The Nuclear Spin of Li^7 from Hyperfine Structure Data

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Theoretical patterns for the 5485($1s2s\ ^3S-1s2p\ ^3P$) line of Li II have been calculated assuming nuclear spin values of 3/2, 2 and 5/2 in units of $h/2\pi$. Comparison of experimental measurements of Schüler and of Granath confirm the previously accepted value of $i=3/2$ for the spin of Li^7. It is also shown that $i=5/2$ can be excluded and that $i=2$ is quite improbable. The calculation follows the method used by Güttinger and Pauli and includes the 6 percent correction for the effect of the $2s$ electron worked out by Breit and Doermann.

A KNOWLEDGE of the nuclear angular momenta and magnetic moments is essential for the formation of a theory of nuclei. One of the methods available at present for obtaining this information is the study of the hyperfine structure (hfs) of the spectral lines.

The λ(5485) ($1s2s\ ^3S-1s2p\ ^3P$) line of Li II is of special interest because the electronic configurations are sufficiently simple to make possible absolute calculations of the nuclear magnetic moment. Its hfs has been investigated experimentally by Schüler[1] and by Granath.[2] Güttinger[3] and Güttinger and Pauli[4] having compared theoretical calculations for $i=3/2$ with Schüler's measurements conclude that either the spin of Li^6 is zero or that it has a small magnetic moment, and that the spin of Li^7 is 3/2.

The work of Güttinger involves the assumption that the interaction between the nuclear magnetic field and the external electrons takes place only through the more closely bound s electron, and does not take into account the fact that the gross multiplet structure and the hfs are of the same order of magnitude. The effect of the latter is considered by Güttinger and Pauli.

For the $i=2$ and the $i=3/2$ the agreement between experiment and a theory like Güttinger's is such that one cannot be sure that it could not be improved upon by considering perturbations between hyperfine levels having the same f as was done by Güttinger and Pauli for $i=3/2$. For this reason Güttinger and Pauli's conclusion about the spin of Li^7 was not considered to be conclusive. Heretofore no calculations have been published considering both these perturbations and the 6 percent correction in the coupling factor for the S state due to the $2s$ electron.[5]

Granath's measurements on the interval ratio of the ^3S level indicate directly that the spin of Li^7 is 3/2. Since only a very few exact measurements of the interval have been made so far it was felt that the theory should be compared with experiment as accurately as possible for the ^3P levels also.

The present paper takes into account the perturbations of Güttinger and Pauli as well as the interaction of both electrons with the nuclear magnetic field for the S state. The spins $i=3/2$, 2, 5/2 are considered so that a more satisfactory decision concerning the spin of the Li^7 nucleus can be made.

Nonrelativistically, the interaction energy between an electron and the nucleus may be taken to be[5] (see end of paper for definition of symbols).

[1] H. Schüler, Zeits. f. Physik **42**, 487 (1927); **66**, 432 (1930).

[2] L. P. Granath, Phys. Rev. **36**, 1018 (1930); **42**, 44 (1932).

[3] P. Güttinger, Zeits. f. Physik **64**, 749 (1930).

[4] P. Güttinger and W. Pauli, Zeits. f. Physik **67**, 743 (1931).

[5] G. Breit and F. W. Doermann, Phys. Rev. **36**, 1732 (1930).

$$H'=\frac{(e/mc)(\mathbf{L}\mathfrak{y})}{1+(E-mc^2+eA_0)/2mc^2}\frac{1}{r^3}+\frac{hec/2\pi}{E+mc^2+eA_0}\left\{-\frac{(\mathfrak{y}\mathbf{S})}{2r^3}+\frac{3(\mathbf{r}\mathbf{S})(\mathbf{r}\mathfrak{y})}{2r^5}\right\}$$
$$+\frac{(hec/2\pi)e|\mathcal{E}|}{(E+mc^2+eA_0)^2}\left\{\frac{(\mathfrak{y}\mathbf{S})}{2r^2}-\frac{(\mathbf{r}\mathbf{S})(\mathbf{r}\mathfrak{y})}{2r^4}\right\}. \quad (1)$$

The last term matters only for s electrons in which case the first two terms may be neglected. For non-s electrons the last term vanishes and the first two survive.

For two electrons we consider the interaction energy to be a sum of two parts $H_1'+H_2'$ one for each electron. According to Breit and Doermann this interaction energy leads to the following expression for the energy differences if we neglect perturbations between terms with the same f and different j:

$$\Delta W=(\tilde{A}/2)[f(f+1)-i(i+1)-j(j+1)]$$

where

$$\tilde{A}(^3S_1)=(8\pi/3)(1+\epsilon)[g(i)\mu_0^2/1840]\psi_s(0)^2,$$
$$\tilde{A}(^3P_1)=[(4\pi/3)\psi_s(0)^2+\overline{2(r^{-3})_p}]g(i)\mu_0^2/1840,$$
$$\tilde{A}(^3P_2)=[(4\pi/3)\psi_s(0)^2+(4/5)\overline{(r^{-3})_p}]g(i)\mu_0^2/1840.$$

Here $1+\epsilon=1.06$. ϵ is due to the $2s$ electron. $\overline{(r^{-3})_p}$ is an average of r^{-3} over the motion of the p electron. The terms in (r^{-3}) are relatively small in these formulas amounting, according to approximate estimates, to 2 percent and 1 percent of $\tilde{A}(^3P_1)$ and $\tilde{A}(^3P_2)$, respectively. They arise from the first two terms in Eq. (1). We suppose therefore that these terms in Eq. (1) may be neglected also for the calculation of nondiagonal elements. This approximation amounts qualitatively to neglecting the interaction of the p electron with the nuclear magnetic field.

According to the calculations of Breit[6] for the ^3P state and of Breit and Doermann[5] for the ^3S state the antisymmetric coordinate functions can be represented sufficiently well by $\psi_{1s}(1)\psi_{2s}(2)-\psi_{1s}(2)\psi_{2s}(1)$ for the S state and by $\psi_{1s}(1)\psi_{2p}(2)-\psi_{1s}(2)\psi_{2p}(1)$ for the ^3P state where ψ_{1s} is practically the same in both cases. Qualitatively this is due to the smallness of the screening due to the $2s$ and $2p$ electrons. Thus these calculations give the ratio of the hfs splittings of the ^3S, $^3P_1$, $^3P_2$ terms which would exist if the hfs were small compared with the gross structure. For the ^3P terms this amounts to knowing the diagonal terms of the matrix for $H'=H_1'+H_2'$ in a representation with $\mathbf{L}^2$, $\mathbf{S}^2$, $\mathbf{J}^2$, $\mathbf{F}^2$, $\mathbf{F}_z$ diagonal in terms of the hfs splitting of ^3S.

The calculations of Güttinger and Pauli may be looked at as determining the ratios of the nondiagonal elements of H' for the ^3P level to the diagonal ones as long as the interaction may be replaced by $A(\mathbf{Is})$ where $\mathbf{s}$ is the total spin vector. These nondiagonal elements are labeled with the same $\mathbf{F}^2$ but different $\mathbf{J}^2$. Supposing for the moment that one can justify the replacement by $A(\mathbf{Is})$, where A is a suitably chosen constant, we may look at A as being determined for ^3P by the calculations of Breit and of Breit and Doermann in terms of $\tilde{A}(^3S_1)$ by the requirement that the diagonal elements should have the ratios found by them. This requirement can be expressed by simple formulas making use of the fact that the diagonal elements of $\mathbf{BI}$, where $\mathbf{B}$ is any matrix vector involving only electronic variables, are given by $(\tilde{A}/2)[f(f+1)-j(j+1)-i(i+1)]$ where $\tilde{A}=(\mathbf{BJ})_j/j(j+1)$. For $\mathbf{B}=\mathbf{As}$ we have $\tilde{A}=A[j(j+1)+s(s+1)-l(l+1)]/2j(j+1)$. For the ^3P terms $s=l$ and $\tilde{A}=A/2$. For the ^3S terms similarly $\tilde{A}=A$.

The use of $A(\mathbf{Is})$ instead of the complete perturbation function may be justified by making use of; (a) the smallness of the coupling of the p electron to the nuclear magnetic field, (b) the spherical symmetry of the orbital functions of the s electron, (c) the Russell-Saunders coupling for the configurations dealt with. It follows from (a) that the operations due to H' on the eigenfunctions of the p electron may be set equal to zero and the matrix elements can involve only the properties of radial functions of the s electron functions. Making use of (c) it is found by direct

[6] G. Breit, Phys. Rev. **36**, 385 (1930).

calculation that any operator $\mathbf{D}_1\mathbf{s}_1+\mathbf{D}_2\mathbf{s}_2$ may be replaced by $(1/2)(\mathbf{D}_1+\mathbf{D}_2)(\mathbf{s}_1+\mathbf{s}_2)$. This reduces the part $(\mu\mathbf{s})/r^2$ of the third term of Eq. (1) directly to the form $[f(r_1)+f(r_2)]\mathbf{I}(\mathbf{s}_1+\mathbf{s}_2)$ which leads to the form $A(\mathbf{Is})$ on performing radial integrations. Finally by using (b) the terms $(\mathbf{rs})(\mathbf{r}\mu)/r^4$ of the third term of Eq. (1) reduce to the same result. Thus in our calculations for the ^3P states we take the interaction energy due to the nuclear magnetic field to be $H'=A(\mathbf{Is})$, $A=(4\pi/3)\psi_s(0)^2g(i)\mu_0^2/1840$ and consider $g(i)\psi_s(0)^2$ to be determined by $(\tilde{A}\,^3S_1)$.

Following the method of Güttinger and Pauli the ^3P term is now discussed taking into account simultaneously its multiplet and hyperfine structures. The representation in which $\mathbf{L}^2$, $\mathbf{S}^2$, $\mathbf{J}^2$, $\mathbf{F}^2$, F_z are diagonal is used. The part of the Hamiltonian which does not involve the nuclear spin is then diagonal also. Its values for different j are called $F(j)$. Only the differences in the values of $F(0)$, $F(1)$, $F(2)$ are of interest to us, and they are directly obtainable from the Li^6 isotope. The part of the matrix of the whole Hamiltonian which involves the ^3P levels may thus be taken to be $H=F(j)+A(\mathbf{Is})$. We take $F(0)=0$ and using the data of Schüler on Li^6 we have $F(1)=-5.15$ cm^{-1} and $F(2)=-3.05$ cm^{-1}. For A we use Granath's measurements on the components (1), (2), (3). These are due to transitions from $^3P_0$ to $^3S_1$ and give directly the intervals of $^3S_1$. Granath's measurements give an interval ratio for ^3S which agrees with $i=3/2$. For $i\neq 3/2$ we obtain two possible values of A depending on whether we use his (1), (3) or (2), (3) interval. The values of A are given in Table I.

TABLE I. *The numerical values of the coupling factor A.*

	From $\Delta W(1,3)$ $=1.06$ cm^{-1}	From $\Delta W(2,3)$ $=0.66$ cm^{-1}
$i=1$	0.333 cm^{-1}	0.313 cm^{-1}
$i=3/2$	0.250	0.250
$i=2$	0.200	0.208
$i=5/2$	0.167	0.179

The energies, frequencies, etc., may be computed approximately neglecting the effect of the matrix elements of H which are not diagonal in j. In this case we call them "unperturbed." If the calculations are made accurately, i.e., if the nondiagonal elements of H are taken into account all the quantities will be called "perturbed" because the perturbations between levels with different j are taken into account. The calculations are very similar to those of Güttinger and Pauli. The results are given in Table II.

The frequencies in Tables II and III should be increased by 18,200 cm^{-1}.

It is seen from Table II that the calculation of Goudsmit and Inglis[7] showing that the

[7] S. Goudsmit and D. R. Inglis, Phys. Rev. **37**, 328 (1931).

TABLE II. *Frequencies ν and relative intensities I for complete patterns.*

	$i=1$		$i=3/2$			$i=2$							$i=5/2$						
	Unperturbed $A=0.333$ cm^{-1} from $\Delta W(1,3)$ ν cm^{-1}	I	Perturbed $A=0.250$ cm^{-1} ν cm^{-1}	I		Unperturbed $A=0.200$ cm^{-1} from $\Delta W(1,3)$ ν cm^{-1}	I	Perturbed $A=0.200$ cm^{-1} from $\Delta W(1,3)$ ν cm^{-1}	I	Perturbed $A=0.208$ cm^{-1} from $\Delta W(2,3)$ ν cm^{-1}	I		Unperturbed $A=0.167$ cm^{-1} from $\Delta W(1,3)$ ν cm^{-1}	I	Perturbed $A=0.167$ cm^{-1} from $\Delta W(1,3)$ ν cm^{-1}	I	Perturbed $A=0.179$ cm^{-1} from $\Delta W(2,3)$ ν cm^{-1}	I	
c	31.31	0.67	31.31	0.79	(3)	31.31	1.20	31.31	0.96	31.31	0.94	(3)	31.31	1.33	31.31	1.06	31.31	1.04	(3)
b	30.96	2.00	30.91	1.78	(2)	30.89	2.00	30.89	1.87	30.88	1.79	(2)	30.87	2.00	30.87	1.84	30.84	1.82	(2)
a	30.25	3.33	30.25	3.42	(1)	30.25	2.80	30.25	3.22	30.22	3.26	(1)	30.25	2.67	30.25	3.11	30.18	3.16	(1)
i	27.76	3.33	27.89	1.83		27.96	2.10	27.96	1.44	27.95	1.41		28.01	1.87	28.02	1.22	27.99	1.18	
f	27.74	7.50	27.81	5.03	(4)	27.84	5.60	27.85	4.41	27.84	4.36	(4)	27.86	5.14	27.87	4.03	27.84	3.98	(4)
l			27.68	2.36		27.76	2.70	27.75	2.41	27.72	2.40		27.80	2.80	27.79	2.42	27.75	2.40	
t						27.66	1.20	27.63	1.20	27.60	1.20		27.68	2.00	27.59	2.00	27.60	2.00	
d	27.53	14.00	27.55	12.00		27.60	10.80	27.57	10.80	27.55	10.80	(5)	27.62	10.00	27.65	10.00	27.54	10.00	(5)
h	27.41	2.50	27.49	3.65	(5)	27.54	3.50	27.54	3.87	27.52	3.90		27.57	3.66	27.58	3.97	27.52	4.00	
k			27.28	0.64		27.34	0.90	27.32	1.19	27.29	1.21		27.36	1.20	27.35	1.55	27.28	1.60	
e	27.03	2.50	27.15	3.98	(6)	27.20	2.80	27.21	3.99	27.18	4.03	(6)	27.24	2.86	27.25	3.99	27.18	4.08	(6)
g	26.70	0.17	26.83	0.53		26.90	0.40	26.90	0.67	26.86	0.69		26.95	0.48	26.96	0.78	26.86	0.80	
q	25.99	2.00	25.94	3.39		26.06	2.70	25.96	3.59	25.95	3.64		26.08	2.80	25.98	3.69	25.95	3.75	
n	25.98	2.50	25.88	3.98	(8)	25.94	2.80	25.86	3.99	25.86	4.03	(8)	25.93	2.86	25.92	3.93	25.83	4.03	(8)
s			25.81	0.63		25.86	0.90	25.81	1.19	25.79	1.21		25.87	1.20	25.82	1.56	25.79	1.60	
p	25.64	1.50	25.54	0.58		25.64	0.50	25.54	0.30	25.52	0.31		25.64	0.34	25.54	0.18	25.48	0.17	
r	25.48	2.00	25.41	2.37	(13)	25.44	2.70	25.39	2.42	25.36	2.40	(13)	25.43	2.80	25.38	2.42	25.32	2.40	(13)
m	25.27	7.50	25.22	5.02	(9)	25.30	5.60	25.23	4.41	25.20	4.36	(9)	25.31	5.14	25.30	4.03	25.17	3.94	(9)
o	24.93	2.50	24.88	2.03	(10)	25.00	2.80	24.90	2.09	24.86	2.07	(10)	25.02	2.86	24.92	2.10	24.82	2.03	(10)

TABLE III. *Schüler's experimental data and theoretical "unresolved" patterns.*

Schüler's exp.			$i=3/2$		$i=2$				$i=5/2$			
			$A=0.250$ cm^{-1}		$A=0.200$ cm^{-1} from $\Delta W(1,3)$		$A=0.208$ cm^{-1} from $\Delta W(2,3)$		$A=0.167$ cm^{-1} from $\Delta W(1,3)$		$A=0.179$ cm^{-1} from $\Delta W(2,3)$	
	ν cm^{-1}	I	ν cm^{-1}	I	ν cm^{-1}	I	ν cm^{-1}	I	ν cm^{-1}	I	ν cm^{-1}	I
(1)	31.31	0.9	31.31	0.79	31.31	0.96	31.31	0.94	31.31	1.06	31.31	1.04
(2)	30.91	1.8	30.91	1.78	30.89	1.87	30.88	1.79	30.87	1.84	30.84	1.82
(3)	30.26	3.3	30.25	3.42	30.25	3.22	30.22	3.26	30.25	3.11	30.18	3.16
(4)	27.74	11.1	27.79	9.22	27.84	8.30	27.82	8.17	27.84	7.67	27.84	7.56
(5)	27.52	20.1	27.54	15.65	27.57	15.87	27.56	15.90	27.60	15.97	27.54	16.00
(6)	27.17	3.5	27.17	4.62	27.19	5.81	27.15	5.93	27.28	5.54	27.21	5.68
(8)	25.91	11.8	25.90	8.00	25.89	8.72	25.89	8.88	25.93	9.18	25.87	9.38
(13)	25.46	2.4	25.41	2.37	25.41	2.72	25.38	2.71	25.38	2.42	25.32	2.40
(9)	25.25	6.5	25.22	5.02	25.21	4.44	25.20	4.36	25.30	4.03	25.17	3.94
(10)	24.93	1.8	24.88	2.03	24.90	2.09	24.86	2.07	24.92	2.10	24.82	2.03

perturbations have only a small effect on the frequencies is verified.

Since the experimental pattern is not completely resolved it is necessary to construct a theoretical "unresolved" pattern. This has been done for "perturbed" patterns only. The intensity of an "unresolved" line is taken to be the sum of the intensities of its components. The frequency is taken as the center of gravity of the frequencies of its components, each component being weighted in proportion to its intensity. In Table II the lines that are thus combined are included in brackets. Schüler's experimental data and the theoretical "unresolved" patterns are given in Table III.

It is seen from this table that on the whole experiment agrees best with the theoretical pattern for $i=3/2$. This is already indicated by the interval ratio of the (1), (2), (3) group. It is also possible to use the distance between component (3) and the (4), (5), (6) group as a test. Schüler's measurements agree best with calculations for $i=3/2$. A check on this was obtained by measuring one of Granath's Lummer plate patterns. The results are $\Delta\nu(3,\ 4)=2.46\pm0.08$ cm^{-1}, $\Delta\nu(3,\ 5)=2.75\pm0.09$ cm^{-1}, $\Delta\nu(3,\ 6)=3.11\pm0.10$ cm^{-1}. The indicated errors are intended to represent the maximum deviations due to errors in the comparator settings and readings. With reference to Table III it is seen that Granath and Schüler agree very well except for the (3), (4) interval for which Granath's measurements agree best with the theory for $i=3/2$. Schüler remarks that his measurements of the positions of (4) are subject to some error and that it should probably be farther from (5). This would improve the agreement with theory and with Granath's measurements. The (3), (5) interval was also measured on one of Granath's Fabry-Perot plates and was found to be 2.74 ± 0.11 cm^{-1}. These measurements are in good agreement with $i=3/2$; they rule out the possibility of $i=5/2$ and show that $i=2$ is improbable.

The experimental intensities attributed to Schüler are taken from a graph in his 1930 article. The intensities thus obtained cannot be considered accurate and should be used for rough comparison only.

According to Schüler component (6) is a few percent stronger than component (3). This gives no information about the spin since it is true for all the theoretical "perturbed" patterns considered.

Component (8) is estimated by Schüler to be 30 percent stronger than (9). Theoretically (8) should have an intensity approximately 1.6 times that of (9) for $i=3/2$. For $i=2$ and $5/2$ (8) is even stronger than (9) relatively. Presumably Schüler's statement that (8) is 30 percent stronger than (9) means that the intensity of (9) is 0.70 times that of (8) which would be in rough agreement with theory and with Schüler's Fig. 1 in his 1930 paper.

A series of Schüler's measurements gives for the ratio of the intensity of component (3) to (2) the value $J(3)/J(2)=1.91$. A second series gives 1.98. He says that these are to be taken as minimum values.

The theoretical values for the intensity ratio $J(3)/J(2)$ are 1.93 for $i=3/2$; 1.72 and 1.82 for

$i=2$; and 1.69 and 1.74 for $i=5/2$. If we assume that the 3.7 percent difference in Schüler's two values is the maximum percentage error of his measurements then both $i=2$ and $i=5/2$ are ruled out and agreement is good for $i=3/2$. Too much weight should not be given to this agreement in view of the difficulties in intensity measurements.

Casimir[8] after considering perturbations in the hfs of Hg observed by Schüler and Jones[9] concludes that the scalar product (**is**) represents the magnetic interaction of the nucleus with the external electrons satisfactorily for the diagonal elements but not satisfactorily for the nondiagonal elements. Goudsmit and Bacher[10] in considering the same perturbations find that the magnitude of the nondiagonal elements is in good accord with the cosine law and show that deviations between theory and experiment dealt with by Casimir are most probably due to insufficient experimental accuracy.

The agreement found here for Li is also essentially due to the cosine nature of the interaction as well as to the fact that the interaction is mainly due to the s electron. The cosine character is responsible for the correct ratios of splittings of the ^3S, $^3P_1$, $^3P_2$ levels and it is seen that the ratio of the nondiagonal terms to the diagonal ones must also be given approximately correctly by the cosine law. This together with Granath's results on the intervals between (1), (2), (3) indicates strongly that the interaction is of the cosine type.

Taking the spin to be 3/2 the effective nuclear magnetic moment and nuclear g value for Li^7 are those obtained by Granath since his data were used to calculate the theoretical patterns. Thus the effective magnetic moment of the Li^7 nucleus is 3.3 in terms of the "theoretical" magnetic moment of a proton, and the nuclear g value is 2.2.

It is a pleasure to acknowledge the kind assistance of Professor G. Breit.

[8] H. Casimir, Zeits. f. Physik **77**, 811 (1932).

[9] H. Schüler and E. G. Jones, Zeits. f. Physik **77**, 801 (1932).

[10] S. Goudsmit and R. F. Bacher, Phys. Rev. **43**, 894 (1933).

Definitions of Symbols

f, j, l, s, i. Fine, inner, azimuthal, electronic spin, nuclear spin quantum numbers.
F, **J**, **L**, **S**, **I**. Corresponding operators.
$-e$. Charge on an electron.
$\boldsymbol{\mu}$. Nuclear magnetic moment.
A_0. Electrostatic potential due to the nucleus.
r. Distance of an electron from nucleus.
$\mathcal{E}$. Electric intensity of the nuclear field.
μ_0. Bohr magneton.
$g(i)$. Ratio of magnetic moment and angular momentum of the nucleus.
$\psi_s(0)^2$. Probability of finding an s electron in a unit volume at the nucleus.
$\psi_{1s}(1)$ etc. Coordinate part of wave function for 1s electron number 1.