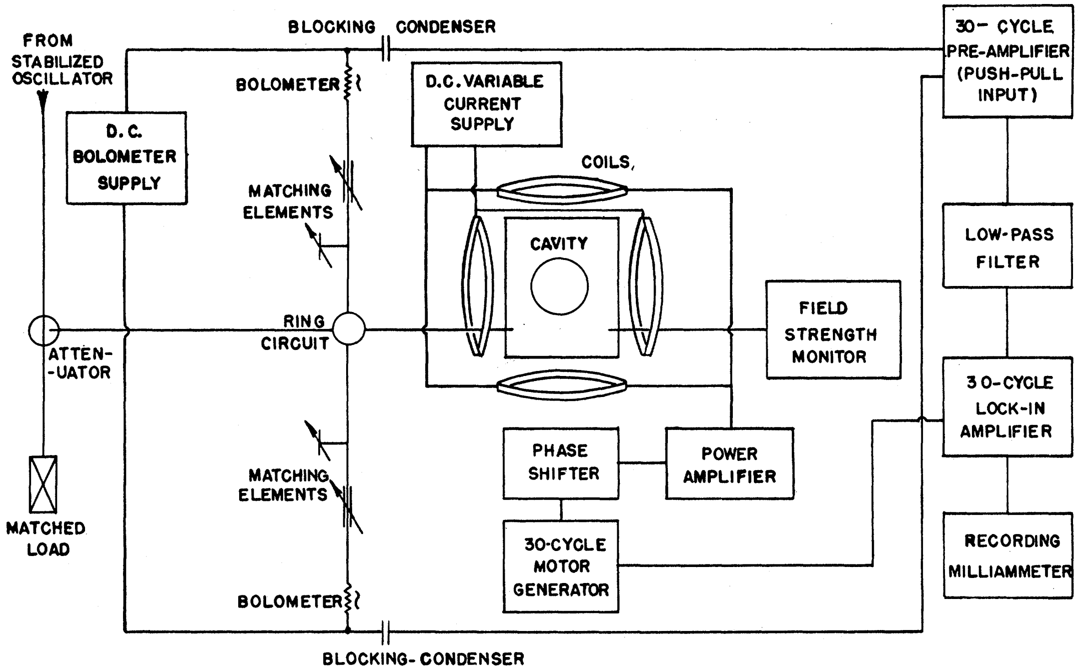

Fig. 3. Detection system.

The rf field level in the cavity was determined by coupling a small amount of power out to the field strength monitor, which consisted of a crystal rectifier and microammeter; it was adjusted by varying the amount of bolometer mismatch. On resonance, the atomic hydrogen in a bottle in the cavity absorbed power, thus mismatching the cavity and sending an "absorption wave" back to the bolometers. In practice, the absorption was modulated at 30 cycles/sec, producing a 30-cycle amplitude modulation in the absorption wave. This wave beat with the local oscillator power in the bolometers, producing a 30-cycle variation in bolometer resistance. This was converted to a voltage signal by the dc bolometer current, amplified, filtered and detected in a phase-sensitive amplifier, whose reference signal was derived from the system used to modulate the absorption. Bolometers were used as microwave detectors instead of crystal diodes because of their lower noise at very low intermediate frequencies.[16]

The absorption was modulated as follows: the $\Delta M_F = 0$ hyperfine transition can only be induced by a rf magnetic field parallel to the static magnetic field (which defines the axis of quantization) while the $\Delta M_F = \pm 1$ transitions can only be induced by an rf field perpendicular to the static field. The cavity was a right circular cylinder, resonant in the TE_{112} mode. This provided a region of rf magnetic field nearly uniform in strength and direction at the center of the cavity where the bottle containing the atomic hydrogen was located. By balancing out all static fields except a weak (0.05 gauss) horizontal field parallel to the rf field in the cavity at the position of the atomic hydrogen, and then applying an oscillating vertical field varying from about 0 to 0.13 gauss, a quasi-static field was set up that oscillated at 30 cycles/sec from parallel to the rf field to nearly perpendicular, thus modulating the absorption.

The nature of the resonant response, (i.e., whether it is absorptive, dispersive or some mixture), depends on the relative phase of the absorption wave and the local oscillator power at the bolometers. This is determined by the cavity tuning and the length of line between the cavity and ring circuit. Although measurement of signal strength at four frequencies on a resonance theoretically determine all the unknown parameters describing the line (frequency of the line center, line width, admixture of dispersive phase, and normalization), the mathematical chore of determining line centers from such data is onerous and the resulting line center determination is badly affected by noise fluctuations. Therefore a technique was devised to insure that the observed line was always purely absorptive. This consisted of inserting a polystyrene rod into a region of strong rf electric field in the cavity and at times modulating the insertion length over a range of $\frac{1}{16}$ in. at 30 cycles/sec. As the loss tangent for the rod was very small, the rod may be considered lossless. The effect of modulating its insertion length, therefore, is to introduce a purely dispersive signal. By adjusting the cavity tuning to be "on resonance" as determined by the field strength monitor and then adjusting the line length between cavity and ring circuit so that the

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[16] R. Beringer and J. G. Castle, Phys. Rev. 78, 581 (1950).

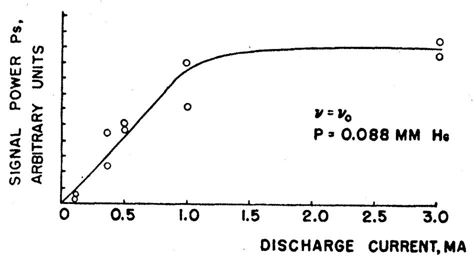

FIG. 4. Signal strength as a function of discharge current and thus of atomic hydrogen concentration.

vibrating rod produced no output signal, a purely absorptive hydrogen signal was assured. After this alignment procedure the rod modulation was stopped. This procedure had to be repeated at each frequency. By this means, the amount of dispersion could be kept less than $\pm 6:10^4$ of the absorption; this corresponds (for a line 3 kc/sec wide) to a shift of the apparent center frequency of ±0.5 cycles/sec, a negligible amount.

POWER LEVEL AND CONCENTRATION EFFECTS

While most data were taken at the microwave power level producing the theoretical optimum signal to noise in the detection system, the effects of varying the rf level were briefly investigated. No indication of any shift in the resonant frequency with changing power level was observed. Also, the changes in line width and signal strength with power level were as predicted by theory, where the predominant relaxation mechanism is electron-exchange collisions between hydrogen atoms, as discussed above.

As with power level, atomic hydrogen concentration was kept constant at an optimal value, i.e., that corresponding to the narrowest line compatible with adequate signal to noise, during most of the data taking. However, measurements at higher concentrations were made at one total pressure. (This corresponds to a fixed molecular hydrogen "buffer" pressure, as the admixture of the active atomic hydrogen was so small.) Although the line was definitely broadened, as expected, there was no observable shift in the central frequency of the transition with atomic hydrogen concentration.

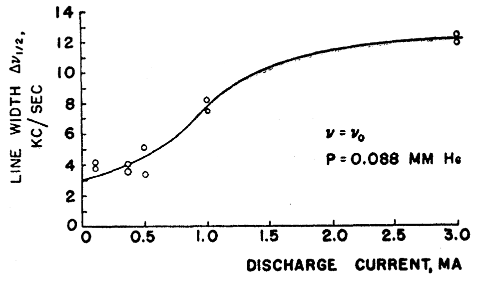

FIG. 5. Line width as a function of discharge current and thus of atomic hydrogen concentration.

The variation of atomic hydrogen concentration was obtained by varying the current passing through the Woods' discharge. The results obtained are shown in Figs. 4 and 5. As there is no independent measure of atomic hydrogen concentration, one of the curves can be considered to be a smooth fit of the data points with the other curve being determined by the assumption that electron-exchange collisions provide the broadening mechanism. Only two arbitrary parameters are used in the fit: the rf field strength at the atoms and a normalization factor in the signal power curve. The value of rf field strength giving best fit is in reasonable agreement with that given by the crystal-rectifier cavity field monitor. The atomic hydrogen concentration could have been independently inferred from the signal power available. However, the amplifier gain was not sufficiently well known.

The shape of the resonance line was observed by measuring signal strength at a series of frequencies on the resonance. Typical lines obtained in this way are shown in Figs. 6 and 7. Lorentz absorption curves have been fitted to the experimental points.

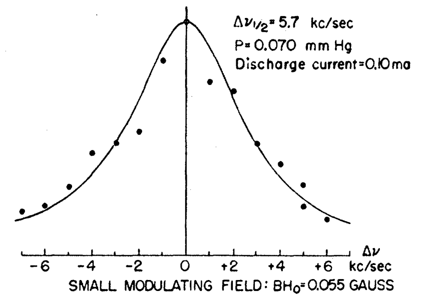

FIG. 6. Line contour using a weak modulating field. $BH_0 = 0.055$ gauss.

Preliminary measurements having determined the optimum power levels and concentrations, data were taken in the following fashion. At each total pressure, one measurement consisted of a determination of the signal strength at each of three frequencies: one near the line center and two at frequencies approximately a resonance half-width away. The order in which the three points were taken varied randomly from measurement to measurement. At each frequency the microwave signal phase was readjusted to insure a purely absorptive signal. After several measurements were made, the total pressure was changed and another series of measurements was made.

The data taken this way were analyzed by fitting a Lorentz curve through each set of three experimental points and taking the central frequency of this fitted curve as the result of the measurement. 103 measurements were made in this way, at a total of three gas pressures. The results are shown in histogram form in Fig. 8 and are tabulated in Table I. As discussed above, the data were analyzed by assuming a linear variation of observed frequency with total gas pressure. The linear relationship assumed was determined by a least-squares fit of the 103 measurements, weighting each measurement equally. The extrapolated value corresponding to zero total pressure then gives the desired value for the hyperfine splitting for an isolated atom. The determination made in this way was liable to four sources of error: the measurement of frequency, asymmetry of the observed resonance, an uncorrected Zeeman shift and a nonlinear pressure shift. It is believed that the frequency measurement technique discussed above introduced an uncertainty of ±7 cycles/sec into the hyperfine determination. The exact value of the WWV frequency used as a reference was obtained from the correction sheets published by the National Bureau of Standards. The phase-adjustment technique used to insure an absorptive response eliminated this as a source of error greater than ±0.5 cycles/sec. The weak (quasi-static) magnetic fields used in the absorption modulation required a correction of 8 cycles/sec to the hyperfine splitting, but introduced negligible uncertainty. The statistical scatter of the data about the least-squares line for the pressure dependence of the hyperfine splitting gave an uncertainty (probable error) of ±58 cycles/sec at zero total pressure. The combined total probable error in the measurement is ±59 cycles/sec.

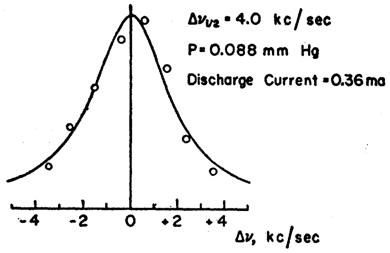

FIG. 7. Line contour using a strong modulating field. $BH_0=0.474$ gauss.

RESULTS

The value obtained in this experiment for the hfs is

$$\Delta\nu_{\rm H}=1420.40580\pm0.00006\ {\rm Mc/sec}.$$

The average of all experimental points without regard to pressure gives a frequency of

$$\Delta\nu_{\rm Av}=1420.40572\pm0.00001\ {\rm Mc/sec}.$$

Thus the pressure correction amounts to a shift upward of

$$80\pm60\ {\rm cycles/sec},$$

an amount too small to be significant statistically. Thus, as has been indicated by Kusch,[4] one cannot conclude either from the data or theory that a pressure shift exists as large as that above. On the other hand, the linear extrapolation can only be avoided if there is reliable information external to the data that the pressure shift is negligible.

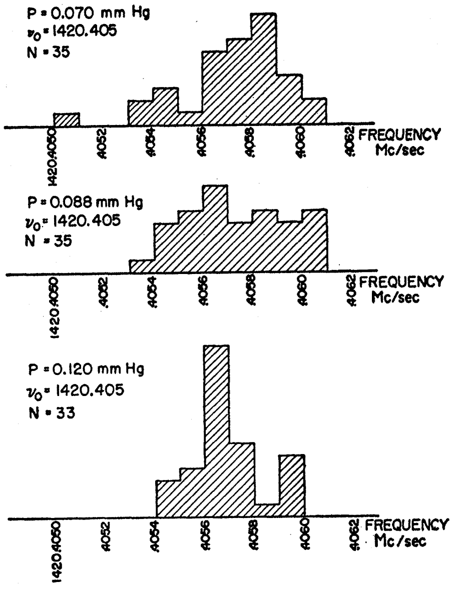

FIG. 8. Histograms showing the hyperfine frequency measurements at three pressures.

The above value $\Delta\nu_{\rm H}$ is to be compared with the value obtained in the most recent atomic beam experiment,[4]

$$\Delta\nu_{\rm H}=1420.40573\pm0.00005\ {\rm Mc/sec},$$

and with the value given by theory,

$$\Delta\nu_{\rm H}=\frac{16}{3}\alpha^2cR_\infty\left(\frac{\mu_p}{\mu_e}\right)\left(\frac{\mu_e}{\mu_0}\right)^2(1+\tfrac{3}{2}\alpha^2)\left(\frac{M_r}{M}\right)^3$$

$$\times\left[1-\left(\frac{5}{2}-\ln2\right)\alpha^2\right]P_rP_s$$

$$=(1420.4161\pm0.0369)P_rP_s\ {\rm Mc/sec},$$

where P_r is a proton recoil correction factor[17] and P_s is a proton-structure correction.[2] The following numerical values have been inserted: $\alpha^{-1}=137.0377\pm0.0016$, $c=(2.997929\pm0.000008)\times10^{10}$ cm/sec, $R_\infty=109737.309$

TABLE I. Results.

Pressure, mm Hg	Number of observations	Frequency,[a] Mc/sec
0.070	35	1420.405719±0.000025
0.088	35	1320.405746±0.000023
0.120	33	1420.405681±0.000017
0(extrapolated)	···	1420.40580 ±0.00006

[a] Zeeman correction = 8 cycles/sec.

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[17] W. A. Newcomb and E. E. Salpeter, Phys. Rev. **97**, 1146 (1955).

± 0.012 cm^{-1}, $(\mu_e/\mu_p)=658.2087\pm 0.0020$, $m=9.1085\pm 0.0006\times 10^{-28}$ gram, $M=1.67243\pm 0.00010\times 10^{-24}$ gram, and

$$\frac{\mu_e}{\mu_C}=1+\frac{\alpha}{2\pi}-\frac{2.9726\alpha^2}{\pi^2}.$$

The two experimental determinations are seen to be in excellent agreement with each other. The uncertainties in the theoretical expression are several orders of magnitude larger than the experimental ones: this is primarily due to uncertainty in the value of the fine structure constant. If this could be determined to better than one part in 10^6, the measurements, together with the theoretical formula, would lead to an experimental evaluation of the structure and recoil corrections, which have been estimated to be of the order of parts in 10^5.[2,17]

APPENDIX I

The effect of a high surrounding gas pressure that confines a radiating atom to a small region can be treated classically as follows. Consider an atom radiating the plane wave

$$\begin{aligned} E(t)&=A\exp[i(\omega_0 t-x/\bar{\lambda})] \quad && t>0 \\ &=0 && t<0. \end{aligned}$$

Here ω_0 is the complex (damped) frequency of radiation and $x=x(t)$ is the coordinate of the atom. The radiation is propagated along the x axis. The radiation spectrum is given by the square of the Fourier transform:

$$|G(\omega)|^2=\frac{1}{2\pi}|A|^2\int_0^\infty\int_0^\infty \exp\left[i(\omega_0-\omega)t-\frac{ix}{\bar{\lambda}}\right] \times\exp\left[-i(\omega_0{}^*-\omega)t'+\frac{ix'}{\bar{\lambda}}\right]dtdt'.$$

Let

$$\Delta x=x(t)-x(t'),\quad \tau=|t-t'|,$$

and assuming that the motion of the atoms is determined by the diffusion equation, $\partial P/\partial t=D\nabla^2 P$,

$$P(\Delta x)=\frac{1}{(4\pi D\tau)^{\frac{1}{2}}}\exp\left[-\frac{(\Delta x)^2}{4D\tau}\right],$$

where P is the position probability function.

Taking an average over an ensemble of similar noninteracting atoms, we have

$$\langle W\rangle_{\text{Av}}=\langle\exp[-i(x-x')/\bar{\lambda}]\rangle_{\text{Av}}=\exp(-D\tau/\bar{\lambda}^2).$$

Assuming no correlation between A and x for each atom,

$$\langle|G(\omega)|^2\rangle_{\text{Av}}=\frac{1}{2\pi}\langle|A|^2\rangle_{\text{Av}}\int_0^\infty\int_0^\infty\langle W\rangle_{\text{Av}}\exp[i(\omega_0-\omega)t] \times\exp[-i(\omega_0{}^*-\omega)t']dtdt'.$$

Writing $\omega_0=\Omega_0+i\gamma$ and assuming $\gamma\ll D/\bar{\lambda}^2$, straightforward integration yields

$$\langle|G(\omega)|^2\rangle_{\text{Av}}=\frac{\langle|A|^2\rangle_{\text{Av}}}{2\pi\gamma}\frac{D/\bar{\lambda}^2}{(D/\bar{\lambda}^2)^2+(\Omega_0-\omega)^2}.$$

Since $D=(\pi/24)^{\frac{1}{2}}vL$, where v is the root-mean-square velocity, the width of this Lorentz-shaped line is

$$\Delta\nu_1=4\pi D/\bar{\lambda}^2=2.8(L/\lambda)\times(\text{normal Doppler breadth}).$$

APPENDIX II

The four hyperfine spin states of the hydrogen atom will be designated as follows: State (1) $F=0$, $M_F=0$; State (2) $F=1$, $M_F=1$, State (3) $M_F=0$, State (4) $M_F=-1$. The spin state of some one of the hydrogen atoms is designated by the column vector $\mathbf{a}$ with the four elements $\mathbf{a}_j$, the index j ranging from 1 to 4. The density matrix describing the statistical character of the spin is defined as

$$\boldsymbol{\varrho}=\langle\mathbf{aa}^*\rangle_{\text{Av}},$$

where $\mathbf{a}^*$ is a row vector, the Hermitian adjoint of $\mathbf{a}$. The average is taken over all the atoms of the gas. The elements of $\boldsymbol{\varrho}$ are $\rho_{ij}=\langle a_i\bar{a}_j\rangle_{\text{Av}}$.

The populations of the various spin states are given directly by the diagonal elements of $\boldsymbol{\varrho}$ and the average value of the magnetic moment of a gas atom is given by the trace

$$\operatorname{tr}(\mu_e\boldsymbol{\sigma}_e+\mu_p\boldsymbol{\sigma}_p)\boldsymbol{\varrho}.$$

Here μ_e and μ_p are the magnetic moments of the electron and proton, respectively.

Assuming that the gas is acted upon by an oscillating magnetic field in the z direction and is in an equilibrium state through the influence of the various relaxation effects, the general form of $\boldsymbol{\varrho}$ can be determined by requiring that the oscillating polarizations of the gas shall be at the frequency of the applied field and that the density matrix shall be invarient under an arbitrary rotation about the z axis. It is found to have the general form

$$\boldsymbol{\varrho}=\begin{bmatrix}\gamma & 0 & \delta\exp(-i\omega t) & 0\\ 0 & \alpha & 0 & 0\\ \delta\exp(i\omega t) & 0 & \beta & 0\\ 0 & 0 & 0 & \alpha\end{bmatrix},$$

where α, β, γ, and δ are real numbers and ω is the frequency of the applied field. This can be written in terms of Pauli spin operators as

$$\begin{aligned}\boldsymbol{\varrho}=\tfrac{1}{2}\delta[\tfrac{1}{8}(\boldsymbol{\sigma}_e+\boldsymbol{\sigma}_p)^2(\exp(i\omega t)-1)+1](\sigma_{ez}-\sigma_{pz})\\ \cdot[\tfrac{1}{8}(\boldsymbol{\sigma}_e+\boldsymbol{\sigma}_p)^2(\exp(-i\omega t)-1)+1]+\tfrac{1}{4}(\alpha-\beta)\\ \cdot(\sigma_{ez}+\sigma_{pz})^2+\tfrac{1}{8}(\beta-\gamma)(\boldsymbol{\sigma}_e+\boldsymbol{\sigma}_p)^2+\gamma\mathbf{I}.\end{aligned}$$

The N hydrogen atoms comprising the gas are imagined paired randomly to form a new ensemble of $N/2$ atom pairs whose spin function prior to an interaction between atoms of a pair can be taken to be a column vector with the 16 components $a_i^{(1)}a_j^{(2)}$, where (1) and (2) refer to the two atoms of a given pair. The density matrix $\boldsymbol{\rho}'$ describing this ensemble has elements

$$\rho'_{ik,\,jl}=\langle a_i^{(1)}a_k^{(2)}\bar{a}_j^{(1)}\bar{a}_l^{(2)}\rangle_{\mathrm{Av}}.$$

Because of the absence of correlation between atoms of atom pairs prior to the interaction this can be written as

$$\rho'_{ik,\,jl}=\langle a_i^{(1)}\bar{a}_j^{(1)}\rangle_{\mathrm{Av}}\cdot\langle a_k^{(2)}\bar{a}_l^{(2)}\rangle_{\mathrm{Av}}=\rho_{ij}\rho_{kl},$$

since (1) and (2) are statistically equivalent. Thus $\boldsymbol{\rho}'$ is the outer product of $\boldsymbol{\rho}$ with itself.

An electron spin exchange between the two atoms of an atom pair is brought about by the spin exchange operator

$$\mathbf{P}=\tfrac{1}{2}(\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2-1),$$

where $\boldsymbol{\sigma}_1$ and $\boldsymbol{\sigma}_2$ are the Pauli spin operators.

Under an electron exchange the 16×16 density matrix is transformed into

$$\boldsymbol{\rho}''=\mathbf{P}\boldsymbol{\rho}'\mathbf{P}^*=\mathbf{P}\boldsymbol{\rho}'\mathbf{P}.$$

This of course describes the statistical character of the atom pairs assuming an electron exchange in each atom pair. The resulting density matrix describes the spin state averages of the individual atoms as well as correlations between spin states of the atoms of the atom pairs. This correlation information is not useful as soon as the pairs are separated into individual atoms.

The useful information is described by a 4×4 density matrix obtained from $\boldsymbol{\rho}''$ by forming a diagonal sum over indices of one of the atoms in the ensemble of atom pairs. This 4×4 density matrix has matrix elements

$$\rho'''_{ij}=\textstyle\sum_k\rho''_{ik,\,jk}.$$

The density matrix $\boldsymbol{\rho}'''$ is evaluated by expressing $\boldsymbol{\rho}$ in terms of Pauli spin operators as indicated above. The 16×16 matrix $\boldsymbol{\rho}'$ can be written as the outer product

$$\boldsymbol{\rho}'=\boldsymbol{\rho}^{(1)}\times\boldsymbol{\rho}^{(2)}.$$

The superscripts are introduced as an aid in identifying the indices subsequently.

The transformed matrix is

$$\boldsymbol{\rho}''=\mathbf{P}\boldsymbol{\rho}^{(1)}\times\boldsymbol{\rho}^{(2)}\mathbf{P}.$$

The final density matrix is obtained by forming the trace over all indices with the superscript (2):

$$\boldsymbol{\rho}'''=\mathrm{tr}_{(2)}\mathbf{P}\boldsymbol{\rho}^{(1)}\times\boldsymbol{\rho}^{(2)}\mathbf{P}.$$

The above matrix $\boldsymbol{\rho}'''$ is expressible as a polynomial in the four spin operators $\boldsymbol{\sigma}_e^{(1)}$, $\boldsymbol{\sigma}_e^{(2)}$, $\boldsymbol{\sigma}_p^{(1)}$, $\boldsymbol{\sigma}_p^{(2)}$.

The trace is evaluated in a straightforward though tedious fashion by making use of the relations

$$\begin{aligned}&\mathrm{tr}\boldsymbol{\sigma}=0,\\&\mathrm{tr}(\boldsymbol{\sigma})^2=12,\\&\mathrm{tr}(\sigma_x^n\sigma_y^{n'})=[1+(-1)^n][1+(-1)^{n'}],\\&\mathrm{tr}_{(2)}\boldsymbol{\sigma}^{(1)}\cdot\boldsymbol{\sigma}^{(2)}=0,\end{aligned}$$

etc. This gives for $\boldsymbol{\rho}'''$,

$$\boldsymbol{\rho}'''(t_1)=\begin{bmatrix}\frac{1}{4}+\delta^2\cos^2\omega t_1 & 0 & \delta\cos\omega t_1 & 0\\ 0 & \frac{1}{4}-\delta^2\cos^2\omega t_1 & 0 & 0\\ \delta\cos\omega t_1 & 0 & \frac{1}{4}+\delta^2\cos^2\omega t_1 & 0\\ 0 & 0 & 0 & \frac{1}{4}-\delta^2\cos^2\omega t_1\end{bmatrix}.$$

Here t_1 is the time at which the electron exchange takes place. Averaging over a range in exchange times equal to $2\pi/\omega$ gives for the density matrix at any fixed time shortly after the electron exchange:

$$\bar{\boldsymbol{\rho}}'''=\begin{bmatrix}\frac{1}{4}+\frac{1}{2}\delta^2 & 0 & \frac{1}{2}\delta\exp(-i\omega t) & 0\\ 0 & \frac{1}{4}-\frac{1}{2}\delta^2 & 0 & 0\\ \frac{1}{2}\delta\exp(i\omega t) & 0 & \frac{1}{4}+\frac{1}{2}\delta^2 & 0\\ 0 & 0 & 0 & \frac{1}{4}-\frac{1}{2}\delta^2\end{bmatrix}.$$

In averaging the off-diagonal elements, the explicit time dependence resulting from the energy difference and oscillating magnetic field must be eliminated before the averaging. This method of averaging is valid when the radio-frequency and resonance frequency are roughly equal.

In the above density matrix, for the conditions of the experiment δ^2 can be neglected in relation to 1. Consequently an electron exchange equalizes the populations of all 4 spin states. The oscillating dipole moment of the gas before the electron exchange is given approximately by

$$\mathrm{tr}\mu_e\sigma_{ez}\boldsymbol{\rho}=2\mu_e\delta\cos\omega t.$$

After the electron exchange, the off-diagonal elements of the density matrix are reduced by $\frac{1}{2}$, resulting in the same reduction in the size of the oscillating moment.