

On the g_J Values of the Alkali Atoms*

The Hyperfine Structure of the Alkali Atoms

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Measurements have been made on the ratios of the g_J values of the alkali atoms. It is found that the g_J values of Li^6 , Li^7 , Na and K^{39} are identical to within one part in 40,000. The g_J of Rb and Cs , however, are greater than the g_J of the other alkalis by 5 and 13 parts in 100,000 respectively. Effects which modify the g_J value of an atom may be expected to depend on the detailed electronic configuration of an atom. Since the g_J values of Li , Na and K are shown, in present experiments, to be equal, it can be presumed, in view of the different electronic structures of these atoms, that perturbing effects are negligible and that the g_J values of these atoms are, in fact, equal to the electron spin gyromagnetic ratio.

INTRODUCTION

THIS paper describes a precision determination of the ratios of the g_J values of the alkali atoms. The measurement was undertaken because the g_J values of one or more of the alkali atoms enter into the experimental determination of at least two important physical quantities, the spin gyromagnetic ratio of the electron and the gyromagnetic ratio of the proton.

In a recent experiment, Kusch and Foley¹ have measured the spin gyromagnetic ratio of the electron by a determination of the ratios of the total electronic g values of two different atomic energy states. Interpretation of the data of those experiments depends on the assumption that the g_J values are properties of an ideal state and are not characteristic, to a significant extent, of a particular atomic system. In particular, the result depends on the ratio of the g_J of indium in the $^2P_{3/2}$ state to that of sodium in the $^2S_{1/2}$ state and on the ratio of the g_J of gallium in the $^2P_{3/2}$ state to that of sodium in the $^2S_{1/2}$ state. The two ratios yield the same value for the spin gyromagnetic ratio of the electron, and from this agreement it may be inferred that perturbations which affect the g_J values of the two $^2P_{3/2}$ states are identical. Since this is not likely to be the case if the perturbations are large, it follows that the g_J values are very nearly those characteristic of a pure $^2P_{3/2}$ state. In a similar way, if it can be shown that the g_J value of sodium is common to most of the alkali atoms, it can again be assumed that its g_J value is characteristic of a pure $^2S_{1/2}$ state and the interpretation of the result of Kusch and Foley becomes much more significant than it is in the absence of the indicated information.

In the paper following the present paper, Taub and Kusch² present a determination of the gyromagnetic ratio of the proton, g_H , in terms of the g_J value of indium in the $^2P_{3/2}$ state and in terms of the g_J value of caesium in the $^2S_{1/2}$ state. By use of the ratio $g_J(^2P_{3/2}, \text{In})/g_J(^2S_{1/2}, \text{Na})$ previously reported¹ and by use of the ratio $g_J(^2S_{1/2}, \text{Cs})/g_J(^2S_{1/2}, \text{Na})$ reported in this paper, it is possible to find the value of g_H in terms of the g_J of sodium. Since the results of the present experiment indicate that the g_J value of sodium does not deviate to a significant extent from the spin gyromagnetic ratio, it is possible to find the g value of the proton in terms of the spin gyromagnetic ratio of the electron and hence in terms of the fundamental quantity, the orbital gyromagnetic ratio of the electron.

As has been pointed out before, a precision measurement of the absolute value of a gyromagnetic ratio is not feasible with currently available methods, because of the difficulty of producing magnetic fields which are known in terms of absolute standards to a high order of precision. The ratios of g values may, however, be measured with extremely high precision.

The general experimental procedures employed in the measurements here reported are identical to those previously discussed.¹

THE HYPERFINE STRUCTURE OF THE ALKALI ATOMS

In order to determine the ratios of the g_J values of any two atoms by an observation of appropriately chosen lines in the h.f.s. spectra of the two atoms, it is necessary to know the interaction constants which determine the frequencies of the lines in a magnetic field. These constants, when $J = \frac{1}{2}$, are $\Delta\nu$, the zero field separation of the two levels for which $F = I + \frac{1}{2}$ and $F = I - \frac{1}{2}$, and the

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¹ P. Kusch and H. M. Foley, *Phys. Rev.* **74**, 250 (1948).

² H. Taub and P. Kusch, *Phys. Rev.* **75**, 1481 (1949).

TABLE I. Values of $\Delta\nu$ and g_J/g_I .

Atom	$\Delta\nu \times 10^{-6}$ (sec. ⁻¹)	g_J/g_I
Li ⁶	228.208±0.005	-4472±3
Li ⁷	803.512±0.015	-1693.7±0.8
Na ²³	1771.61±0.03	-2487.8±2.5
K ³⁹	461.723±0.010	-14130±100
Rb ⁸⁵	3035.7±0.15	-6853±40
Rb ⁸⁷	6834.1±1.0	-2016±7
Cs ¹³³	9192.76±1.0	-5018±3

ratio g_J/g_I . These quantities can be determined directly from an observation of the h.f.s. spectrum of the atom in question.

For the purposes of this experiment as well as for the requirements of the experiment on the determination of the g value of the proton, the values of $\Delta\nu$ of Li⁶, Li⁷, Na²³, K³⁹ and Cs¹³³ have been redetermined. The $\Delta\nu$ of Li⁶, Li⁷ and K³⁹ have been measured by the method of observing the transitions, $\Delta F = \pm 1$, $\Delta m = \pm 1$ at very weak fields. This method has been extensively discussed by Kusch and Millman.³ We find that the values of $\Delta\nu$ are the following:

$$\begin{aligned} & \text{Li}^6(228.208 \pm 0.005) \times 10^6 \text{ sec.}^{-1} \\ & \text{Li}^7(803.512 \pm 0.015) \times 10^6 \text{ sec.}^{-1} \\ & \text{K}^{39}(461.723 \pm 0.010) \times 10^6 \text{ sec.}^{-1}. \end{aligned}$$

The $\Delta\nu$ of Na²³ and Cs¹³³ are inconveniently high (1770 and 9190 mc) for a direct measurement of this quantity at weak fields. Large $\Delta\nu$ have been determined⁴ in the past by measurement at intermediate fields of lines described by the low field quantum numbers $(F, m) \leftrightarrow (F, m \pm 1)$ or of lines described by the high field quantum numbers $(m_J, m_I) \leftrightarrow (m_J, m_I \pm 1)$. The Breit-Rabi formula, which describes³ the energy levels of an atom in a state in which $J = \frac{1}{2}$, permits a determination from such data of $\Delta\nu$ and of the ratio g_J/g_I . This method is of rather poor precision since a fractional error in the observation of the line frequencies may appear as a much larger fractional error in $\Delta\nu$.

Another procedure, not heretofore employed in the determination of $\Delta\nu$, is, however, available. This procedure depends on the fact that some of the lines $(F, m) \leftrightarrow (F, m \pm 1)$ attain a maximum frequency at characteristic values of the magnetic field. (See, for example, some curves in references 3 and 4, which indicate the dependence of the frequency of such lines on magnetic field.)

The frequency of a line arising from the transition $(I \pm \frac{1}{2}, m) \leftrightarrow (I \pm \frac{1}{2}, m - 1)$ is given by:

$$f = (\Delta\nu/2) \{ [1 + 4mx/(2I+1) + x^2]^{\frac{1}{2}} - [1 + 4(m-1)x/(2I+1) + x^2]^{\frac{1}{2}} \} \pm g_I \mu_0 H/h, \quad (1)$$

where

$$x = (g_J - g_I) \mu_0 H/h \Delta\nu. \quad (2)$$

³ Kusch, Millman, and Rabi, Phys. Rev. **57**, 765 (1940).

⁴ S. Millman and P. Kusch, Phys. Rev. **58**, 438 (1940).

All the lines appear as components of doublets of frequency separation $2g_I \mu_0 H$, except when the magnetic level $m = \pm(I + \frac{1}{2})$ is involved in the transition. The mean frequency of the doublet, f_m , is as given by Eq. (1) except that the term $g_I \mu_0 H$ does not occur. If we call $x_1 = -2m/(2I+1)$ and $x_2 = -2(m-1)/(2I+1)$, the value of x at which f_m has a maximum is given by:

$$x = (x_1 x_2 + 1)/(x_1 + x_2) + [(x_1 x_2 + 1)^2/(x_1 + x_2)^2 - 1]^{\frac{1}{2}}. \quad (3)$$

The value of $f_m/\Delta\nu$ may then be determined by Eq. (1). It can be shown that a maximum occurs only when $-(I - \frac{3}{2}) \leq m \leq 0$, $-(I - \frac{1}{2}) \leq m - 1 \leq -1$. In the case of Na²³ where $I = \frac{3}{2}$, the only line for which a maximum occurs is the line $(F, 0) \leftrightarrow (F, -1)$. For Cs where $I = 7/2$, a maximum will occur for the lines $(F, -2) \leftrightarrow (F, -3)$, $(F, -1) \leftrightarrow (F, -2)$ and $(F, 0) \leftrightarrow (F, -1)$.

From an observation of the maximum mean frequency of a doublet it is thus possible to determine $\Delta\nu$ with the same precision as that with which the frequency has been measured. This method of determining $\Delta\nu$ has a marked advantage over other methods since in the region of field at which the frequency is a maximum, the line frequencies are almost entirely field independent. Accordingly, small inhomogeneities in the magnetic field will not affect the width and shape of the lines. A significant measurement of a line frequency may be made to a precision limited only by the accuracy of the frequency measuring equipment and by the natural width of the lines, and the possibility of systematic error arising from unsymmetrical broadening is avoided. It is not necessary to determine the frequency of the line at precisely the maximum, for $f/\Delta\nu$ varies very slowly with field in the neighborhood of the maximum. Accordingly, from an approximate knowledge of g_J/g_I and from the measured doublet separation $2g_I \mu_0 H$, it is possible to find an approximate value of H . If $\Delta\nu$ is also approximately known, x may be found to a sufficiently good degree of approximation to permit the determination of a new value of $\Delta\nu$ with a precision limited only by the precision of frequency determination. If observations of the frequencies of both components of a doublet are made over a fairly large range of field on either side of the field for maximum frequency, it is possible to determine the value of g_J/g_I ; for if an incorrect value of g_J/g_I is assumed, the calculated value of $\Delta\nu$ will be either an increasing or a decreasing function of field and g_J/g_I may be adjusted until the calculated value of $\Delta\nu$ is independent of field.

For the case of Cs, the maximum mean frequency of the doublet $(F, -2) \leftrightarrow (F, -3)$ occurs at $x = 0.1(11 + (21)^{\frac{1}{2}}) = 1.55926$. At this field and for this line, $2f/\Delta\nu = 0.1((12)^{\frac{1}{2}} - (7)^{\frac{1}{2}})(11 + (21)^{\frac{1}{2}})$ which

gives a mean doublet frequency of about 1485 mc. This is inconveniently high. The maximum mean frequency of the doublet $(F, -1) \leftrightarrow (F, -2)$ occurs at $x = 0.5(3 + (5)^{\frac{1}{2}}) = 2.618034$. At this field, $2f/\Delta\nu = 0.5((5)^{\frac{1}{2}} - 2)(3 + (5)^{\frac{1}{2}}) = 0.27009$. This corresponds to a line frequency of about 1240 mc. The field of 8600 gauss is readily attained in our apparatus.

In the course of three independent runs, twenty-five individual observations were made of the frequencies of each member of the doublet at values of x ranging from 2.4 to 2.75. This range included not only the value of the field at which the mean of the doublet attains a maximum frequency, but included also the fields at which each component of the doublet separately attains a maximum frequency. From the maximum of the mean a value $\Delta\nu = 9192.76 \times 10^6 \text{ sec.}^{-1}$ is obtained. This known value of $\Delta\nu$ permits a calculation to be made, in terms of g_J/g_I , of the maximum frequency of each component of the doublet. We thus find that $g_J/g_I = -5018$. Using this value of the ratio g_J/g_I , the twenty-five values of $\Delta\nu$ calculated from the individual observations give a mean $\Delta\nu$ as stated above with an average deviation of $0.10 \times 10^6 \text{ sec.}^{-1}$. Further, the individually calculated $\Delta\nu$ show no variation with magnetic field as would be expected if the value g_J/g_I had been incorrectly chosen. We take $\Delta\nu(\text{Cs}) = (9192.76 \pm 0.10) \times 10^6 \text{ sec.}^{-1}$ and $g_J/g_I = -5018 \pm 3$. The precision measures attached to the values are considerably greater than the probable error deduced from the internal consistency of the data and are given because of a small uncertainty in the frequency of the quartz crystal against which all frequencies were measured.

As an additional check, measurements have also been made at intermediate fields ($x \sim 0.6$) of the frequencies of the four lines $(F, 3) \leftrightarrow (F, 2)$ and $(F, -2) \leftrightarrow (F, -3)$. From these data we find $\Delta\nu(\text{Cs}) = 9192.51 \times 10^6 \text{ sec.}^{-1}$ and $g_J/g_I = -5017$. The discrepancy between this value of $\Delta\nu$ and the one previously given can be accounted for by an error in the mean frequency of the doublet $(F, 3) \leftrightarrow (F, 2)$ of 1 part in 10^5 . We consider the agreement to be good; the agreement indicates that the frequencies of lines are given by Eq. (1) to a very high order of precision.

Further evidence of the validity of our procedures can be obtained by a comparison of the present result with the ratio $g_I(\text{Cs})/g_I(\text{Li}^7) = 0.33743$ recently measured by Bitter⁵ by use of the nuclear absorption method. All nuclear g values heretofore published, and obtained⁶ by molecular beam methods, assume that the g_J values of the alkali atoms are equal to g_s which is, in turn, assumed to be exactly 2. If we use the previously published value of $g_I(\text{Li}^7)$ and the new value of $g_I(\text{Cs})$ obtained by

TABLE II. Observations from which the ratios of the g_J values of the alkali atoms are calculated.

Run	Atom	Line	Calc. H'
I	Li ⁷	(2, -1) (2, -1)	604.479
		(2, -2) (1, -1)	604.486
II	Li ⁷	(2, -1) (2, -2)	604.460
		(2, -2) (1, -1)	509.088
	Li ⁶	(3/2, -3/2) (3/2, -1/2)	509.090
		Na	(2, -1) (2, -2)
III	Li ⁷	(2, -1) (2, -2)	509.084
		(2, -2) (1, -1)	605.236
	K ³⁹	(2, -1) (2, -2)	605.232
		(2, -2) (1, -1)	605.246
IV	Na	(2, -1) (2, -2)	605.201
		(2, -2) (1, -1)	603.584
	Cs	(F, 1) (F, 0)	603.604
			603.684
V	Na	(2, -1) (2, -2)	603.525
		(2, -2) (1, -1)	603.534
	Cs	(F, 1) (F, 0)	603.583
VI	Na	(2, -1) (2, -2)	603.237
		(F, 1) (F, 0)	603.329
	Cs	(F, 3) (F, 2)	603.305
VII	Na	(2, -1) (2, -2)	603.881
		(F, 1) (F, 0)	603.971
	Cs	(F, 3) (F, 2)	603.957
VIII	Na	(2, -1) (2, -2)	603.930
		(F, -1) (F, -2)	604.001
	Cs	(F, 2) (F, 1)	604.024
IX	Na	(2, -1) (2, -2)	603.707
		(F, 0) (F, -1)	603.724
	Rb ⁸⁷	(F, 1) (F, 0)	603.732
		Rb ⁸⁵	
X	Na	(2, -1) (2, -2)	603.891
		(F, 0) (F, -1)	603.930
	Rb ⁸⁷	(F, 1) (F, 0)	603.941
		Rb ⁸⁵	

making the same assumption about g_J , we find for the ratio the value 0.3375. The agreement of our value with that of Bitter is well within our experimental error and indicates the possibility of obtaining accurate values of the ratio g_J/g_I by the indicated procedures.

For Na the only lines which have a maximum frequency are the components of the doublet $(F, 0) \leftrightarrow (F, -1)$. The mean frequency of the doublet has a maximum at $x = 2 + \sqrt{3} = 3.732$. This corresponds to a field of 2360 gauss. At this field $2f/\Delta\nu = (2 - \sqrt{3})^{\frac{1}{2}}$, and the mean frequency is about 458 mc. The mean of a number of observations in the region of maximum frequency gives $\Delta\nu(\text{Na}^{23}) = (1771.61 \pm 0.03) \times 10^6 \text{ sec.}^{-1}$. The value of $g_I(\text{Na}^{23})$ given by Millman and Kusch⁴ has been used, and we find it to be entirely consistent with our data.

In the experiments to be described in the next section of this paper we use the values of $\Delta\nu$ and g_J/g_I given in Table I. All quantities are taken from previously published work^{3, 4, 6} except where new measurements are presented in this paper.

⁵ F. Bitter, Phys. Rev. **75**, 1326 (1949).

⁶ S. Millman and P. Kusch, Phys. Rev. **60**, 91 (1941).

THE ELECTRONIC g_J VALUES OF THE ALKALI ATOMS

In this section are discussed the results of the intercomparison of the g_J values of the atoms Li^6 , Li^7 , Na^{23} , K^{39} , Rb^{85} , Rb^{87} and Cs^{133} , in their ground states. The general experimental procedures are similar to those previously described.¹ The atomic beam apparatus is fitted with a special oven chamber which permits the rapid interchange of ovens. Suitable lines in the h.f.s. spectrum of each of two alkali atoms are measured in succession at a suitably chosen magnetic field. Since the magnetic field always drifts to some extent during the time required to make the necessary observations, all of the lines are measured several times in rotation and from a suitable reduction of data, line frequencies are found which correspond to some fixed magnetic field. From the observed frequencies of the lines, from the known zero field h.f.s. separation and from the known ratio g_J/g_I , it is possible, by application of Eq. (1), to find the value of $H' = \mu_0 H/h \times 10^{-6}$ at which the lines were observed. The nominal g_J of the atom is assumed in this calculation. If the g_J values of the two atoms depart from their nominal values, g_J^0 , by differential amounts, the values of H' will differ. However, under the conditions of the experiment, H' is the same for both atoms; hence the g_J ratio is adjusted to make H' the same. Suppose that $H_1' - H_2' = \Delta H'$. Then $g_{J1}/g_{J2} = (1 + \Delta H'/H')g_{J1}^0/g_{J2}^0$.

In Table II are recorded the results of the observations of lines in the spectra of each of two alkali atoms at the same value of the magnetic field. The quantity H' has been found by assuming that $g_J = 2$. In the cases of Cs and Rb, H' has been calculated from the mean frequency of the doublet listed in Table II. In the cases of Cs and Rb, the effect of uncertainties in the $\Delta\nu$ is trivial, since the lines are observed in the Zeeman region or in the low intermediate field region and the $\Delta\nu$ enters the calculation only as a small correction term. In cases where two lines, not components of the same doublet, are measured, it is possible, provided g_J/g_I is known, to find H' without prior knowledge of $\Delta\nu$, since the $\Delta\nu$ may itself be calculated from the two observed line frequencies. Adopting this procedure in case *I*, we find $\Delta\nu(\text{Li}^7) = 803.509 \times 10^6$ sec.⁻¹ and $H' = 604.478$. Of the three determinations of the $\Delta\nu$ of Li^7 which are possible from the data of Table II, this one deviates by the largest amount from the previously given value of 803.512×10^6 sec.⁻¹. By comparison of the value of $H' = 604.478$ with the values given for run *I* in Table II, it is seen that the value of H' derived from measurements on the line $(2, -2) \leftrightarrow (1, -1)$ is excessively sensitive to the assumed value of $\Delta\nu$ and the values of H' derived from this line are therefore not used

in further deductions. The same considerations apply to the case of K^{39} , where the internally obtained $\Delta\nu(\text{K}^{39}) = 461.731 \times 10^6$ sec.⁻¹ and $H' = 605.248$. Evidently the very small difference between this value of $\Delta\nu$ and that given in Table I has changed the apparent H' found from the line $(2, -2) \leftrightarrow (1, -1)$ by a very large amount. From the two runs, *IV* and *V*, we find that the $\Delta\nu(\text{Na})$ is 1771.59 and 1771.60×10^6 sec.⁻¹, and here again the line $(2, -2) \leftrightarrow (1, -1)$ is discarded in further deductions. It is to be noted, however, that the very good agreement of the $\Delta\nu$'s calculated from these data with the values more directly obtained is good indication of the validity of the data.

From the runs *I*, *II* and *III* we conclude that the g_J of Li^6 , Li^7 , Na^{23} and K^{39} are identical to within 1 part in 40,000. However, in the runs *IV-VIII* the mean $\Delta H' = H'(\text{Cs}) - H'(\text{Na}) = 0.081 \pm 0.004$. Note that eight different lines in the spectrum of Cs have been measured. We conclude that $g_J(\text{Cs})/g_J(\text{Na}) = 1 + \Delta H'/H' = 1.000134 \pm 0.000007$, where the precision measure is the statistical probable error.

Inspection of the runs *IX* and *X* indicates that $g_J(\text{Rb}) > g_J(\text{Na})$. The apparent discrepancy between the g_J of Rb^{87} and the g_J of Rb^{85} is within the experimental error of the observations. We conclude from these observations that $g_J(\text{Rb})/g_J(\text{Na}) = 1.00005 \pm 0.00001$, where the precision measure is again the statistical probable error.

DISCUSSION

Relativistic effects which influence the g_J value of an electron have been considered by Margenau⁷ and others. The g_J values are reduced by about 1 part in 10^5 and the reduction is roughly the same for all the alkali atoms.^{1,8} The order of magnitude of this effect is too small to be detected in the present experiments.

The fact that the g_J of Li, Na and K are identical seems to indicate that, within the precision of these measurements, the g_J of these atoms is equal to the spin gyromagnetic ratio, g_s . For if perturbations were to affect the value of g_J , they would presumably affect the different atoms by different amounts. The larger g_J values of Rb and Cs presumably arise from some perturbation. The possible origin of such perturbations has been previously discussed.¹ It is not possible, at the present time, to give a quantitative theory of the effect.

We are indebted to Miss Zelda Marblestone who has reduced much of the data used in this series of experiments.

⁷ H. Margenau, Phys. Rev. **57**, 383 (1940).

⁸ M. Phillips, Phys. Rev. **60**, 100 (1941).