Redetermination of the Hyperfine Splittings of Hydrogen and Deuterium in the Ground State*

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The hyperfine splittings of hydrogen and deuterium in the $1^2S_{\frac{1}{2}}$ state have been remeasured by the atomic beam method. It is found that

$$\Delta\nu(\text{H}) = (1420.40573 \pm 0.00005) \times 10^6 \text{ sec}^{-1},$$
$$\Delta\nu(\text{D}) = (327.384302 \pm 0.000030) \times 10^6 \text{ sec}^{-1}.$$

The result for hydrogen is in agreement with a recent measurement of Wittke and Dicke. It is in significant disagreement with an earlier atomic beam measurement.

RECENTLY, Wittke and Dicke[1] have made a new determination of the hyperfine splitting of hydrogen in the ground state. The result is in disagreement with an earlier result of Prodell and Kusch[2] by almost three times the sum of the stated uncertainties of the two results. While no interpretation of the experimental value of the hfs splitting itself is concerned with the discrepancy because of a lack of knowledge of the fine structure constant to a precision comparable to the discrepancy between the two results, the resolution of the discrepancy is, nevertheless, of importance in the comparison[3] of the hyperfine structure separation of hydrogen in the $1S$ and $2S$ states and in the search for a differential hfs anomaly for hydrogen and deuterium in the $1S$ and $2S$ states.

Dicke[4] has suggested that a systematic error may have occurred in the atomic beam method through a continuous change in phase of the rf magnetic field along the rf circuit (hairpin) traversed by the atom. Such a change of phase can occur through a differential resistance or radiation at the two ends of the hairpin. The change in phase may be reversed by mechanical reversal of the hairpin with respect to the direction of the beam provided that the whole electrical environment of the hairpin, including its shielding, is reversed. In the previous modification of the experiment, no complete reversal was possible. In the present experiment, the hairpin was rigidly and symmetrically mounted in a rigid shield with minimal apertures to allow transit of the beam and the whole system could readily be reversed with respect to the beam. The apparatus generally was as previously described.[2] However, the Pirani gauge had been remarkably improved in steadiness and a much better frequency standard was available for the present work. The wire deflecting magnets had been replaced by conventional iron magnets of increased deflecting power.

The oscillator output was beat against a signal, derived from the frequency atandard, of 1420 and 328 Mc/sec for H and D, respectively. The beat frequencies of about 405 and 615 kc/sec were measured on a *BC* 221 frequency meter which was, in turn, calibrated against the standard. The oscillators themselves were as previously described. The rf amplitude was adjusted to values in the neighborhood of the optimum value where the line has its theoretical transit-time width and the probability of transition at the line center is a maximum. A probe in the coaxial line which fed the hairpin was connected through a crystal to a galvanometer. In most cases a detectable change in the galvanometer current occurred as the oscillator frequency was varied over several times the line width. The observed effect is, of course, a result both of variation of the rf current in the hairpin and of the frequency-dependent characteristics of the detecting circuit. The effect of a variable rf field amplitude will be discussed in the section on errors.

To determine the central frequency of the line, pairs of observations were made of the frequencies on both sides of the intensity maximum at which the readings of the galvanometer in the Pirani gauge circuit were equal. Since the Pirani gauge circuit had, for long periods of time, a slow and constant thermal drift, alternate pairs of readings were made for an opposite direction of traverse of the line frequency and effects of drift were thus cancelled out. In a random way and at the discretion of the observer, the center was measured for a range of widths whose extremes differed by a factor of five though a statistically significant body of data is not available for widths which differ by this large factor. The data for H were taken on eight days and those for D on six. The adjustment of all available parameters (rf circuit, rf amplitude, deflecting fields, beam intensity, etc.) was changed between different days and sometimes within a given day. Data were taken for both directions of traverse of the hairpin by the beam and by five different observers.

For hydrogen the line (1,0; 0,0) was measured. The frequency of the line is very nearly independent of magnetic field at low field, but a small correction, quadratically dependent on field, must be subtracted

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[1] J. P. Wittke and R. H. Dicke, Phys. Rev. **96**, 530 (1954); J. P. Wittke, dissertation, Princeton University, 1955 (unpublished).
[2] A. G. Prodell and P. Kusch, Phys. Rev. **88**, 184 (1952).
[3] Reich, Heberle, and Kusch, Phys. Rev. **98**, 1194 (1955).
[4] R. H. Dicke (private communication).

from the line frequency to determine the zero-field hfs separation. To determine the field, about 0.32 gauss, the frequency of the line (1,0; 1,−1) was measured. The quadratic correction was about 280 cps. For deuterium, the central frequency of a doublet was measured. The doublet is unresolved, and at the fields used in these experiments the separation of the components is about 400 cps. The line of lower frequency, $(\frac{3}{2},\frac{1}{2};\frac{1}{2},-\frac{1}{2})$, and that of higher frequency $(\frac{3}{2},-\frac{1}{2};\frac{1}{2},\frac{1}{2})$ are characterized[5] by matrix elements proportional to the rf amplitude and $(1\pm x)$ respectively. In the present case x, the usual magnetic field parameter, is about 0.0026. If the rf amplitude is less than its optimum value, the component with a larger matrix element will be characterized by both a greater width and a higher probability of transition at the center than will the component of the smaller matrix element. If, however, the rf field is greater than its optimum value, the line of larger matrix element has a lower probability of transition at the center and a greater width than does the other line.

Salwen[6] has given tables of both the transition probability and line width as a function of rf amplitude. It is easily shown that over a considerable range of rf amplitude about its optimum value, the shift of the center of the doublet arising from the differential transition probabilities is wholly negligible (∼1 cps). Atoms with a very low velocity may make such large excusions in their trajectories that they may collide with the surfaces of the deflecting magnets or with other obstacles. In the present case, however, the magnetic moment of atoms in the terminal states of the two transitions are so nearly identical that no significant loss of intensity in either of the two lines with respect to the other can occur.

For D, the magnetic field was determined from the frequency of the line $(\frac{3}{2},-\frac{1}{2};\frac{3}{2},-\frac{3}{2})$. The quadratic field correction was of the order of 1000 cps.

RESULTS, CORRECTIONS, AND UNCERTAINTIES

The following results are obtained:

$$\Delta\nu(\mathrm{H})=(1420.40573\pm0.00005)\times10^{6}\ \mathrm{sec}^{-1},$$

$$\Delta\nu(\mathrm{D})=(327.384302\pm0.000030)\times10^{6}\ \mathrm{sec}^{-1}.$$

In each case the result depends on the determination of the center of an observed line to about 1 part in 750 of the line width. A detailed consideration of the various uncertainties follows.

(a) *Statistical uncertainty.*—A total of 440 observations was made for H and 360 for D. The probable error of the mean value of $\Delta\nu$ was 12 cps for hydrogen and 6 cps for deuterium. The difference occurs because the H line is broader than the D line, because of a better absolute frequency stability of the oscillator used for D than of that used for H and because uncertainties in the frequency standard have a larger absolute effect on the measurement of the H line than on that of the D line. No statistically significant variation of the result dependent on the observer, rf amplitude, deflecting field, or any other adjustable parameter has been found. A completely independent set of observations for both H and D, with a hairpin somewhat less perfectly shielded than the one finally used, gave a result in both cases within the limits specified above for the final result.

(b) *Magnetic field determination.*—The lines used to determine the magnetic field have a linear frequency dependence on field and the frequency presumably gives an average value of the field over the transition region. The quadratic correction term, however, depends on the average value of the square of the field and it has been assumed that this is equal to the square of the average field. The lines with a linear field dependence had their natural half-width, in the case of D about 25 kc/sec. While no theoretical or experimental investigations of the effects of field inhomogeneity exist, it seems reasonable to assume that the inhomogeneity does not exceed 10% of the total field, which, for D, would give a frequency spread in the line of about 28 kc/sec. If the field is assumed to vary linearly from one end of the hairpin to the other with an extreme variation of 10%, the difference between $\langle H^2\rangle_{\mathrm{Av}}$ and $(\bar{H})^2$ is about 0.075%. If the variation is assumed to be quadratic with a total variation of 10% and a minimum field at the center of the hairpin, the difference is 0.083%. The effect is thus less than 1 cps for D and very much less for H.

A random fluctuation of the field of the order of a few milligauss was noted. The fluctuations were so rapid that a critical measurement of the half-width of the field-dependent line could not be made in a single observation. However, sufficient measurements of the low-frequency, field-dependent line were made to insure that an average applicable to the calculation of the quadratic correction was found.

(c) *Doublet error.*—It is estimated that an upper limit to the displacement of the apparent center of the deuterium doublet from the true center is ±3 cps.

(d) *Overlap error.*—The rf field had a direction relative to that of the constant field such that both σ and π transitions could be excited. Only those lines were observable, however, which correspond to the high-field transitions $\Delta m_J=\pm1$, since the deflecting magnets operate at a field where high-field quantization occurs. Therefore the line (1,1; 0,0) but not the line (1,−1; 0,0) occurs for H. The line (1,1; 0,0), at higher frequency than the line (1,0; 0,0) under observation is separated from it by about 13 line widths. The overlap of the lines then shifts the central frequency at half-intensity of the line (1,0; 0,0) upwards by 8 cps and the true $\Delta\nu$ is then the apparent $\Delta\nu$ reduced by 8±4 cps. In the case of D, the two adjacent σ lines are both observable and symmetrically spaced on either side of the doublet under observation. These lines, therefore, give no overlap

[5] H. C. Torrey, Phys. Rev. **59**, 293 (1941).
[6] H. Salwen (to be published).

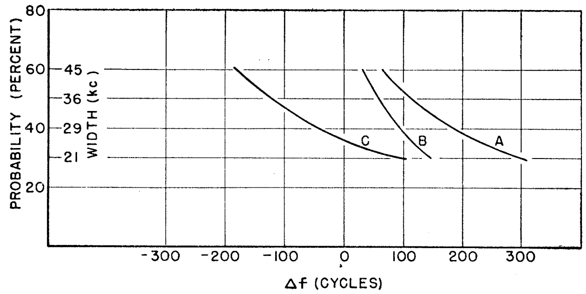

FIG. 1. The shift in the resonance line of hydrogen when the rf amplitude varies linearly. Curves A and B correspond to an optimum value of the amplitude and a 5 and 2.5% variation over 35 kc/sec respectively. Curve C corresponds to an amplitude about 1.3 times the optimum value and a variation of 5% over 35 kc/sec. The sequence in which the widths are shown should be inverted; i.e., a probability of 60% corresponds to a width of 21 kc/sec.

correction. The line $(\frac{3}{2},\frac{3}{2};\frac{1}{2},\frac{1}{2})$ however gives an overlap correction of 1 ± 1 cps.

(e) *Nonconstant* rf *amplitude.*—It is inevitable that some variation of the rf amplitude will occur over the width of the line and this variation may shift the apparent center of the line. The effect may be calculated from Salwen's[6] tabulation of line widths and transition probabilities in a beam which issues from a source containing atoms in thermal equilibrium. In Fig. 1 are shown some results for a resonance line whose natural half-width is 35 kc/sec. The curves A and B are calculated for an optimum rf amplitude at the center of the line and a linear variation of 5 and 2.5% respectively over a range of 35 kc/sec. The line widths which correspond to the probabilities are indicated. The curve C corresponds to an amplitude at the line center of 1.3 times the optimum value and a variation of the amplitude of 5% over 35 kc/sec. It is to be noted that the shift reverses in sign with respect to A and B for the same sign in the change of amplitude and for widths near the half-width. All available evidence suggests that the amplitude did not vary by more than 0.5% over the line width in hydrogen. Moreover, the variation had a variable sign and the rf amplitude at the line center had a variable magnitude from run to run. Accordingly a maximum error of 20 cps at the half-width point is assigned. The data of each run were analyzed to detect a statistically significant variation of $\Delta\nu$ as measured at the narrow and wide portions of the resonance line. In no case was an effect discovered. In the case of H, the 100 observations in the total body of data taken at the smallest widths, with a mean width of 22.7 kc/sec differed in mean frequency from the 100 observations at the greatest width, with a mean width of 40.8 kc/sec by 28 cps. The difference is much less than the statistical uncertainties allow. For hydrogen we allow, however, an uncertainty of ±20 cps arising from the effect under discussion. For deuterium, where the line is narrower we allow ±15 cps.

(f) *Phase change in the hairpin.*—There is no statistically significant variation of the apparent $\Delta\nu$ as the direction of traverse of the beam through the hairpin is reversed. Any effect of a continuous change in phase over the length of the hairpin should average out in the reversal. Nevertheless, an identical traverse in both directions is limited by mechanical tolerances. We assign ±5 cps as a maximum residual error for both H and D.

(g) *Frequency errors.*—Frequent comparison was made of the local frequency standard with WWV and the standard was always within 2 parts in 10^8 of WWV. Because the local standard was frequently reset, the residual error was random in magnitude and presumably in sign. A generous estimate of error arising from the difference between our standard and WWV is, therefore, ±28 cps for H and ±7 cps for D.

In the course of his measurements of the hfs of hydrogen, Wittke[1] has made a study of the possibility of systematic error in the intercomparison of a local standard of frequency and WWV due to a diurnal variation of a Doppler shift in the transmitted signal. He concludes that there is no detectable systematic effect at Princeton, New Jersey and we assume that no significant error occurs in New York. Finally, the signal transmitted by WWV is corrected whenever the deviation from the nominal frequency is greater than 1 part in 10^8. The maximum error for H is thus ±14 cps and for D, ±3 cps.

All the estimates of possible systematic error appear to be rather generous in magnitude. The rms sum of the uncertainties is ±40 cps for H and ±20 cps for D. We, however, give in the final result a somewhat larger uncertainty to allow for an unfavorable accumulation of error.

At the present time the origin of the error in the previous determination of $\Delta\nu(\mathrm{H})$ by the atomic beam method is not clear. It appears, however, that inadequate shielding of the hairpin, with a consequent differential radiation at the two ends may have been responsible for the error. Our present result is in satisfactory agreement with the result, $\Delta\nu(\mathrm{H})=(1420.40580\pm0.00005)\times10^6$ sec^{-1} of Wittke and Dicke. If it is assumed that there is no significant dependence of $\Delta\nu$ on the pressure of the molecular hydrogen into which the atomic hydrogen is mixed, the data of Wittke and Dicke give for $\Delta\nu(\mathrm{H})$ the value 1420.40571 Mc/sec. It is not wholly clear, both from the data and from theoretical estimates, that the pressure dependence of $\Delta\nu(\mathrm{H})$ is as great as found by Wittke and Dicke.

The hyperfine structure anomaly as previously defined[2] and with the same values of the auxiliary constants is now $(1.703\pm0.005)\times10^{-4}$.

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