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Fine and Hyperfine Structure of the 3^2P Term in Lithium*

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The fine and hyperfine structures of the 3^2p term in Li^7 have been studied by the technique of level-crossing spectroscopy. A preliminary value for the fine-structure separation is $\Delta\nu=2882.9\pm1.2$ Mc/sec. It is expected that the present technique can be extended to obtain a result that is reliable to a few parts per million. It is noteworthy that the fine-structure intervals in lithium are 8% and 12% *smaller* for the $2p$ and $3p$ levels, respectively, than the corresponding intervals in hydrogen. A theory is developed for interpreting the separation between hyperfine level crossings. Its application depends on a detailed knowledge of the core-polarization effects of the $3p$ electron. Evidence is presented indicating that the core-polarization effects in the np states ($n=2$, 3) scale as $\langle 1/r^3\rangle_{np}$ for the valence electron. Assuming this to be true, we estimate that $a_s(3p)=-3.05(12)$ Mc/sec for Li^7. The limited precision achieved so far in this work has prevented observation of the Li^7 quadrupole interaction.

INTRODUCTION

SINCE its discovery in 1959,[1] level-crossing spectroscopy has been a useful technique for investigating atomic fine and hyperfine structures. In particular, a number of experiments have been performed[2] and are in progress[3] on the fine structure of simple atomic systems whose principal goal is an improvement in our knowledge of the fine-structure constant α. The present best value for α is based on the fine structure separation in the 2^2P term in deuterium.[4] In order to obtain a result accurate to about ten ppm, the resonance line had to be split to one thousandth of its natural width ($\approx$100 Mc/sec). The fine structure in the $2P$ state of H is about 10 000 Mc/sec so that the ratio of interval to linewidth is about 100. For the $(1s^23p)3^2P$ term in lithium the fine-structure interval is approximately 2833 Mc/sec and the linewidth about 1.5 Mc/sec with a corresponding ratio of 1900. An evaluation of α from the measured doublet separation in Li, however, depends upon the calculation of precise three-electron wave functions. In addition, important relativistic and radiative corrections have to be evaluated. Finally, the possibility of three-electron interactions must be considered. Despite these difficulties, an experimental value for the lithium fine structure accurate to a few ppm may still serve to stimulate the necessary theoretical work. The most recent value for α has been deduced from measurements on the hyperfine structure of muonium.[5] It is in excellent agreement with the deuterium result.

While we expect that the present technique can yield results with a precision of a few ppm, we are reporting preliminary values for the fine and hyperfine separations since no other values for these splittings have been published. Work is continuing on a precision measurement and will be reported at a later time.

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[1] F. D. Colegrove, P. A. Franken, R. R. Lewis, and R. H. Sands, Phys. Rev. Letters **3**, 420 (1959).

[2] See Ref. 1 and K. C. Brog, Ph.D. thesis, Case Institute of Technology, 1963 (unpublished).

[3] R. T. Robiscoe, Phys. Rev. **138**, A22 (1965).

[4] E. S. Dayhoff, S. Triebwasser, and W. E. Lamb, Jr., Phys. Rev. **89**, 106 (1953).

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THEORY OF THE EXPERIMENT

The theory underlying the level-crossing technique has received excellent and extensive treatment.[6] The experimental apparatus described below consists of a source of resonance radiation, a beam of scattering atoms placed in a magnetic field, and a detection system. The observed signal results from an interference produced in the light scattered from two Zeeman levels when these are made degenerate by varying the magnetic field. The angle between the incident and scattered light determines whether the signal will have a dispersion- or Lorentzian-type shape.

The Zeeman pattern for a ^2P term is reproduced in Fig. 1. Two level crossings are observable. For a system with $L=1$, $S=\frac{1}{2}$ one can solve exactly for the energy levels as a function of magnetic field. The field at which two levels cross is found by equating their energies. In this way one obtains

$$\frac{\mu_0 H}{\Delta\nu}=\frac{g_s+2g_l}{3g_l(g_s+g_l)}, \quad \text{crossing of } P_{3/2}(m_J=-\tfrac{3}{2}) \text{ and } P_{1/2}(m_J=+\tfrac{1}{2}) \qquad (1)$$

and

$$\frac{\mu_0 H}{\Delta\nu}=\frac{g_s+2g_l}{3g_lg_s}, \quad \text{crossing of } P_{3/2}(m_J=-\tfrac{3}{2}) \text{ and } P_{1/2}(m_J=-\tfrac{1}{2}). \qquad (2)$$

In these equations μ_0 is the Bohr magneton, $\Delta\nu$ is the zero-field fine structure interval, and g_s and g_l are the electronic spin and orbit g factors.

In our experiments natural lithium was used both in the atomic beam oven and in the lamp. The natural isotopic abundances are 93% Li^7 and 7% Li^6. The isotope shift of the 3233 Å line has not been measured,[7] and light from Li^7 atoms in the lamp might well be exciting Li^6 atoms in the beam. However, the low abundance of Li^6 scattering atoms is sufficient to depress their contribution to the point where it is completely masked by the Li^7 signal. In any case, the possible line shifts caused by the small contamination of Li^6 are not important for the present level of precision. This conclusion was borne out experimentally as described below.

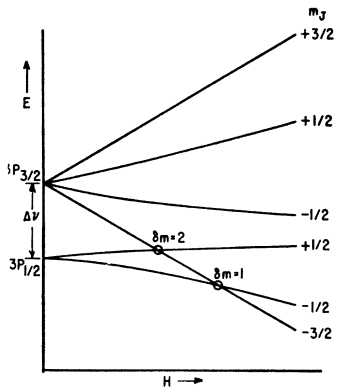

FIG. 1. Zeeman effect on a ^2P term. The observable level crossings are indicated by circles.

The Li^7 nucleus has a spin of $\frac{3}{2}$. The magnetic field at which the experiment is performed is sufficient to uncouple I and J so that only their projections on the field direction are good quantum numbers. Consequently, each of the m_J crossing levels consists of four closely spaced levels. Interference signals from only four of the sixteen crossings are observable since the nuclear and electronic motions are uncoupled and the photon interacts with the electronic structure. Hence the selection rule $\Delta m_I=0$.

At a field, H_c, for which crossing would occur in the absence of nuclear spin, two hyperfine states still have an energy separation given approximately by $\delta=am_Im_J-a'm_Im_J'$. They can be made to cross by adding or subtracting a small field increment ΔH, given by $\delta=\Delta H(\partial E/\partial H)_{H_c}$. Here E represents the energy difference between crossing levels in the absence of hyperfine structure. The crossing field for a pair of levels with the same value of m_I is then

$$H(m_I)=H_c+\Delta H=H_c+[m_I(am_J-a'm_J')]/(\partial E/\partial H)_{H_c}. \qquad (3)$$

The actual expression for the energy increment, δ, is more complicated owing to state mixing by the Zeeman and hyperfine operators and is given in the section below entitled Discussion.

EXPERIMENTAL APPARATUS AND PROCEDURE

The apparatus consists of a cylindrical vacuum jacket, fabricated of copper, and placed at the center of a 12-in. Harvey-Wells electromagnet (model L-128). Figure 2 shows a schematic side view of the apparatus, which is three inches in breadth and fits snugly into the magnet gap. The field is applied perpendicular to the plane of the incoming and scattered light and is homogeneous to about one part in 10^5 over the scattering region (a few cubic centimeters). Modulation coils are provided for lock-in detection of the crossing signal. The beam source is a conical molybdenum oven positioned about one-half inch below the scattering region. The beam effuses through a one-half inch diameter multichanneled aperture[8] at the top of the oven and is collected on a liquid nitrogen trap after passing vertically through the scattering chamber. This arrangement of tiny openings produces a dense, collimated beam, with an estimated density of at least 5×10^{12} atoms/cc at a beam oven temperature of about

[6] P. A. Franken, Phys. Rev. **121**, 508 (1961); M. E. Rose and R. L. Carovillano, *ibid.* **122**, 1185 (1961).

[7] R. H. Hughes, Phys. Rev. **99**, 1837 (1955).

[8] J. A. Giordmaine and T. C. Wang, *Quantum Electronics*, edited by C. H. Townes (Columbia University Press, New York, 1960), p. 67.

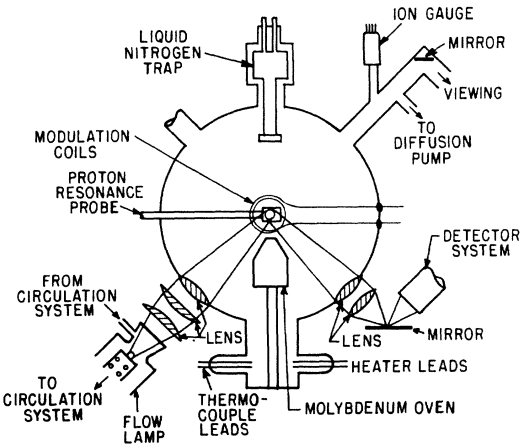

FIG. 2. Schematic diagram of level-crossing apparatus.

500°C. Residual pressure no greater than 3×10^{-5} Torr is maintained in the apparatus.

Light from a flow-type lamp[9] is incident and scattered at an angle of 45° to the direction of the atomic beam and the horizontal (see Fig. 2). The optimum lamp oven operating temperature was found to be 625°C for production of the 3233-Å line. The power in the rf discharge was typically 20 W at 26 Mc/sec. Spectroscopically pure neon was circulated at a pressure of 1.0–1.5 Torr. The source is imaged at the center of the apparatus with the arrangement of three $f/1.5$ quartz lenses shown in Fig. 2. The light is scattered by the atomic beam about one-half inch above the top of the oven and passes out through another set of quartz lenses as indicated in the figure. After reflection from a metallic mirror, the light travels through an aluminized light pipe to the photodetector (a Dumont No. 7664 photomultiplier). A mirror arrangement also permits the incident and scattered light to be viewed directly. A narrow-band interference filter at 3233 Å or a Shott UG-11 color filter was placed in the light path. The UG-11 filter has a considerably broader bandwidth than the interference filter, but provides higher transmission at the peak wavelength. It proved to be more satisfactory. The multiplier signal was passed through a phase-sensitive detector and displayed on a servo recorder.

Coating of the inner lens surfaces by atoms scattered out of the lithium beam presented a major difficulty in the experiment. A few monolayers severely cut down uv transmission. This effect limited the time available for observation to about four hours. At the end of this period the apparatus had to be taken apart, the lenses cleaned, and everything reassembled. The 45° geometry shown in Fig. 2 was chosen to minimize the rate of lens coating.

Several effects are present which may lead to systematic errors. These are magnetic perturbations, magnetic field offset, field inhomogeneity, and magnetic scanning of the lamp profile. We consider them in this order. By using bifilar current-carrying elements within the beam oven and by spot welding these with nonmagnetic constantan jumpers, we minimized magnetic fields produced by the heaters. Such stray field perturbations are expected to be no greater than a few parts in 10^5. The field difference between the positions of the NMR probe and the scattering region of the beam is no more than two parts in 10^5. This was determined from previous mapping measurements of the magnetic field in both horizontal and vertical directions in and near the median plane between the pole pieces of the magnet. The mapping measurements also indicate that the field produced by the Harvey-Wells magnet is homogeneous to about one part in 10^5 over a few cubic centimeters. Theoretical estimates of the lamp profile indicate that the lamp intensity is constant over the crossing region. Therefore, none of the known systematic errors can cause changes in the crossing fields of more than a few parts in 10^5. This falls within the random error of our results.

EXPERIMENTAL RESULTS

The 3^2P state of lithium was first detected by observing the zero-field level crossing (Hanle effect) with a signal-to-noise ratio of approximately 100:1. The Hanle effect in the 2^2P state was also studied. On the basis of the lifetimes estimated on the Bates and Damgaard Coulomb-approximation method,[10] the linewidths were expected to be in the ratio 1:7. A ratio of 1:6 was actually observed though no attempt was made to optimize the amplitude of the modulating field for each state.

Figure 3 shows the four low-field hyperfine crossings superimposed on the fine-structure crossing. Four well-resolved dispersion-type curves with a peak-to-peak separation of approximately 2.4 kc/sec can be seen. Markers give the NMR magnetometer frequency in kc/sec for protons in a mineral-oil sample. The crossing field is determined from the center of the pattern at which the hyperfine crossings would coalesce if there were no hyperfine interaction. The position of the center is obtained by averaging the positions of the four individual crossings. It is important to note here that the lithium used in the beam source was a natural sample containing about 6% of Li^6. No distortion of the crossing pattern due to the presence of the Li^6 was observed.[11] The crossing field H_c and the separation

[9] B. Budick, R. Novick, and A. Lurio, Appl. Opt. 4, 229 (1965).

[10] D. R. Bates and A. Damgaard, Phil. Trans. Roy. Soc. London A242, 101 (1949).

[11] Brog's measurements on the $2P$ state [see Ref. 2] show that the pattern for Li^6 ($I=1$) contains three crossings at approximately the positions of the two central crossings in the Li^7 pattern. If the Li^6 pattern were superimposed on the Li^7 pattern with sufficient intensity to cause distortion, the central Li^7 crossings would display a larger amplitude than the outside crossings. However, all crossings were observed to have equal amplitudes.

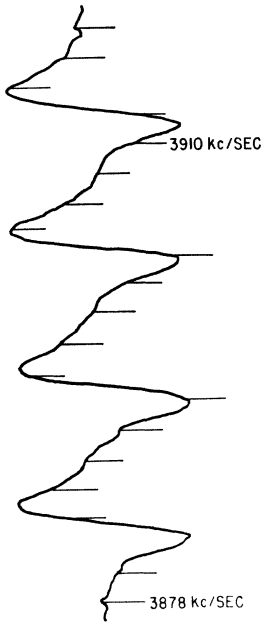

FIG. 3. Level-crossing signal observed in Li^7 $3P$ state. The markers and numbers in the figure refer to proton NMR magnetometer readings.

of adjacent hyperfine crossings $(\Delta H)_c$ were found to be

$$H_c = 3897.2 \pm 0.2 \text{ kc/sec},$$
$$(\Delta H)_c = \quad 9.62 \pm 0.20 \text{ kc/sec}.$$

The quoted uncertainty in H_c is the standard deviation for five curves. The magnetic field was swept both up and down through the level crossing and the results averaged to eliminate sweep corrections. The uncertainty in ΔH_c is twice the average deviation for five curves. This factor of two is intended to allow for the possible shifts resulting from overlap of adjacent crossings.

We deduce the $3P$ doublet separation from Eq. (1), which expresses the relation between the crossing field and the fine-structure splitting. With

$$H_c = 915.30 \pm 0.05 \text{ G},$$
$$g_s = 2 \ (1.00116),$$
$$g_l = 1,$$

we obtain

$$\Delta\nu \ (3P \text{ state of } Li^7) = 2882.9(12) \text{ Mc/sec}$$
$$= 0.09616(4) \text{ cm}^{-1},$$

where the uncertainty has been increased to allow for the possible effect on g_l of the finite mass of the nucleus.[12] With further refinements in technique it should be possible to determine the crossing fields to a few parts in 10^6. We have also observed anticrossings in the $3P$ state similar to those reported by Eck, Foldy, and Wieder[13] for the $2P$ state of lithium.

[12] The specific-mass effect appears to be much smaller than the normal-mass effect; cf., R. H. Hughes, Phys. Rev. **99**, 1837 (1955).

[13] T. G. Eck, L. L. Foldy, and H. Wieder, Phys. Rev. Letters **10**, 239 (1963).

DISCUSSION

The fine structure separations in lithium are 8% and 12% *smaller* for the $2P$ and $3P$ levels, respectively, than the corresponding intervals in hydrogen (see Table I). At first glance this result is surprising for

TABLE I. Fine structure intervals in hydrogen and lithium (cm^{-1}).

	H	Li
$2P$	0.366	0.33534
$3P$	0.1084	0.09616

two reasons. One would have expected an effective nuclear charge larger than one for lithium and hence a larger fine-structure interval. In addition, any deviations from the hydrogen value caused by penetration of the K shell should be smaller for the $3P$ state than for the $2P$ state. However, a number of interactions other than shielding are present in a three-electron atom which could easily reverse these expectations. Some of them are discussed by Blume and Watson.[14]

Part of the motivation for the present experiment was the hope that with the narrow linewidths obtainable in the $3P$ state, contributions of the nuclear quadrupole interaction to the hyperfine-structure separations would be observable. Simple estimates of such contributions based on previously reported values for the Li^7 quadrupole moment[15,16] show that the quadrupole interaction is about $\frac{1}{10}$ Mc/sec. Since the precision achieved in the present work is about one megacycle per second, quadrupole effects are not observable, and discussion of them will be reserved for a later paper dealing with more precise measurements.

Some knowledge of the magnetic hyperfine interactions in the $3P$ state can be obtained from the observed splitting of the level-crossing signals. Since the observations were made in a field large enough to cause substantial mixing of the $^2P_{3/2}$ and $^2P_{1/2}$ states, it is convenient to discuss the hyperfine interaction in a representation in which the fine-structure and electronic Zeeman operators are diagonal. Thus the zeroth-order Hamiltonian is taken as

$$\mathcal{H}_0 = \xi \mathbf{l}\cdot\mathbf{s} + g_J\mu_0 \mathbf{J}\cdot\mathbf{H}. \quad (4)$$

A representation in which this operator is diagonal was used to find the matrix elements of the hyperfine and nuclear Zeeman operators.

$$\mathcal{H}' = g_I\mu_0 \mathbf{I}\cdot\mathbf{H} + \mathfrak{y}_N \cdot \mathbf{H}_e, \quad (5)$$

[14] M. Blume and R. E. Watson, Proc. Roy. Soc. (London) **A270**, 127 (1962).

[15] H. Wieder, Ph.D. thesis, Case Institute of Technology, 1964 (unpublished).

[16] L. Wharton, L. P. Gold, and W. Klemperer, J. Chem. Phys. **37**, 2149 (1962) and Phys. Rev. **133**, B270 (1964); S. L. Kahalas and R. K. Nesbet, Phys. Rev. Letters **6**, 549 (1961) and J. Chem. Phys. **39**, 529 (1963).

where $\mathbf{H}_e$ is the electronic magnetic field at the nucleus. This includes contributions from the orbital and spin motion of the $3P$ electron as well as spin contributions from the core electrons (core polarization). The nuclear Zeeman effect does not contribute to the splitting because of the $\Delta m_I=0$ selection rule. In view of the limited precision of the present experiment, it is sufficient to consider only the matrix elements of the hyperfine operator which are diagonal in the $\mathcal{H}_0$ representation (see above). We use first-order perturbation theory to evaluate the position of each crossing and hence the interval between crossings. In this approximation all of the intervals are equal and are given by

$$\Delta H_c=\left(\frac{\partial E}{\partial H}\right)_{H_c}^{-1}[-(50/33)a_{3/2}(p)-(16/33)a_{1/2}(p) -(5/33)\xi a_{3/2}(p)-(6/11)a_c]. \quad (6)$$

Here $a_{3/2}(p)$ and $a_{1/2}(p)$ are the hyperfine constants for the $^2P_{3/2}$ and $^2P_{1/2}$ states, respectively, in the absence of core polarization, ξ is the ratio of radial integrals defined by Schwartz,[17] and a_c is the core-polarization interaction constant. The result given in Eq. (6) includes the effect of off-diagonal core polarization matrix elements. Goodings[18] has shown that the hyperfine interaction constants for the $^2P_{3/2}$ and $^2P_{1/2}$ states are given by

$$a_{3/2}=a_{3/2}(p)+a_c,$$
$$a_{1/2}=a_{1/2}(p)-a_c, \quad (7)$$

and $a_{1/2}(p)=5a_{3/2}(p)$. Thus the spacing between hyperfine crossings can be expressed as a linear combination of $a_{3/2}(p)$ and a_c. From tables given by Kopfermann[19] and formulas given by Schwartz[17] we find $\xi=1.00006$, and from the theory of the electronic Zeeman effect

$$(\partial E/\partial H)_{H_c}=-(24/11)\mu_0=-3.05\ (\text{Mc/sec})/\text{G}. \quad (8)$$

In terms of these parameters the spacing is

$$\Delta H_c=(1/\mu_0)\tfrac{1}{8}[15a_{3/2}(p)+2a_c]. \quad (9)$$

The theoretical expressions for the hyperfine splittings are identical for the $2p$ and $3p$ states. From the present results we find that

$$(1/\mu_0)\tfrac{1}{8}[15a_{3/2}(p)+2a_c]_{3p}=2.26(5)\ \text{G},$$

and from the work of Wieder[15]

$$(1/\mu_0)\tfrac{1}{8}[15a_{3/2}(p)+2a_c]_{2p}=7.67(1)\ \text{G}.$$

Comparison of these results shows that the ratio of the hyperfine intervals in the two states is very closely equal to the ratio of the fine-structure intervals.[20] The numbers are 0.294(7) and 0.2868(2) for the two ratios, respectively. This strongly suggests that all of the hfs interactions scale as $\langle 1/r^3\rangle_{np}$. We are therefore led to the conclusion that a_c scales as $\langle 1/r^3\rangle_{np}$.

Ritter[21] has recently determined the hfs of the $2^2P_{1/2}$ state of Li^7 by an optical double resonance technique and found that $a_{1/2}=46.17(35)$ Mc/sec. Using this value and the observed hfs splitting of the $2P$ level-crossing signal, Wieder[15] finds that $a_c=-10.5(3)$ Mc/sec for the $2P$ state of Li^7. In accordance with our hypothesis that the hfs interactions scale as $\langle 1/r^3\rangle_{np}$, we find that[22] $a_c=-3.05(12)$ Mc/sec for the $3P$ state of Li^7. By combining this estimate with the observed hfs splitting of the $3P$ level-crossing signal, we can evaluate the other hfs constants for this state. These constants and the corresponding constants for the $2P$ state of Li^7 are listed in Table II.

TABLE II. Magnetic hyperfine interaction constants for Li^7 (Mc/sec).

Constant	$2P$[a]	$3P$[b]
a_c	−10.5(3)	−3.05(12)
$a_{1/2}$	+46.17(35)	+13.5(2)
$a_{3/2}$	−3.36(30)	−0.96(13)

[a] See Refs. 15 and 21.
[b] These values are based on the hypothesis that the constants scale as $\langle 1/r^3\rangle_{np}$ (see text) and that $a_{1/2}$ is positive.

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[17] C. Schwartz, Phys. Rev. **97**, 380 (1955).
[18] D. A. Goodings, Phys. Rev. **123**, 1706 (1961).
[19] H. Kopfermann, *Nuclear Moments* (Academic Press Inc., New York, 1958).
[20] T. Eck (private communication).
[21] G. J. Ritter, Can. J. Phys. **43**, 770 (1965).
[22] The value given for a_c is the average of values obtained by using the ratios of the hfs and fine-structure intervals.