

THE HYPERFINE STRUCTURE OF *S* AND *P* TERMS OF
TWO ELECTRON ATOMS WITH SPECIAL
REFERENCE TO Li^+ BY G. BREIT AND F. W. DOERMANN
DEPARTMENT OF PHYSICS, NEW YORK UNIVERSITY

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ABSTRACT

The proper form of the interaction energy between the nuclear magnetic moment and the electronic system of a many electron atom is discussed. The results of the Dirac equation for a single electron are taken as the guiding principle. A form for the interaction energy is set up as an expression involving Pauli's spin matrices. No convergence difficulties occur in the form here given.

The interaction Hamiltonian is applied to the 3S and 3P terms of two electron atoms for the case of Russell-Saunders's coupling. An exact formula is derived for the resultant hyperfine structure of 3S terms and corrections to the Goudsmit Bacher formulas for 3P terms are given. It is shown that the Landé interval rule for 3S hyperfine structure levels is exact, and that therefore the ratio of intervals can be used to determine nuclear spin moments.

The formulas are applied to the Li^+ 5485A line. Proper functions for *S* levels are worked out by the variational method and applied to the calculation of the magnetic moment of Li_7 . With Schüler's wave-length data the nuclear *g* factor is 2.13 on the assumption that the nuclear spin is $3/2$.

The accuracy of the calculation is discussed. It is likely to be good to at least 2% in *g*. As a by-product of the calculation the lowest energy level of ortholithium has been computed as ≤ -1.1354 in units of the ionization potential of Li^{++} . The empirical value is -1.1358 .

INTRODUCTION

THE effect of nuclear spin on optical spectra has been treated mathematically by Casimir,¹ Fermi,² and Hargreaves.³ A somewhat more qualitative discussion has been given by Goudsmit and Bacher.⁴ In the first three of these discussions only one valence electron has been taken into account while in the last the more general problem of several valence electrons has been considered. Qualitatively the conclusions of Goudsmit and Bacher are doubtless correct. They do not pretend, however, to be exact quantitatively since the coupling between the nuclear spin and the electron system is supposed to be taking place only through one of the electrons—the most closely bound *s* electron. It is desirable to have a more exact quantitative theory taking into account the coupling of all electrons. This is particularly necessary if, say, two of them are *s* electrons. The desirability of having such a theory lies in its application to the absolute value of nuclear magnetic mo-

¹ See Goudsmit and Young, *Nature*, March 22, 1930.

² E. Fermi, *Zeits. f. Physik* **60**, 320 (1930).

³ J. Hargreaves, *Proc. Roy. Soc.* **124**, 568 (1929); **127**, 141 (1930); **127**, 407 (1930).

⁴ S. Goudsmit and R. F. Bacher, *Phys. Rev.* **34**, 1501 (1929).

ments. The observations of Schüler⁵ and of Granath⁶ show that the 3S level of Li^+ is split into three components under the action of the nuclear magnetic field and the separation between the two extreme components can be said to be 1.03 cm.^{-1} . There seems to be no doubt that the three components in question are single. They are well and definitely resolved and so there is every reason to expect eventually a reliable determination of the nuclear magnetic moment from the determination of their frequency difference. The whole electron system consists in this case of only two electrons. The solution of the Schroedinger wave equation offers in this case a simpler problem than that of the heavy alkalis. An attempt at its approximate solution and its application to the calculation of the magnetic moment of the Li_7 nucleus is one of the objects of this paper. The other object is to formulate a theory for the interaction between the nucleus and the extranuclear electrons. A few words must be said as to why the formulation of such a theory is still subject to speculation.

For one electron an unambiguous result can be obtained by means of Dirac's equation. This has been done by Fermi and Casimir. The problem is not so clear when two or more electrons are discussed. There exists no satisfactory mathematical treatment of the relativistic two electron problem. It becomes necessary to use approximate equations. The simplest form for these is obtained through the introduction of Pauli's two row, two column spin matrices. It is known that interactions between electrons can be satisfactorily represented by means of these as long as the electronic velocities are not excessive. It might be expected that the interaction of nuclei and electrons can be reduced to the same basis. There is one important distinction between these two cases. The force between a nucleus and an electron is attractive while that between two electrons is repulsive. When an electron is close to the nucleus its velocity cannot be treated as small. For s electrons an important contribution to the interaction energy is due to the influence of the nucleus when the electron is very close to it. We have no reason to expect the interaction energy of the nucleus and the electron to be of the same form as that used for the approximate interaction energy of two electron spins. In fact it will be seen below that the two forms are different.

In order to derive the proper form of the interaction energy we consider first of all the one electron problem from the point of view of Dirac's equation, i.e. we write down the formulas found already in Fermi's paper. The two smaller Dirac wave-function components are then eliminated and an equation in the two large components is obtained. This equation involves Pauli's spin matrices and is equivalent to Dirac's for the discussion of the lighter nuclei. Having thus derived the proper interaction energy for one electron the result is generalized to the case of two or more. This forms the first section of the paper. In the second section the separations of spectral terms caused

⁵ H. Schüler, *Zeits. f. Physik* **42**, 487; (1927).

⁶ L. P. Granath, *Phys. Rev.* **36**, 1018, (1930), (letter). See also the forthcoming paper by P. Güttinger in the *Zeits. f. Physik* in which the feasibility of $i=3/2$ is explained and an approximate g value for the nucleus is derived.

by nuclear interactions are worked out. In the third the results of the second section are applied to Li^+

(I). THE INTERACTION ENERGY FOR ONE ELECTRON

We consider one electron of charge $-e$ under the influence of a single nucleus. The electrostatic potential due to the nucleus is A_0 . The electrostatic field due to the nucleus is central so that A_0 is a function only of r , the distance from the nucleus. The vector potential due to the nucleus is A . In special applications we take

$$A = \frac{[\mathbf{u} \times \mathbf{r}]}{r^3}. \quad (1)$$

With the abbreviations

$$\mathbf{p} = \mathbf{P} + (e/c)\mathbf{A}, \quad \mathbf{P} = (h/2\pi i)\nabla, \quad p_0 = E/c + (e/c)A_0 \quad (2)$$

Dirac's equation for a stationary state is

$$(p_0 + \alpha_1 p_1 + \alpha_2 p_2 + \alpha_3 p_3 + \alpha_4 mc)\psi = 0. \quad (3)$$

We suppose the α_s to be those given in Dirac's original paper. Equation (3) is, of course, a set of four equations in four ψ_s . It is convenient to eliminate ψ_1, ψ_2 as has been done by Darwin.⁷ The reader will verify that without approximations

$$\left\{ p_0 - mc - (\mathbf{p}\delta) \frac{1}{p_0 + mc} (\mathbf{p}\delta) \right\} \psi = 0 \quad (4)$$

where now the σ_k ($k=1, 2, 3$) are Pauli's matrices and the column matrix ψ contains only two rows: ψ_3, ψ_4 . Equation (4) must be satisfied for any solution of (3). It is not altogether equivalent to (3) if it is used for the determination of the eigenwerte E . In (3) it is required that $\psi_1^* \psi_1 + \psi_2^* \psi_2 + \psi_3^* \psi_3 + \psi_4^* \psi_4$ be integrable. Equation (4) is equivalent to (3) only if this last condition is added. If ordinary perturbation methods of quantum theory are applied to (4) it is more convenient to use the integrability of $\psi_3^* \psi_3 + \psi_4^* \psi_4$ as the restricting condition. As will be seen presently this circumstance is only of secondary importance. For the present we use (4) and derive its consequences as though $\psi_3^* \psi_3 + \psi_4^* \psi_4$ were integrable. Performing the operations indicated in the second term, using (2) and introducing the electric and magnetic fields by means of

$$\mathcal{E} = -\text{grad } A_0, \quad \mathcal{H} = \text{curl } A \quad (5)$$

we obtain

$$\begin{aligned} E = mc^2 - eA_0 + \frac{c^2}{E + mc^2 + eA_0} & \left[\mathbf{P}^2 + \frac{e}{c}(\mathbf{P}\mathbf{A} + \mathbf{A}\mathbf{P}) + \frac{e^2}{c^2}A^2 + \frac{he}{2\pi c}(\mathcal{H}\delta) \right] \\ & + \frac{h}{2\pi i} \frac{c^2 e}{(E + mc^2 + eA_0)^2} \left[(\mathcal{E}\mathbf{P}) + \frac{e}{c}(\mathcal{E}\mathbf{A}) + i[\mathcal{E} \times \mathbf{P}] \delta \right. \\ & \left. + i \frac{e}{c}[\mathcal{E} \times \mathbf{A}] \delta \right] \end{aligned} \quad (6)$$

⁷ C. G. Darwin, Proc. Roy. Soc. 118, 654 (1928).

this is still an exact consequence of (2). At this point we make an approximation. The magnetic moment μ enters (6) only through \mathbf{A} . It is sufficient to consider first order effects in μ and therefore in \mathbf{A} . Quadratic terms in \mathbf{A} are disregarded from here on. The perturbation energy may therefore be taken to be

$$H' = \frac{c^2}{E + mc^2 + eA_0} \left[\frac{e}{c} (\mathbf{PA} + \mathbf{AP}) + \frac{he}{2\pi c} (\mathcal{I}\mathcal{C}\mathcal{O}) \right] \\ + \frac{hc^2e}{2\pi(E + mc^2 + eA_0)^2} \left[\frac{e}{c} [\mathcal{E} \times \mathbf{A}] \mathcal{O} - i \frac{e}{c} (\mathcal{E}\mathbf{A}) \right]. \quad (7)$$

In this expression the first bracketed term corresponds to the ordinary interaction energy which is used in the ordinary discussions of two electrons. In the major portion of the configuration space eA_0 is negligible in comparison with $E + mc^2$ which itself is very nearly $2mc^2$. In this region the first bracketed term of (7) is on using (1)

$$H'' = \frac{e}{mc} \frac{\mathbf{M}\mathbf{y}}{r^3} + \frac{eh}{4\pi mc} \left\langle (\nabla\mathcal{O}) (\nabla\mathbf{y}) \frac{1}{r} \right\rangle \quad (8)$$

where

$$\mathbf{M} = [\mathbf{r} \times \mathbf{P}] \quad (8')$$

is the angular momentum operator and ∇ operates only on r^{-1} in the $\langle \rangle$. Only the expression (8) can be derived from the analogy of the electron and the nucleus to little magnets. For s terms the second term of (8) becomes indeterminate. A definite theory can be formulated by means of (8) if \mathbf{y} is defined as the limit of a spatial distribution of magnetic moment of very small extension in the limiting case of the extension approaching zero. It will be seen that the result of this limiting process is different from the application of the complete expression (7). For s electrons the result of (7) is (-2) times the result of (8). Hargreaves obtains zero for the perturbing effect of (8) in the case of s terms. He could have obtained any desired result since he has not defined the limiting process for the definition of the divergent integrals. Nevertheless his conclusion is correct. The exact effect of the first bracketed term of (7) is zero for s terms, the presence of eA_0 in the denominator making the radial integrals convergent. We see that the picture of the nucleus and electron as little magnets can be applied in this instance only with extreme caution.

If the field is central \mathcal{E} is perpendicular to \mathbf{A} and the imaginary part of the second bracketed term of (7) disappears. Its real part containing $[\mathcal{E} \times \mathbf{A}]$ is then combined advantageously with the second part of the first bracketed term containing $(\mathcal{I}\mathcal{C}\mathcal{O})$. The perturbation energy becomes

$$\begin{aligned}
H' = & \frac{(e/mc)(M\mathbf{y})}{1 + (E - mc^2 + eA_0)/2mc^2} \cdot \frac{1}{r^3} \\
& + \frac{hec/2\pi}{E + mc^2 + eA_0} \left\{ -\frac{(\mathbf{y}\delta)}{r^3} + \frac{3(\mathbf{r}\delta)(\mathbf{r}\mathbf{y})}{r^5} \right\} \\
& + \frac{(hec/2\pi)(e|\mathcal{E}|)}{(E + mc^2 + eA_0)^2} \left\{ \frac{(\mathbf{y}\delta)}{r^2} - \frac{(\mathbf{r}\delta)(\mathbf{r}\mathbf{y})}{r^4} \right\} \quad (9)
\end{aligned}$$

The perturbation energy (9) can now be applied to the calculation of the splitting of an s term. The first term of (9) can be disregarded because $M\psi = 0$ for s terms and because the radial integration gives a finite result on account of eA_0 in the denominator. It is well known that the conservation of angular momentum makes it sufficient to calculate the average value of the coefficient of $\mu_x\sigma_x$ in the second line of (9). If this average be w and the nuclear spin k the s level is split into two components displaced by the amounts $w, (-1 - k^{-1})w$ from the normal position.⁸ The first component is the one of higher fine quantum number $f = k + \frac{1}{2}$. The first term of the second line of (9) contributes nothing to the average, again on account of the presence of eA_0 in the denominator which makes the integration over r give a finite result. Using (5) we have on partial integration

$$w = - \int_0^\infty \frac{8\pi\mu}{3} \frac{hec}{2\pi} \frac{2\psi\psi'}{E + mc^2 + eA_0} dr \cong \frac{8\pi\mu}{3} \left(\frac{he}{4\pi mc} \right) \psi^2(0) \quad (10)$$

in agreement with Fermi.

The final result is not quite correct, but is very nearly so as long as the region in which $eA_0 \ll mc^2$ is negligible in comparison with the spatial extension of $\psi\psi'$ and as long as $E - mc^2 \ll mc^2$. Both of these conditions are satisfied by light nuclei. The difference between (10) and the correct result is of the order of the square of the fine structure constant.⁸ This example shows that the substitution of the integrability of $\psi_3^*\psi_3 + \psi_4^*\psi_4$ for the integrability of $\psi_1^*\psi_1 + \psi_2^*\psi_2 + \psi_3^*\psi_3 + \psi_4^*\psi_4$ is safe for the present purpose. We see also that the "empirical terms" used by Hargreaves are essentially the same as the terms derived above from Dirac's equation.

If instead of using Dirac's equation we were to use the perturbation energy (8) we should run into convergence difficulties. These may be avoided by endowing the magnetization of the nucleus with a finite spatial extension, say, by supposing that the magnetization is spread uniformly through the volume of a very small sphere. The first term then has no effect. The second gives rise to

$$w = \frac{\mu eh}{4\pi mc} \int \frac{\psi^2(P)}{3} \int f(P') \Delta_P \left(\frac{1}{r_{PP'}} \right) dV_{P'} dV_P$$

⁸ See e.g. G. Breit, Phys. Rev. **35**, 1447 Equations (2), (3) (1930).

where P' refers to a point of the magnetization distribution, and $f(P')\mu dV_{P'}$ is the amount of magnetization in the element of volume $dV_{P'}$. The above double integral is easily evaluated if $I = \int f(P')(1/r_{PP'})dV_{P'}$ is interpreted as the electrostatic potential at the point P due to a charge distribution of density $f(P')$. The total charge is $1 = \int f(P')dV_{P'}$. Outside the nucleus $\Delta_P I = 0$. Inside the nucleus Poisson's equation gives

$$\Delta_P I + 4\pi f(P) = 0,$$

and therefore

$$\int (\Delta_P I) dV_P = -4\pi.$$

In the limit of a very concentrated distribution $f(P')$ we may set therefore

$$\Delta_P \int f(P') \frac{1}{r_{PP'}} dV_{P'} = -4\pi \delta(P) \quad (11)$$

and we obtain then

$$w = -\frac{4\pi\mu}{3} \frac{ch}{4\pi mc} \psi^2(0). \quad (12)$$

This result must be multiplied by (-2) in order to give Fermi's result (10). The magnetic doublet model and Dirac's equation give in this case widely different results. The present evidence is that Dirac's equation is to be preferred so that (10) is the correct result.

The perturbation energy (9) must now be generalized to include the case of two or more electrons. As has been explained in the introduction we are unable to start with a relativistic treatment of two electrons and we must instead use (9) as an indication for the proper generalization. A number of possible generalizations could be made. Thus one could go back to (7) and use the field quantities \mathcal{E} , \mathcal{H} taking \mathcal{E}_1 to be the electric intensity at x_1, y_1, z_1 , due to the nucleus and also due to electron 2. Or else one may take \mathcal{E}_1 , \mathcal{H}_1 to be due only to the nucleus. For the first choice we would have to prove that the imaginary term in (7) contributes nothing to the result. Also some generalization of A_0 would have to be made. Having no basis for forming such a generalization we make instead

$$H' = H_1' + H_2' \quad (13)$$

where H_1' is the result of using x_1, y_1, z_1, δ_1 , instead of x, y, z, δ in all of the terms of (9). The coupling between the nucleus and each electron is thus represented by a term in the Hamiltonian which depends only on the coordinates of that electron.

It may also be shown that for 3S terms the alternative generalization based on (7) leads to the same final result as (13) provided $\mathcal{E}_i = -\text{grad } A_{0i}$ ($i = 1, 2$). The proof is not of sufficient interest to be quoted.

II. CALCULATION OF PERTURBATIONS IN TERMS OF SCHROEDINGER ψ IN CONFIGURATION SPACE

We use the method of sums.⁹ Consider first the 3S terms. It is convenient to define the following spin functions

$$S_1 = S_\alpha^1 S_\alpha^2, S_0 = 2^{-1/2}(S_\alpha^1 S_\beta^2 + S_\alpha^2 S_\beta^1), S_{-1} = S_\beta^1 S_\beta^2. \tag{14}$$

The upper indices refer to electrons 1 and 2. The functions S_α, S_β are as usual the column matrices $\begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix}$. The upper row corresponds to the spin being in the positive direction of the z axis. In the case of Russell-Saunders coupling there are three unperturbed functions for the 3S state. Each of these is the product of a coordinate function and of one of the three functions (14). The coordinate function ψ depends only on the shape and size of the electronic triangle and not on its orientation.¹⁰ The wave-function of the coupled system nucleus+electrons contains also the angular momentum specification of the nucleus. Denoting the angular momentum of the nucleus by k there are $2k+1$ nuclear functions

$$N_k = \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, N_{k-1} = \begin{pmatrix} 0 \\ 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \dots N_{-k} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ 1 \end{pmatrix} \tag{15}$$

The vector matrix \mathbf{u} operates on these. The matrices for the components of \mathbf{u} we take to be the same as Fermi's. Among these the only matrix having diagonal elements is μ_z . It is a diagonal matrix with elements $\mu(1, k-1/k, \dots -1)$. The complete system of $3(2k+1)$ unperturbed eigenfunctions can be represented by means of

$$u_i^m = S_i N^m \psi \begin{pmatrix} i = 1, 0, -1 \\ m = k, k-1, \dots -k \end{pmatrix} \tag{16}$$

It is most conveniently arranged in a table:

Angular momentum:	$k+1$	k	$k-1$	-----	$-k+1$	$-k$	$-k-1$
	u_1^k	u_1^{k-1}	u_1^{k-2}	-----	u_1^{-k}		
		u_0^k	u_0^{k-1}	-----	u_0^{-k+1}	u_0^{-k}	
			u_{-1}^k	-----	u_{-1}^{-k+2}	u_{-1}^{-k+1}	u_{-1}^{-k}

In Slater's method we are concerned only with diagonal elements of the perturbation energy matrix. The functions N^m are normal orthogonal and so are the S_i . We are therefore concerned only with coefficients of μ_z . This shows that the combined effect of the perturbations due to $\mathbf{M}_1\mathbf{u}$ and $\mathbf{M}_2\mathbf{u}$ is zero. In fact this perturbation is of the form $(\mathbf{B}_1 + \mathbf{B}_2)\mathbf{u}$. It, by itself, commutes with the total angular momentum. When it operates on u_1^k it gives $(B_{1z} + B_{2z})\mu u_1^k$ as well as other terms which do not count in the calculation

⁹ J. C. Slater, Phys. Rev. **34**, 1293 (1929).
¹⁰ E. Wigner, Zeits. f. Physik **43**, 624 (1927).

of the diagonal element $\int u_1^{*k} H' u_1^k$. The operation on u_{-1}^{-k} gives $-(B_{1z} + B_{2z})\mu u_{-1}^{-k}$. Thus $\int u_1^{*k} H' u_1^k = -\int u_1^{*k} H' u_1^k = 0$. The term of highest fine structure quantum number is therefore undisturbed. Considering the other functions in turn we see that there is no splitting due to terms not involving δ_1, δ_2 . This may also be verified by a short calculation of the average value of $A(r_1)\partial/\partial\phi_1 + A(r_2)\partial/\partial\phi_2$ in the six dimensional configuration space $x_1 \dots z'_2$ for the case of $\psi = \psi(r_1, r_2, \cos\theta_{12})$. The terms in δ_1, δ_2 are easily treated if it is observed that, so far as the calculation of diagonal matrix elements is concerned, the symmetric operator $A_1\delta_1 + A_2\delta_2$ gives rise only to the following terms

$$(A_1\delta_1 + A_2\delta_2)(S_1, S_0, S_{-1}) \rightarrow (A_{1z} + A_{2z})(S_1, 0, -S_{-1}). \tag{17}$$

Letting now the energy perturbations of the three levels be w_1, w_2, w_3 , in the order of decreasing fine quantum numbers, we have from the first three columns of the table

$$\begin{aligned} w_1 &= \int \psi^*(A_{1z} + A_{2z})\psi, \quad w_1 + w_2 = \frac{k-1}{k}w_1, \quad w_1 + w_2 + w_3 \\ &= \left(-1 + \frac{k-2}{k}\right)w_1 \\ w &= w_1\left(1, -\frac{1}{k}, -\frac{k+1}{k}\right). \end{aligned} \tag{18}$$

Here

$$A_{1z} = \frac{hec}{2\pi(2mc^2 + Ze^2/r_1)^2} \left\{ 2mc^2 \left(\frac{3z_1^2}{r_1^5} - \frac{1}{r_1^3} \right) + \frac{2Ze^2}{r_1^6} z_1^2 \right\}.$$

Performing one of the integrations over 1 for A_{1z} and over 2 for A_{2z} and then using the symmetry of ψ^2 in 1 and 2 we have

$$\begin{aligned} w_1 &= 16\pi/3 \mu\mu_0 \int \psi^2(0, 0, 0; x, y, z) dx dy dz \\ &(\mu_0 = eh/4\pi mc > 0). \end{aligned} \tag{19}$$

The only approximations made in deriving (19) are: (1) a definite case of Russell-Saunders coupling, (2) neglect of the square of the fine structure constant. The integral in (19) represents the probability of one electron being in a unit volume near the nucleus. The connection of this result with Goudsmit and Bacher is seen if one writes

$$\psi = (1/2^{1/2})[\phi_n(q_1)\phi_m(q_2) - \phi_n(q_2)\phi_m(q_1)]. \tag{20}$$

If n refers to the inner electron state

$$\begin{aligned} \int \psi^2(0, q) dq &\cong \frac{1}{2} \phi_n^2(0), \quad \text{and} \\ w_1 &= (8\pi/3)\mu\mu_0\phi_n^2(0). \end{aligned} \tag{21}$$

In this approximation (19) (18) are identical with the corresponding formulas of Goudsmit and Bacher. A discussion of the difference between (19) and (21) will be given in the third section.

If $k=1/2$ formula (18) remains correct if it is read from left to right and the last term is omitted. This is obvious from the order in which w_1, w_2, w_3 have been derived.

We may now consider 3P terms. There are three linearly independent coordinate eigenfunctions, each of these combining with the three spin functions (14) and thus forming a set of nine functions. The coordinate functions may be called $\psi_1, \psi_0, \psi_{-1}$ corresponding to components 1, 0, -1 of the orbital angular momentum in the z direction. The functions $\psi_i S_k$ do not themselves correspond to definite parts of the 3P term but certain linear combinations of them do. These linear combinations are

$$\begin{aligned} {}^3P_0 &: 3^{-1/2}(\psi_1 S_1 - \psi_0 S_0 + \psi_{-1} S_{-1}) \\ {}^3P_1 &: 2^{-1/2}(\psi_1 S_0 - \psi_0 S_1), 2^{-1/2}(\psi_1 S_{-1} - \psi_{-1} S_1), 2^{-1/2}(-\psi_{-1} S_0 + \psi_0 S_{-1}) \quad (22) \\ {}^3P_2 &: \psi_1 S_1, 2^{-1/2}(\psi_0 S_1 + \psi_1 S_0), 6^{-1/2}(\psi_1 S_{-1} + 2\psi_0 S_0 + \psi_{-1} S_1), \\ & 2^{-1/2}(\psi_0 S_{-1} + \psi_{-1} S_0), \psi_{-1} S_{-1}. \end{aligned}$$

The functions $\psi_1, \psi_0, \psi_{-1}$ are supposed to be chosen so as to transform themselves under rotations as $2^{-1/2}(x+iy), -z, 2^{-1/2}(-x+iy)$. The set of functions (22) is convenient because each one of them corresponds to a definite value of the angular momentum in the direction of the z axis. There is no splitting for the 3P_0 and we consider first the 3P_1 term. The nucleus is brought in by means of the N_k just as in the case of 3S terms. The table which led to (18) is still correct, though now the functions u_i^m are different. Equation (18) still is valid although (19) is different. The validity of (18) is of course a consequence of the "cosine" law of interaction with the nucleus. It is very easy to prove this by writing $u_i^m = v_i N^m$. Denoting the coefficient of μ_z in the interaction energy by a_z we have on applying the diagonal sum theorem from both ends of the table $w_1 = I_1 = -I_{-1}$; $w_2 + w_1 = (k-1)/k I_1 + I_0 = -((k-1)/k) I_{-1} - I_0$ where $I_l = \mu \int v_i^* a_z v_l$. This shows that $I_0 = 0$ and (18) follows at once. It remains to determine w_1 . We may omit the correction in the denominator of the first term of (9). The second two terms are easily combined and we have

$$w_1 = (e\mu/mc) \int v_1^* (r_1^{-3} M_{1z} + r_2^{-3} M_{2z}) v_1 + \mu \int v_1^* (\mathcal{B}_1 \delta_1 + \mathcal{B}_2 \delta_2) v_1 \quad (23)$$

where

$$\mathcal{B}_1 = \frac{hec}{2\pi \{2mc^2 + (Ze^2/r_1)\}^2} \left\{ 2mc^2 \left(3z_1 \frac{\mathbf{r}_1}{r_1^5} - \frac{\boldsymbol{\zeta}}{r_1^3} \right) + \frac{2Ze^2}{r_1^6} z_1 \mathbf{r}_1 \right\}. \quad (24)$$

Here $\boldsymbol{\zeta}$ is a unit vector along the z axis. \mathcal{B}_2 is obtained from \mathcal{B}_1 on substituting z_2, r_2 everywhere for z_1, r_1 . Performing the operations δ_1, δ_2 in (23) we have on letting

$$\mathbf{B} = \mathbf{B}_1 + \mathbf{B}_2 \quad (25)$$

$$w_1 = \frac{e\mu}{2mc} \int \psi_1^*(r_1^{-3}M_{1z} + r_2^{-3}M_{2z})\psi_1 + \frac{e\mu}{2mc} \int \psi_0^*(r_1^{-3}M_{1z} + r_2^{-3}M_{2z})\psi_0 \\ + (\mu/2) \int \{\psi_0^*B_z\psi_0 - \psi_1^*2^{-1/2}(B_x + iB_y)\psi_0 - \psi_0^*2^{-1/2}(B_x - iB_y)\psi_1\} \quad (26)$$

This form for w_1 is correct quite regardless of any approximations which may be made as to the representation of the coordinate wave-functions $\psi_1, \psi_0, \psi_{-1}$. The most general forms of these functions are known and formula (26) is capable of giving exact results as long as the hypothesis of Russell-Saunders coupling applies.¹¹ In practical applications it appears to be unnecessary to use the general expressions for $\psi_1, \psi_0, \psi_{-1}$ and it will usually be sufficient to use the approximate representation of these coordinate functions as antisymmetric combinations of products of functions involving the coordinates of only one particle. We may then write

$$\begin{aligned} \psi_1 &= (3^{1/2}/4\pi)(F \sin \theta_1 e^{i\phi_1} - \tilde{F} \sin \theta_2 e^{i\phi_2}) \\ \psi_0 &= - (6^{1/2}/4\pi)(F \cos \theta_1 - \tilde{F} \cos \theta_2) \\ \psi_{-1} &= - (3^{1/2}/4\pi)(F \sin \theta_1 e^{-i\phi_1} - \tilde{F} \sin \theta_2 e^{-i\phi_2}) \end{aligned} \quad (27)$$

with

$$\begin{aligned} F &= f_1(r_1)f_2(r_2); \quad 4 \int F^2 r_1^2 r_2^2 dr_1 dr_2 = 1 \\ \tilde{F} &= f_1(r_2)f_2(r_1). \end{aligned} \quad (27')$$

The functions in (27) are chosen so as to give (22). The radial function f_1 is characteristic of the p state while f_2 describes the s state. If a single electron were in that s state it would be described by a normalized function ψ_s . Clearly

$$4\pi\psi_s(0)^2 = f_2(0)^2 / \left(\int f_2(r_2)^2 r_2^2 dr_2 \right). \quad (28)$$

It is now found on substitution of (27) (27')

$$(e/2mc) \int \psi_1^*(r_1^{-3}M_{1z} + r_2^{-3}M_{2z})\psi_1 = (eh/4\pi mc) \overline{(r_1^{-3})} \quad (29)$$

where

$$\overline{(r_1^{-3})} = 4 \int F^2 r_1^{-3} r_1^2 r_2^2 dr_1 dr_2 \quad (29')$$

is the average of r^{-3} for a p electron described by a radial function f_1 . Also in

$$\frac{1}{2} \int \psi_0^* B_z \psi_0$$

¹¹ E. Wigner, reference 10; G. Breit, Phys. Rev. **35**, 569 (1930).

we need

$$(3/16\pi^2) \int F^2 \cos^2 \theta_1 B_{1z} = (1/5)\mu_0 \overline{(r_1^{-3})} - (1/20)\mu_0 \overline{(r_1^{-4})} (Ze^2/mc^2).$$

A numerical estimate shows that the term in $\overline{r_1^{-4}}$ is much too small ordinarily to be worried about and this as well as similar terms will be neglected here. The most important contribution to (26) comes from terms of the type

$$(3/16\pi^2) \int F^2 \cos^2 \theta_1 B_{2z} = (2\pi/3)\mu_0 \psi_s(0)^2$$

using (28). The remaining contributions are from

$$-\frac{1}{2} \int \{ \psi_1^* 2^{-1/2} (B_x + iB_y) \psi_0 + \psi_0^* 2^{-1/2} (B_x - iB_y) \psi_1 \} = (3/5)\mu_0 \overline{(r_1^{-3})}.$$

It is thus found on substituting all the integrals into (26) that

$$w_1 = \mu\mu_0 \{ (4\pi/3)\psi_s(0)^2 + 2\overline{(r^{-3})}_p \}. \quad (30)$$

This completes the calculation for the 3P_1 level.

For the 3P_2 term we have five electronic functions given by the last row of (22). These may be designated as v_l and the complete specification of the system is given by $u_l^m = v_l N^m$. Only now $l = (2, 1, 0, -1, -2)$ and the v_1, v_0, v_{-1} are, of course, now different from those just used for the 3P_1 term. In this case the table following equation (16) must be extended so as to have five rows. The method of sums does not suffice now to give all of the separation ratios. Denoting as before the coefficient of μ_z by a_z and letting $I_l = \mu \int v_l^* a_z v_l$ the method of sums shows directly that $I_2 = -I_{-2}$, $I_1 = -I_{-1}$, $I_0 = 0$ but it does not establish a relation between I_1 and I_2 . A calculation is easily made however for both I_1 and I_2 . We have:

$$I_2 = \frac{\mu e}{mc} \int \psi_1^* (r_1^{-3} M_{1z} + r_2^{-3} M_{2z}) \psi_1 + \mu \int \psi_1^* B_z \psi_1. \quad (31)$$

Substitution of the integrals used in deriving (30) gives

$$I_2 = \mu\mu_0 [(8\pi/3)\psi_s(0)^2 + (8/5)\overline{(r^{-3})}_p]. \quad (32)$$

Also

$$\begin{aligned} I_1 = (\mu e/2mc) \int \psi_1^* (r_1^{-3} M_{1z} + r_2^{-3} M_{2z}) \psi_1 \\ + (\mu/2) \int \{ \psi_0^* B_z \psi_0 + \psi_1^* 2^{-1/2} (B_x + iB_y) \psi_0 + \psi_0^* 2^{-1/2} (B_x - iB_y) \psi_1 \} \end{aligned} \quad (33)$$

so that I_1 can be obtained directly from (30) by subtracting $(6/5)\overline{(r^{-3})}_p$ inside the parenthesis. We have

$$I_1 = \mu\mu_0[(4\pi/3)\psi_s(0)^2 + (4/5)\overline{(r^{-3})}_p] = I_2/2. \quad (35)$$

Using the sum theorem we obtain for the first order energy perturbations

$${}^3P_2 = \mu\mu_0[(4\pi/3)\psi_s(0)^2 + (4/5)\overline{(r^{-3})}_p] \left(2, \frac{k-2}{k}, -\frac{3}{k}, -\frac{k+3}{k}, -2\frac{(k+1)}{k} \right) \quad (36)$$

which may be compared with

$${}^3P_1 = \mu\mu_0[(4\pi/3)\psi_s(0)^2 + 2\overline{(r^{-3})}_p] \left(1, -\frac{1}{k}, -\frac{k+1}{k} \right) \quad (36')$$

$${}^3S_1 = \mu\mu_0(8\pi/3)(1 + \epsilon)\psi_s(0)^2 \left(1, -\frac{1}{k}, -\frac{k+1}{k} \right). \quad (36'')$$

Here ϵ is a fractional correction due to the difference between (19) and (21).

III. APPLICATION TO THE SPECTRUM OF Li^+

The pattern of the ${}^3S-{}^3P$ line of Li^+ which has been observed by Schüler and Granath will now be considered using formulas (36) (36') (36''). The quantities $\overline{(r^{-3})}_p$ and ϵ are of the nature of correction terms and neglecting them these formulas become identical with those of Goudsmit and Young. The $\psi_s(0)^2$ for a hydrogenic s electron is related to the fine structure constant by

$$2\pi\psi_s(0)^2\mu_0^2 = R\alpha^2Z^3/n^3 \quad (37')$$

which is convenient for calculation. For $Z=3$ and $n=1$ we have in agreement with Goudsmit and Young $(8/3)R\alpha^2Z^3/1840n^3 = 0.228 \text{ cm}^{-1}$. Letting $(1840\mu/\mu_0) = g(k)$ we have therefore the approximate formulas:

$$\begin{aligned} {}^3P_2 &= 0.228(g(k)/4) \left(2, \frac{k-2}{k}, -\frac{3}{k}, -\frac{k+3}{k}, -\frac{2(k+1)}{k} \right) \\ {}^3P_1 &= 0.228(g(k)/4) \left(1, -\frac{1}{k}, -\frac{k+1}{k} \right) \\ {}^3S_1 &= 0.228(g(k)/2) \left(1, -\frac{1}{k}, -\frac{k+1}{k} \right) \end{aligned} \quad (37)$$

which are essentially the same as those of Goudsmit and Bacher. An application of (37) and the calculation of relative intensities of the different components of the pattern can be made for different values of k . As has been pointed out by Granath the experimental pattern seems to agree best with $k=3/2$. Most of the pattern appears to have a complicated structure which is due to unresolved components. Only the group of lines due to transitions from 3P_0 to 3S_1 is simple and consists of three fairly well resolved lines. It seems difficult at present to draw any definite conclusions from the other parts of the pattern on account of lack of resolution. We consider it more im-

portant therefore to have an accurate calculation of the correction factor $1 + \epsilon$ in (36'') than the exact evaluation of (36) (36'). There is, of course, no difficulty in evaluating $(\overline{r^{-3}})_p$. In the present instance the correction due to $(\overline{r^{-3}})_p$ amounts to about 1 percent change of scale for 3P_2 and 2 percent for 3P_1 .

In order to calculate the factor $1 + \epsilon$ in formula (36'') we must use the exact formula (19) which differs from (37) by the correction factor

$$1 + \epsilon = 2 \int \psi^2(0, q) dq / \psi_{1s}(0)^2. \quad (38)$$

The integral in the numerator is here the same as the integral in (19) the letter q having been written collectively for (x, y, z) . The denominator of (38) is the $\psi_s(0)^2$ of (37') for $n=1, Z=3$.

We have tried a number of approximate forms for $\psi(q_1, q_2)$ using the variational method for the calculation of the term value of the 3S state and then, having adjusted the constants to satisfy the minimizing requirement, calculated by means of the minimized functions the corresponding value of $1 + \epsilon$. In all cases ϵ is a small quantity. Some of the functions give eigenwerte in good agreement with the spectroscopic term value while others give considerably too small absolute values of the eigenwert. It is of interest to see the results of the bad as well as the good functions. A very rough approximation to the solution can be obtained by tentatively expressing ψ as an antisymmetric combination of products of hydrogenic functions in the field of a certain nuclear charge. This charge is deliberately taken to be the same for both functions. The two functions entering are orthogonal and the calculation is very easy, only the common scale of the two functions being varied. In terms of the ionizing potential of Li^{++} the energy of the 2S state is known to be $\lambda = -1.1358$. In the same units the above function gives $\lambda = -1.1279$ and $1 + \epsilon = 0.96$. This is a deliberately poor function, possessing only one adjustable constant and giving a relatively poor agreement with the experimental λ . Hylleraas¹² has considered the 3S terms of two electron spectra particularly for He. In his paper functions are tried for the ortho state of He which may be called the one and the two term approximations. These give for He $\lambda = -1.0855$ and $\lambda = -1.0871$. The values of $1 + \epsilon$ for He would be 1.009 and 1.04 respectively. For Li^+ we have used only the one term function of Hylleraas giving $\lambda = -1.1337$, $1 + \epsilon = 1.02(6)$. From the analogy to He one would suppose that the two term function of Hylleraas would give an appreciably larger ϵ . The calculations with the two term function of Hylleraas are complicated, however, and we have found it more convenient to use another three constant function. It has also been possible to correct the first function of Hylleraas by a numerical method. In the latter case there is no definite way of using the eigenwert agreement as a check on the calculations and the procedure itself is somewhat arbitrary. Nevertheless it appears to be definite enough to show that $1 + \epsilon > 1.02$ and

¹² Hylleraas, Zeits. f. Physik **54**, 347 (1929).

that $1 + \epsilon \cong 1.06$. The numerical method is based on the following consideration. In the units of length ($\hbar^2/8\pi^2mZe^2$) and energy ($RhcZ^2$) used by Hylleraas the differential equation to be satisfied by ψ is

$$\left[\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial}{\partial r_1} + \frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2} \frac{\partial}{\partial r_2} + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{\lambda}{4} + \frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{Zr_{12}} \right] \psi = 0. \quad (39)$$

The angle θ is the angle between the radii r_1 , r_2 and r_{12} is the distance between electrons 1 and 2. A certain approximation to the exact solution can be obtained by supposing that ψ is a function only of r_1 and r_2 the angle θ being not very important for this particular state. The one term function of Hylleraas does not involve θ or r_{12} and is therefore an approximation of the above type. A systematic neglect of the dependence on θ leads of course to a definite eigenwert and to a definite eigenfunction if the variational method of solution is used. Substituting a general function $\psi(r_1, r_2)$ into the variational equation it is easy to obtain a differential equation for this ψ . This equation is

$$\left[\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial}{\partial r_1} + \frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2} \frac{\partial}{\partial r_2} + \frac{\lambda}{4} + \frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{Z\rho} \right] \psi = 0$$

$$\rho = r_1 \text{ if } r_1 > r_2$$

$$\rho = r_2 \text{ if } r_1 < r_2. \quad (39')$$

We assume for the present that the eigenvalue of λ and the function ψ of (39') is a sufficient approximation to λ and ψ of (39). For the 3S state ψ is antisymmetric in r_1, r_2 and vanishes therefore at $r_1 = r_2$. It may be represented in two dimensions. Along the axis of $r_2 = 0, \rho = r_1$. The last three terms behave as $1/r_2$. If ψ and its first and second derivatives are finite on this axis we must require in order to satisfy (39') that the term $2/r_2 \partial\psi/\partial r_2 + \psi/r_2$ should be finite i.e.

$$\left(\frac{\partial \log \psi}{\partial r_2} \right)_{r_2=0} = -\frac{1}{2}. \quad (40)$$

Any trial ψ can be checked qualitatively by means of (40) and it is important to require that (40) be satisfied in the region of large numerical values of ψ . This is especially advisable in the present instance because the result we wish to obtain is proportional to $\int \psi(r_1, 0)^2 r_1^2 dr_1$ and depends primarily on the relative values of ψ^2 at $r_2 = 0$ as compared with its value at other points of the r_1, r_2 plane.

The one term function of Hylleraas was tested by means of (40) and it was found that although the logarithmic derivative was fairly close to its correct value the differences were greater than could be desired. At a certain point of the r_1 axis (40) is satisfied exactly. This point lies at a higher value of $r_1 = r_{10}$ than that which corresponds to the maximum of $r_1^2 \psi^2$. At the maxi-

imum ψ does not decrease rapidly enough in absolute value with increasing r_2 . The dependence of ψ on r_2 has therefore been corrected by a numerical procedure so as to satisfy (40) in most of the important region. For values of $r_1 < r_{10}$ this was done by fitting the exponential curve $Ce^{-r_2/2}$ to the curve of ψ against r_2 . The fit was made quite accurate by calculating logarithmic derivatives $\partial \log \psi / \partial r_2$ of the Hylleraas function and choosing such an r_2 for every r_1 that $\partial \log \psi / \partial r_2 = -\frac{1}{2}$. This procedure is of course somewhat arbitrary because $e^{-r_2/2}$ is not an exact solution of the wave equation and because $\partial \log \psi / \partial r_2 = -\frac{1}{2}$ only at $r_2 = 0$. Nevertheless, as long as the correction applies only to a small region in the neighborhood of $r_2 = 0$ it is essentially correct. For values of $r_1 > r_{10}$ it is impossible to correct the function

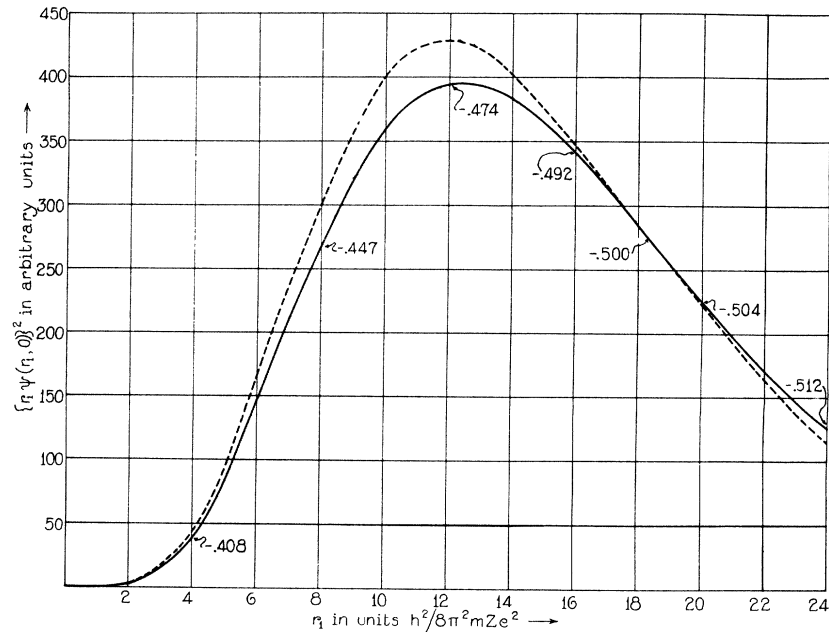


Fig. 1. The dotted curve is computed from the corrected, the full drawn curve from the uncorrected Hylleraas function. The values of $\partial \log \psi / \partial r_2$ are indicated along the curve.

by means of an exponential curve. The correction was made, therefore, by choosing for a given $r_1 = r_1'' > r_{10}$ a corresponding value of $r_1 = r_1' < r_{10}$ for which $\partial \log \psi / \partial r_2$ deviates from $-1/2$ by a numerically equal amount. The known corrections to ψ for $r_1 = r_1'$ and different values of r_2 were now applied to $r_1 = r_1''$ for the same values of r_2 . This means that the deviation of $\partial \log \psi / \partial r_2$ was taken as the criterion of the magnitude of the correction to ψ . The whole procedure has of course a meaning only as long as the corrections are small and can be applied therefore only in the region around the maximum of $r_1 \psi(r_1, 0)$. This maximum is at $r_1 = 12.5$ in the units of length used by Hylleraas. The correction becomes zero at $r_1 = 18.5$. The values of $(r_1 \psi(r_1, 0))^2$ at these points are 397.5 and 270 on an arbitrary scale. The relation of the corrected and the uncorrected $(r_1 \psi(r_1, 0))^2$ curves is shown in the Fig. 1.

Using these corrections the changes in $\int r_1^2 \psi^2(r_1, 0) dr_1$ and $\iint r_1^2 r_2^2 \psi^2(r_1, r_2) dr_1 dr_2$ were calculated. The corrections were taken into account only from $r_1=0$ to $r_1=24$. The resultant change in

$$\int r_1^2 \psi^2(r_1, 0) dr_1 \quad / \quad \iint r_1^2 r_2^2 \psi^2(r_1, r_2) dr_1 dr_2$$

came out to be 4 per cent. The value of $1+\epsilon$ for the one term Hylleraas function is 1.02; the corrected value of $1+\epsilon$ is 1.06.

Our correction procedure may of course be criticized on account of its arbitrariness. It must be remarked however that the sign and the order of magnitude of the result depend primarily on the fact that an increase in the absolute value of ψ is required at the maximum by the logarithmic derivative condition. Thus even though mathematically the procedure lacks rigor we believe that for the present problem it is essentially correct.

Finally we have calculated the result by the variational method using the following trial function.

$$\psi = \phi(kr_1, kr_2); \quad \phi = (r_1 - c)e^{-(a/2)r_1 - (b/2)r_2} - (r_2 - c)e^{-(a/2)r_2 - (b/2)r_1}.$$

This function is easily adapted to the variational procedure. It contains three constants a, b, c . The constants c and k can be treated algebraically in the variational procedure. Extensive arithmetic need be done only in connection with different values of a . The reason for this simplification is that the minimized value of k is always close to $k=1$ if $b=1$, the difference from 1 being usually of the order of 1 percent or less. The first step is to choose a value of a and to take $b=1$. Supposing that $k=1$ the minimizing is done for c analytically. Taking this value of c the result is minimized for k analytically. It is then usually unnecessary to minimize for c again because $k \cong 1$. The procedure is repeated for different values of a and the absolute minimum of λ is fixed by interpolation.¹³ We reproduce the final formulas for the minimizing procedure because they may be found useful in other connections. For $k=1$

$$\lambda/4 = (M - L_0 + L_1)/N \quad (41)$$

where

$$\begin{aligned} M &= 8a^{-3}b^{-3} + 24b^{-1}a^{-5} - 12a^{-1}b^{-1}\beta^{-7}(3\beta^{-1} - 2a^{-1}) \\ &\quad - c[4a^{-2}b^{-3} + 12a^{-4}b^{-1} - 8ab\beta^{-6}(3\beta^{-1} - a^{-1})] \\ &\quad + c^2[2a^{-1}b^{-3} + 2a^{-3}b^{-1} - 4ab\beta^{-6}]; \quad \beta = (a+b)/2 \\ L_0 &= 24a^{-4}b^{-3} + 48a^{-5}b^{-2} - 48\beta^{-7} - c[16a^{-3}b^{-3} + 24a^{-4}b^{-2} - 40\beta^{-6}] \\ &\quad + c^2[4a^{-2}b^{-3} + 4a^{-3}b^{-2} - 8\beta^{-5}] \end{aligned} \quad (42')$$

¹³ The trick of minimizing for k is the same as that used by Hylleraas, ref. 12, and amounts physically to satisfying the requirement of having the kinetic energy = $-(1/2)$ times the potential energy in a system with Coulomb forces.

$$\begin{aligned}
ZL_1 = & 24[a^{-4}b^{-2}(a+b)^{-1} + a^{-3}b^{-2}(a+b)^{-2} + a^{-2}b^{-1}(a+b)^{-4} \\
& + 2a^{-1}b^{-1}(a+b)^{-5}] - (33/2)\beta^{-7} - c\{8[2a^{-3}b^{-2}(a+b)^{-1} \\
& + a^{-2}b^{-2}(a+b)^{-2} + a^{-2}b^{-1}(a+b)^{-3} + 3a^{-1}b^{-1}(a+b)^{-4}] \\
& - (25/2)\beta^{-6}\} + c^2\{4[a^{-2}b^{-2}(a+b)^{-1} + a^{-1}b^{-1}(a+b)^{-3}] - (5/2)\beta^{-7}\}.
\end{aligned} \tag{42''}$$

Z = nuclear charge.

$$N/4 = 24a^{-5}b^{-3} - 18\beta^{-8} - 12c(a^{-4}b^{-3} - \beta^{-7}) + 2c^2(a^{-3}b^{-3} - \beta^{-6}) \tag{42'''}$$

With $L = L_0 - L_1$ the minimum for k comes at

$$k = L/2M, \quad \lambda/4 = L^2/(MN).$$

The correction factor $1 + \epsilon$ is obtained as

$$1 + \epsilon = k^3 I / (N/4) \tag{43}$$

where

$$I = 24a^{-5} - 12c(a^{-4} - \beta^{-4}) + 2c^2(a^{-3} + b^{-3} - 2\beta^{-3}). \tag{43'}$$

Using these formulas we obtain for $a = 1/3$; the minimized values $c = 1.446$, $k = 1.0057$, $-\lambda/4 = 1.1344$; $1 + \epsilon = 1.082$. The minimized value of a is 0.380 giving $-\lambda/4 = 1.1354$; $1 + \epsilon = 1.063$. On the other side of the best value of a say at $a = 0.395$, $1 + \epsilon = 1.055$ and $-\lambda/4 = 1.1353$. The calculations have been carried out to several more significant places and for several more values of a than given here. It is seen that $1 + \epsilon$ varies slowly for the functions minimized for changes in c and k . We believe therefore that 1.063 is a fairly accurate result. It will be noted that this result is in agreement with that obtained by correcting Hylleraas' one term function, and that the agreement between the empirical value of $-\lambda/4 = 1.1358$ and the theoretical $-\lambda/4 = 1.1354$ indicates that the trial function used by us is good.

It is of course usually said that an eigenfunction may be quite inaccurate even if a good eigenwert is obtained. We must consider this in somewhat more detail. Eckart¹⁴ has already given a criterion for the accuracy of eigenfunctions. His reasoning may be extended so as to apply to the specific calculation of a given quantity.

With Eckart we let the solution obtained by the variational method with a given trial function be ϕ and the true eigenfunctions (in this case of the 3S system) we denote in order of decreasing term values by ψ_1, ψ_2, \dots ; the corresponding negatives of the energy we write as W_1, W_2, \dots . The functions ψ_1, ψ_2, \dots are supposed to be normalized and $\phi = a_1\psi_1 + a_2\psi_2 + \dots$ where $a_1^2 + a_2^2 + \dots = 1$. Eckart shows that if the trial function ϕ leads to

¹⁴ Carl Eckart, Phys. Rev. **36**, 878 (1930). In this very useful and interesting paper will be found also many other eigenfunctions. The one used for 3S states of two electron systems is very similar to ours. The eigenwert for Li^+ obtained by Eckart is almost as good as the one obtained by us. For our work we considered it important to minimize for c as well as the other constants because the result is fairly sensitive to c . See also D. S. Hughes and C. Eckart, Phys. Rev. **34**, 694 (1930) for the calculation of the isotope effect in the Li^+ spectrum.

an energy value of absolute amount W then $1 - a_1^2 < (W_1 - W)/(W_1 - W_2)$. We wish to calculate the average of some quantity $f(q)$ over the configuration space q . The function ϕ gives the approximate result $\bar{f}_0 = \int f(q)\phi^2(q)dq$ while the correct result is $\bar{f} = \int f(q)\psi^2(q)dq$. The error is

$$\bar{f}_0 - \bar{f} = (a_1^2 - 1)f_{11} + a_2^2 f_{22} + a_3^2 f_{33} + \dots + 2a_1 a_2 f_{12} + \dots$$

where $f_{ik} = \int \psi_i \psi_k f dq$. The terms in f_{ii} are of the order of $1 - a_1^2$ which in the present instance is of the order of 4×10^{-3} . The relative error due to these terms can be therefore neglected. The only important terms are those containing $f_{1i} (i \neq 1)$. Thus

$$\bar{f}_0 - \bar{f} \cong 2a_1 \sum_{i=2}^{\infty} a_i f_{1i} \cong 2 \sum_{i=2}^{\infty} a_i f_{1i}. \tag{44}$$

Any a_i^2 for $i > 1$ is $< 1 - a_1^2 < (W_1 - W)/(W_1 - W_2)$ and the general order of magnitude of (44) is that of $((W_1 - W)/(W_1 - W_2))^{1/2}$. The numbers f_{1i} are however also of influence. In order to estimate their order of magnitude we must use the special form of f . In our problem

$$f = \frac{1}{2}(\delta(0, q_2) + \delta(0, q_1))$$

q_1 and q_2 being the collective coordinates of electrons 1 and 2. We have then

$$f_{12} = \int \psi_1(0, q)\psi_2(0, q)dq. \tag{45}$$

Approximately

$$\begin{aligned} \psi_1 &\cong 2^{-1/2}[\phi_{1s}(q_1)\phi_{2s}(q_2) - \phi_{1s}(q_2)\phi_{2s}(q_1)] \\ \psi_2 &\cong 2^{-1/2}[\phi_{1s}(q_1)\phi_{3s}(q_2) - \phi_{1s}(q_2)\phi_{3s}(q_1)] \end{aligned}$$

where the ϕ_{1s} is a hydrogenic function in a central field of nuclear charge Z and ϕ_{2s}, ϕ_{3s} are hydrogenic functions in a central field of nuclear charge $Z - 1$. The hydrogenic functions ϕ_{2s}, ϕ_{3s} are orthogonal to each other. In this approximation $f_{12} \cong (1/2)\phi_{2s}(0)\phi_{3s}(0)$. It will now be remembered that $\phi_{ns}(0)^2$ in a field of charge Z is proportional to Z^3/n^3 . Thus $\phi_{2s}(0)^2/\phi_{1s}(0)^2 \cong (2/3)^3(1/2)^3 = 1/27$ in the present instance. We may take $f_{12} < (1/30)f$. It is now seen that we are likely to over-estimate the error by setting $a_3 = a_4 \dots = 0$, and attributing all the error to a_2 . Doing this, $\bar{f}_0 - \bar{f} = 2a_2 f_{12} \cong (a_2/15)f$ and a_2 itself is of the order of $1/15$. Thus the accuracy is likely to be about $(1/2)$ percent.

This estimate of the probable error together with the agreement of this calculation with the numerically corrected Hylleraas one term function makes us think that the value 1.06 which we calculated by both methods is probably correct to 1 percent. We thus conclude

$$1 + \epsilon = 1.06. \tag{46}$$

Using this value in (36'') (37) and the separation between components (1) and (3) observed by Schüler we can derive the value of μ . According to Gran,

ath⁶ a slight correction must be applied to Schüler's value of v_{vac} for component (3). Applying this correction and supposing that the nuclear spin is $k = 3/2$ we get

$$1840\mu/k = g = 2.13. \quad (46')$$

Thus Schüler's and Granath's present data and the present calculation indicate that the magnetic moment of the Li_7 nucleus is approximately equal to three times the theoretical magnetic moment of a proton. If the magnetic moment were exactly three times the theoretical protonic moment the g value in (46') would be $g = 2$. We have at present no explanation to offer for the result $g = 2.13$. It appears that the difference of 2 and 2.13 is a greater one than can be accounted for by experimental errors or by errors in our calculation. It must be remembered however that the measured position of component (1) may be slightly affected by the proximity of component (2) and that the whole separation between (1) and (3) is of the order of 1 cm^{-1} .

Note added in proof: If the coupling of the electronic orbits and spins is of the Russell-Saunders type and if the electronic interactions are not too large and yet considerably larger than the interactions with the nucleus it is possible to give general and simple formulas applying to the case of one electron being in an s state. The other electron is then supposed to be in an L state of azimuthal number l . We may write the energy perturbation as:

$$w = (\mu/k)(b/2)[f(f+1) - k(k+1) - j(j+1)] \quad (47)$$

where the perturbation Hamiltonian is taken to be $H' = (\mathbf{B}\mathbf{u}) = (\mu/k)(\mathbf{B}\mathbf{k})$ and \mathbf{k} denotes the angular momentum matrix vector of the nucleus in units $\hbar/2\pi$. If the electronic angular momentum J is made diagonal in the sense of containing $\delta(j', j'')$ as a factor for every matrix element and if for a given j the matrix J_z is also diagonal then the diagonal elements of B_z for that j mb ; $m = (j, j-1, \dots, -j)$. The proof of this for B_z is exactly similar to the proof for σ_z in the usual derivation of Lande's g factor. The momentum J_z remains conserved under the perturbation B_z . We now imagine the coupling between the electron spins and between the two orbital momenta to be removed. The matrix elements may be referred to pairs of states such as $({}^2S_{1/2})_{m_1}$ and $({}^2L_{l+1/2})_{m_2}$. A canonical transformation does not change the sum of diagonal matrix elements belonging to a given $m = m_1 + m_2$. The values of b for 3L and 1L are thus related to the values for 2S , 2L by sum rule equations:

$$\begin{aligned} (l+1)b({}^3L_{l+1}) &= (\tfrac{1}{2})b({}^2S) + (l + \tfrac{1}{2})b({}^2L_{l+1/2}) \\ l\{b({}^3L_{l+1}) + b({}^3L_l) + b({}^1L_l)\} \\ &= (\tfrac{1}{2})b({}^2S) + 2lb({}^2L_{l+1/2}) + (l - \tfrac{1}{2})b({}^2L_{l-1/2}) \text{ etc.} \end{aligned}$$

The values of b for the one electron terms are known:

$$b({}^2L_l) = 2\mu_0 l(l+1)/j(j+1) \cdot (\overline{r^{-3}}); \quad b({}^2S) = (16\pi/3)\mu_0 \psi_S^2(0).$$

The value of $b({}^1L_l)$ is easily computed directly and the remaining b are determined by the above relations. Thus:

$$\begin{aligned}
b({}^3L_{l+1})/\mu_0 &= (8\pi/3)\psi_S^2(0)/(l+1) + 4l(\overline{r^{-3}})/(2l+3) \\
b({}^3L_l)/\mu_0 &= (8\pi/3)\psi_S^2(0)/(l^2+l) + 2(\overline{r^{-3}}) \\
b({}^3L_{l-1})/\mu_0 &= -(8\pi/3)\psi_S^2(0)/l + 4(l+1)(\overline{r^{-3}})/(2l-1) \quad (47') \\
b({}^1L_l)/\mu_0 &= 2(\overline{r^{-3}}).
\end{aligned}$$

Formulas (36), (36') are special cases of (47), (47'). The fact that sum relations such as used here exist has already been mentioned on p. 210 of Pauling and Goudsmit, *Structure of Line Spectra*. According to an informal communication of Professor Goudsmit these sum rules have been used by him in the derivation of the general formula in *Phys. Rev.* **35**, 440 (1930). Formulas (47), (47') apply only to the case of Russell-Saunders coupling but have the advantage of simplicity.