PHYSICAL REVIEW VOLUME 85, NUMBER 3 FEBRUARY 1, 1952

Wave Function of Ionized Lithium*

P. J. LUKE,† R. E. MEYEROTT,‡ AND W. W. CLENDENIN
Yale University, New Haven, Connecticut

(Received October 18, 1951)

A nonrelativistic wave function for the $1s2s\ {}^3S$ state of singly ionized lithium has been found by using an expansion of the function in Legendre polynomials of the cosine of the angle between the lines joining the electrons to the nucleus. Previous work had indicated that the distance dependent coefficient of the angle-independent term of the expansion predominates over the others. This made it possible to obtain an accurate function by computing to high precision an approximate value of the coefficient as a function of the distances of the electrons from the nucleus. The calculation of this function of the two distances was facilitated by the separability of the wave equation satisfied by the function. An additive correction to this function and also the distance dependent coefficients of higher order Legendre polynomials, all of which were comparatively small, could then be calculated by relaxation and numerical variational methods of less accuracy. Application of tests based on the virial theorem and Green's theorem to the wave function were used as criteria of accuracy. The Ritz integral led to the energy value $-1.135724\ RhcZ^2$, where R is Rydberg's constant for lithium, Z is the atomic number, and h and c are Planck's constant and the velocity of light, respectively. This result compares favorably with the experimental value, corrected for the relativistic effect and nuclear motion, of $-1.135722\pm0.000025\ RhcZ^2$. The hyperfine structure integral $1+\epsilon$ of Breit and Doermann was found to have the value 1.06191 ± 0.00003.

I. INTRODUCTION

A WAVE function for the $1s2s\ {}^3S$ state of singly ionized lithium has been obtained by Breit and Doermann,[1] using a variational procedure. This function gave a value of the energy parameter in agreement with the experimental value to about 1 part in 3000 and was used to compute the hyperfine splitting with an uncertainty of about 1 percent. The object of the present paper is to extend this work by obtaining a more accurate wave function, and, particularly, to develop a method suitable for this purpose. The method of solution, which was suggested by Breit and used in the present work, consists of the following steps and reasoning.

Disregarding spin dependence the wave function of an S state can be represented exactly in terms of the length of the lines joining the two electrons to the nucleus and the angle between them. The agreement with experiment of the function obtained by Breit and Doermann indicates that the function may be approximated by neglecting its dependence on the angle between the two lines. The function is therefore expanded in a series of Legendre functions of the cosine of this angle. The coefficients of the Legendre functions depend on the two distances and will be occasionally referred to as "functional coefficients." Substitution into the Schrödinger equation yields an infinite set of coupled equations between these functions of the two distances. The solution is started by first neglecting all but the coefficient of the Legendre function of order zero, i.e., by assuming an angle independent approximation. In this approximation the wave equation is separable as is clear from the work of Breit and Doermann. For a prescribed energy, exact particular solutions can be constructed, therefore, in such a way as to satisfy boundary conditions for each electron at the nucleus and at infinity. On account of the antisymmetry of the space function in the two electrons it is also necessary to make the wave function vanish when the two electrons are at the same distance from the nucleus. By employing a finite number of terms and an energy value which is only slightly inaccurate, the latter condition can be satisfied only approximately. An initial approximation is obtained by minimizing the integral of the square of the wave function for the line in two-dimensional space on which the wave function must vanish. A correction to the wave function is then worked out by a method similar to Southwell's relaxation procedure. This correction term is a solution of the differential equation for the angle independent function and is arranged to cancel the residue of the initial approximation on the line of equal distances. The improved angle independent function is then used in the coupled equations to determine the functional coefficients of higher order Legendre functions. Changes in the coefficient of the Legendre function of order zero necessitated by the last step are then worked out, and the consistency of the whole solution is reexamined.

II. GENERAL EXPANSION

The wave equation considered here is the Schrödinger equation for a particle without spin. The effect of spin dependent terms on the energy may be calculated by means of this wave function employing standard perturbation methods and will not be discussed until the end of the paper. In calculating the wave function it is convenient to take as coordinates the Euler angles which specify the orientation of the electronic triangle formed by the nucleus and the two electrons, the distances r_1, r_2, and the angle θ which specify the size and

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* Assisted by the joint program of the ONR and AEC.

† Now at the Applied Physics Laboratories of Johns Hopkins University, Silver Spring, Maryland.

‡ Now at the Argonne National Laboratory, Chicago, Illinois.

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

shape of the triangle. Here r_1 and r_2 are, respectively, the distances of electrons 1 and 2 from the nucleus, and θ is the angle between r_1 and r_2. For S states the wave function does not depend on the Euler angles.[2] The differential equation for ψ is Eq. (39) of Breit and Doermann's paper, *viz.*,

$$[\partial^2/\partial r_1^2+\partial^2/\partial r_2^2+(1/r_1^2+1/r_2^2)(\partial/\sin\theta\partial\theta)(\sin\theta\partial/\partial\theta)$$
$$+\lambda/4+1/r_1+1/r_2-1/(Zr_{12})]\varphi=0. \quad (1)$$

Here $\varphi=r_1r_2\psi$ and r_{12} is the interelectronic distance. The units of the energy parameter λ and of length are $\mu e^4Z^2/2\hbar^2=RhcZ^2$ and $\hbar^2/2\mu e^2Z=a_H'/2Z$, respectively, where e, $\hbar$, are, respectively, the electronic charge, Planck's constant divided by 2π while Z is the atomic number; the symbol μ is used for the reduced mass of the auxiliary two-body problem in which one electron is supposed to move in the field of the Li^7 nucleus. A partial justification for the employment of this kind of reduced mass is obtained by observing that the most important effect on the hyperfine structure arises from the coupling of the $1s$ electron to the nucleus and that if the $2s$ electron were absent the employment of the reduced mass has been justified by Breit and Meyerott.[3] The Bohr radius a_H' is the value which the Bohr radius of hydrogen would have if hydrogen had an atomic mass 7. The boundary condition on φ is that it vanish when either r_1 or r_2 is zero or infinity. In addition, since the term is of the triplet system, the wave function is antisymmetric in space coordinates and

$$\varphi(r_1, r_2, \theta)=0, \quad (r_1=r_2). \quad (2)$$

Further, it is possible and also convenient to work in the region $r_1>r_2$ and determine the rest of the function by means of Eq. (2).

To solve Eq. (1), the function φ is expanded in a series of Legendre polynomials

$$\varphi(r_1, r_2, \theta)=\Sigma_{l=0}^{\infty}(2l+1)^{\frac{1}{2}}\Phi_l(r_1, r_2)P_l(\cos\theta). \quad (3)$$

The interelectronic distance r_{12} is also expanded as

$$1/r_{12}=(1/r_1)\Sigma_{n=0}^{\infty}(r_2/r_1)^nP_n(\cos\theta), \quad (r_1>r_2). \quad (4)$$

Substitution of these expansions in Eq. (1) and integration over θ leads to a set of coupled differential equations for the functions Φ_l. These are

$$[\partial^2/\partial r_1^2+\partial^2/\partial r_2^2-l(l+1)(1/r_1^2+1/r_2^2)+\lambda/4$$
$$+1/r_1+1/r_2-M_{ll}/2Z]\Phi_l=\Sigma_m{}'M_{lm}\Phi_m/(2Z). \quad (5)$$

Here the coefficient M_{lm} is

$$M_{lm}=(2l+1)^{\frac{1}{2}}(2m+1)^{\frac{1}{2}}(1/r_1)$$
$$\times\Sigma_0^{l+m}(r_2/r_1)^n\int_0^{\pi}P_lP_mP_n\sin\theta d\theta \quad (6)$$

and the primed summation over m is for $m\neq l$. The summation over n is broken off because of the fact that the integral of three Legendre functions vanishes if the index of one exceeds the sum of the indices of the other two.[4] Nonvanishing values of the integral start therefore with $n=|l-m|$ and extend to $n=|l+m|$.

Solution of the wave equation will be simplified if one of the terms in the expansion of Eq. (3) is much larger than the others. The following considerations show that Φ_0 predominates over the other terms. The homogeneous equation,

$$[\partial^2/\partial r_1^2+\partial^2/\partial r_2^2-l(l+1)(1/r_1^2+1/r_2^2)+\lambda/4$$
$$+1/r_1+1/r_2-M_{ll}/(2Z)]\chi_l=0 \quad (7)$$

defines a set of orthonormal eigenfunctions $\chi_l^{(n)}$, with eigenvalues $\lambda_l^{(n)}$ with the understanding that χ_l satisfies the boundary conditions on φ. The function corresponding to the lowest eigenvalue is the best first approximation to φ and it can be seen from Eq. (7) that this is $\chi_0^{(0)}$ with eigenvalue $\lambda_0^{(0)}$, since both the term $l(l+1)(1/r_1^2+1/r_2^2)$ and the change in M_{ll} raise the energy for $l>0$. The equation for $\chi_0^{(0)}$, which is essentially Eq. (39′) of Breit and Doermann,

$$[\partial^2/\partial r_1^2+\partial^2/\partial r_2^2+\lambda_0^{(0)}/4+(Z-1)/Zr_1+1/r_2]\chi_0^{(0)}$$
$$\equiv[\mathfrak{L}+(\lambda_0^{(0)}/4)]\chi_0^{(0)}=0 \quad (8)$$

is just the Schrödinger equation for the inner electron moving in the unscreened nuclear potential $-Ze^2/r_2$ and the outer electron in the potential $-(Z-1)e^2/r_1$ corresponding to complete screening by the inner electron. This picture leads one to expect $\chi_0^{(0)}$ to be a good first approximation to φ. With the eigenvalue $\lambda_0^{(0)}$, there exists no other solution of Eq. (7), so that each Φ_l for $l>0$ must be a solution of the inhomogeneous equation, Eq. (5). If each Φ_l is expanded in a series

$$\Phi_l=\Sigma_lc_l^{(n)}\chi_l^{(n)} \quad (9)$$

the coefficients $c_l^{(n)}$, obtained from Eq. (5) are

$$c_l^{(n)}=4(\chi_l^{(n)}, \Sigma_m{}'M_{lm}\Phi_m)/[2Z(\lambda-\lambda_l^{(n)})]. \quad (10)$$

If only the interaction with $\Phi_0\approx\chi_0^{(0)}$ is considered, this becomes

$$c_l^{(n)}=4(\chi_l^{(n)}, (r_2^l/r_1^{l+1})\chi_0^{(0)})/[Z(2l+1)^{\frac{1}{2}}(\lambda-\lambda_l^{(n)})]. \quad (10a)$$

The functions $\chi_l^{(0)}$ have no nodes in the interior of the region for all l, $\chi_l^{(n)}$ have nodes for $n>0$. Therefore $|(\chi_l^{(n)}, \chi_0^{(0)})|<|(\chi_l^{(0)}, \chi_0^{(0)})|<1$, and since $r_2^l/r_1^{l+1}<1$ for all but a small part of the region near $r_2=r_1$ and for $r_1<1$, the inequality

$$|(\chi_l^{(n)}, (r_2^l/r_1^{l+1})\chi_0^{(0)})|<|(x_l^{(0)}, (r_2^l/r_1^{l+1})\chi_0^{(0)})|<1$$

also holds. This, together with the fact that $|\lambda-\lambda_l^{(n)}|$ increases with increasing n shows that $|c_l^{(0)}|>|c_l^{(n)}|$,

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[2] In principle the possibility of separating the Euler angles has been covered by E. Wigner, Z. Physik, **43**, 624 (1927). An explicit treatment of separation of angles employing only elementary methods is found in G. Breit, Phys. Rev. **36**, 383 (1930).

[3] G. Breit and R. E. Meyerott, Phys. Rev. **72**, 1023 (1947).

[4] See, e.g., Whittaker and Watson, *Modern Analysis* (Cambridge University Press, London, 1948), p. 331, ex. 11.

and therefore a rough approximation to Φ_l is $c_l^{(0)}\chi_l^{(0)}$, or

$$\Phi_l \cong 4(\chi_l^{(0)}, (r_2^l/r_1^{l+1})\chi_0^{(0)})\chi_l^{(0)}/[Z(2l+1)^{\frac{1}{2}}(\lambda-\lambda_l^{(n)})]. \quad (11)$$

Equation (11) shows that in this approximation Φ_l is negative if $\chi_0^{(0)}$ is positive, and that the order of magnitude of Φ_l decreases with increasing l. That Φ_l and Φ_0 should have opposite signs is to be expected. Indeed on account of the electronic repulsion, there should be a preference for the situation in which the electrons are on opposite sides of the nucleus. This preference is exhibited by negative coefficients for P_l in Eq. (3) when l is odd.

III. ITERATIVE PROCEDURE AND ANGLE INDEPENDENT APPROXIMATION

Returning to Φ_0, it is seen that this function may be separated into two parts,

$$\Phi_0 = \Phi_0^{(0)} + \Phi_0^{(1)} \quad (12)$$

with $\Phi_0^{(0)} = c_0^{(0)}\chi_0^{(0)}$ the solution of the homogeneous equation obtained by setting $l=0$ and neglecting the right side in Eq. (5), and $\Phi_0^{(1)} = \Sigma_1^\infty c_0^{(n)}\chi_0^{(n)}$ a suitably chosen particular solution of the inhomogeneous equation.

If the problem consisted only in obtaining a solution of Eq. (5) for $l=0$ and with prescribed $\Phi_m(m>0)$ there would be no objection to adding to $\Phi_0^{(1)}$ an arbitrary constant multiple of $\Phi_0^{(0)}$. Such an addition would modify, however, the values of the Φ_l obtained by solving Eq. (5) for $l>0$. An iterative procedure of solving the equations becomes impossible, therefore, unless a closer specification of $\Phi_0^{(1)}$ is made. In principle any definite specification can come under consideration and the uniqueness of the solution of the Schrödinger equation assures one of the equivalence of all convergent procedures. Considerations based on the Schrödinger perturbation theory, for which we are indebted to Professor Breit, have indicated, however, that for securing convergence it is advantageous to require that $\Phi_0^{(1)}$ be orthogonal to $\Phi_0^{(0)}$ at all stages of the iterative process.

The method of solution of Eq. (5) used in the work reported on is as follows:

(a) The function $\Phi_0^{(0)}$ is determined by a special method capable of relatively high accuracy on account of the separability of Eq. (8); $\Phi_0^{(0)}$ will be referred to as the angle independent approximation.

(b) Using $\Phi_0^{(0)}$ on the right side of Eq. (5), $\Phi_l^{(0)}$ is calculated.

(c) Newly computed functions $\Phi_m^{(0)}$ are introduced on the right side of Eq. (5) and the functions Φ_l improved.

(d) The function $\Phi_0^{(1)}$ is calculated using the functions Φ_l obtained as in (*c*).

If necessary, $\Phi_0^{(1)}$ is introduced into the calculation of the functions Φ_l and the cycle continued until the desired precision is obtained.

It is essential to have a good solution $\Phi_0^{(0)}$, because it is the only part of Φ giving direct contributions to the hyperfine structure in distinction to contributions through the normalization integral, because it is the largest term in φ in most of the configuration space, and because it is important in determining the Φ_l for $l>0$. The function $\Phi_0^{(0)}$ satisfies Eq. (8) and the boundary conditions on φ. Since Eq. (8) is separable for $r_1>r_2$, the solution can be expressed as a linear combination of products of the type $w(r_1)v(r_2)$. The boundary conditions at $r_1=\infty$ and $r_2=0$ can be satisfied by taking functions such that $w(\infty)=v(0)=0$. The antisymmetry condition at $r_1=r_2$ can be satisfied only by adjusting the coefficients of an infinite series of such products and then only if the energy is exactly right. A relatively good approximation can be obtained, however, using a finite number of terms, and a correction function which will be relatively small can be found by other methods. It is therefore convenient to put

$$\Phi_0^{(0)} = \varphi_0 + \varphi_1, \quad \varphi_0 = \Sigma_1^N c_j w_j(r_1)v_j(r_2). \quad (13)$$

These functions satisfy the differential equations

$$[\mathcal{L} + (\lambda_0^{(0)}/4)](\varphi_0+\varphi_1) = 0, \quad (14)$$

$$[\mathcal{L} + (\lambda_0^{(0)}/4)]\varphi_0 = 0. \quad (14.1)$$

The function φ_0 is the initial approximation of the introduction. The sum $\varphi_0+\varphi_1$ is the angle independent approximation of the heading of the present section. A value -1.13550 was chosen initially for $\lambda_0^{(0)}$. By means of the perturbation formula for energy[5] the improved value -1.13544667 was arrived at and used in the final calculations. The value -1.1354 obtained by Breit and Doermann has been used as a guide in the choice of the first trial value of $\lambda_0^{(0)}$. The solution for $\Phi_0^{(0)}$ was obtained as follows. Separating variables in the equation for φ_0 one finds the following equations for w_j and v_j

$$w_j'' + [-(Z-1)^2/(4Z^2k^2) + (Z-1)/(Zr_1)]w_j = 0, \quad (14.2)$$

$$v_j'' + [-1/(4j^2) + 1/r_2]v_j = 0, \quad (14.3)$$

where primes indicate differentiation with respect to r_1 or r_2. The parameters are related by the equation

$$\lambda_0^{(0)} + (Z-1)^2/(Z^2k^2) + 1/j^2 = 0. \quad (14.4)$$

One of the parameters j or k may be chosen at will and it is convenient to take $j=1, 2, 3\cdots$ so that the functions v_j are hydrogenic functions which do not depend on the value of $\lambda_0^{(0)}$. The completeness of this system of functions assures the possibility of the expansion. After a change of the independent variable, Eq. (14.2) assumes Whittaker's form of the equation for the confluent hypergeometric function. The functions w_j

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[5] Meyerott, Luke, Clendenin, and Geltman, Phys. Rev. **85**, 393 (1952).

were taken to be proportional to the Whittaker functions for the values of k determined by Eq. (14.4). By employing this choice for the solution of Eq. (14.2) one assures the condition that the wave function vanish term by term for $r_1=\infty$ as long as $r_2<r_1$. It is not necessary to do anything about $r_2>r_1$ because for such values the solution is obtained by antisymmetrizing the solution for $r_1>r_2$. Values of w_j computed at large r_1 from the asymptotic series were used as starting values for a numerical integration of Eq. (14.2) toward the origin using the method of Hartree.[6] At small r_1, w_j was computed by means of the series in ascending powers of r_1. The two tables of w_j were checked for smoothness of joining at $r_1=0.9$ in units $a_H'/2Z$.

In order to make $\varphi_0(r, r)$ as small as possible the coefficients c_j are adjusted so as to minimize the expression

$$f=\int[\varphi_0(r, r)]^2 ds \bigg/ \int\int[\varphi_0(r_1, r_2)]^2 dr_1 dr_2, \qquad (15)$$

where s is measured along the line $r_1=r_2$. This procedure determines only the ratios c_j/c_1, but the normalization condition

$$\int\int[\varphi^{(0)}(r_1, r_2)]^2 dr_1 dr_2=1$$

determines the remaining common factor in the c_j.

The calculation of the initial approximation was combined with improvements in the value of the energy. These can be made by means of a formula which follows from Green's theorem or else by means of a nearly equivalent formula which follows from a variational statement of the problem. It will be supposed that the value of $\lambda_0^{(0)}$ in Eq. (14.1) for which φ_0 has been computed is slightly in error. This imperfect value will be denoted by $4\Lambda_0$ so that

$$[\lambda_0^{(0)}]_{\text{preliminary}}=4\Lambda_0, \qquad (16)$$

while the value of $\lambda_0^{(0)}$ in Eq. (14) will be supposed to be accurate and for it

$$\lambda_0^{(0)}=4\Lambda. \qquad (16.1)$$

Writing

$$\mathfrak{L}=\Delta-V;\quad \Delta=\partial^2/\partial r_1^2+\partial^2/\partial r_2^2 \qquad (16.2)$$

and

$$\Phi=\Phi_0^{(0)} \qquad (16.3)$$

one applies Green's theorem to Φ and φ_0 interpreting Δ as the divergence of a gradient and obtaining

$$\Lambda-\Lambda_0=-\int_C \varphi_0(\partial\Phi/\partial n)ds \bigg/ \int\int_A \Phi\varphi_0 dr_1 dr_2 \qquad (16.4)$$

where the first integral is taken over a contour C enclosing area A and where $\partial/\partial n$ denotes differentiation with respect to a normal to C drawn outward from A. The second integral is over the area enclosed by C. In the application, A is the area of the 45° sector of the r_1, r_2 plane bounded by the lines $r_2=0$, $r_1=r_2$ and extending to infinite values of $(r_1^2+r_2^2)^{\frac{1}{2}}$. If φ_0 is a sufficiently good approximation to Φ to make $\partial\varphi_0/\partial n$ sufficiently close to $\partial\Phi/\partial n$ one has the approximation

$$\Lambda-\Lambda_0\cong-\int_C \varphi_0(\partial\varphi_0/\partial n)ds \bigg/ \int\int_A \varphi_0^2 dr_1 dr_2 \qquad (16.5)$$

in which all quantities are known from the initial approximation φ_0. In the work reported on the approximation of Eq. (16.5) was not as accurate as was desired without an estimate of $\partial\varphi_1/\partial n$ for use in Eq. (16.4). A way of calculating the energy correction is furnished by a variational formulation of the problem which is especially suitable for the application of the numerical variational method[5] used in the calculation of φ_1. According to this

$$\delta\Lambda=0,\quad \Lambda=\int\int\{(\nabla\Phi)^2+V\Phi^2\}dr_1 dr_2 \bigg/ \int\int\Phi^2 dr_1 dr_2 \qquad (17)$$

takes place of the differential equation for Φ, arbitrary variations being supposed to be performed on this function. Representing Φ as

$$\Phi=\varphi_0+\varphi_1, \qquad (17.1)$$

with φ_0 fixed and satisfying

$$-\Delta\varphi_0+V\varphi_0=\Lambda_0\varphi_\theta, \qquad (17.2)$$

the variational statement of the problem can be put in the form of $\delta\Lambda=0$ as in Eq. (17) but with

$$\Lambda-\Lambda_0=\left\{\int\int_A[(\nabla\varphi_1)^2+(V-\Lambda_0)\varphi_1^2]dr_1 dr_2 - \int_C \varphi_0(\partial\varphi_0/\partial n)ds\right\} \bigg/ \int\int_A \Phi^2 dr_1 dr_2, \qquad (18)$$

account being taken of the fact that $\varphi_0+\varphi_1=0$ on C. For small values of φ_0 on C the contour integral in curly braces in the preceding formula can be expected to be larger than the integral over the area because φ_1 depends approximately linearly on $\varphi_0(C)$ while $\partial\varphi_0/\partial n$ approaches a finite and nonvanishing limit. It is presupposed that the contour integral does not vanish to a higher order than φ_0, such a condition implying special circumstances. Under the foregoing conditions Eq. (18) gives again the approximation of Eq. (16.5). While this approximation should apply for infinitesimal φ_1, it was found necessary to correct for the integral over the area in the numerator of Eq. (18) employing values of φ_1 available with sufficient approximation from calculations made by means of the numerical variational method. In this manner it has been found possible to carry out successive improvements in Λ and φ_1, the procedure showing every evidence of stability.

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[6] D. R. Hartree, Mem. Proc. Manchester Lit. and Phil. Soc. **77**, 91 (1932).

Equation (18) shows that the calculation of φ_1 and $\Lambda-\Lambda_0$ involves the knowledge of φ_0 in a somewhat secondary manner for the calculation of the normalization integral and that besides its value on C must be known also. The normalization integral requirements can be taken care of in principle with any accuracy by tabulating φ_0 at small enough intervals. The requirements on C are tied in with the treatment of φ_1 by means of a two-dimensional net. Work with the latter would be prohibitively heavy if the net were made much finer than that used. There is consequently a practical limitation in the fact that on the line $r_1=r_2$ the function φ_0 is available in the form of a numerical table only. The error caused by this circumstance will be discussed in a later section.

In carrying out the numerical work the values of φ_1 were first obtained by means of Southwell's relaxation method and then the somewhat more laborious numerical variational method was applied to these preliminary values. The values were sequenced twice. It is not certain that this number of iterations was sufficient to stabilize the values within the accuracy used, but it is believed that this was the case.

The improvement in the wave function produced by changing the number of hydrogenic functions in φ_0 from 1 to 3 may be inferred from Table I in which values of f of Eq. (15) are tabulated against the number of hydrogenic terms used. These values are for $\lambda_0^{(0)}=-1.13550$ rather than -1.1354467 which was used in most of the calculations. If the latter value of $\lambda_0^{(0)}$ is used the value of f_{min} for the three term function becomes 4.48×10^{-6}. By means of Eqs. (16.1), (18) the correction to $\lambda_0^{(0)}$ is obtained as

$$4(\Lambda-\Lambda_0)=29.0\times10^{-6} \tag{19}$$

while Eqs. (16.1), (16.4) give

$$4(\Lambda-\Lambda_0)=30.0\times10^{-6}. \tag{20}$$

The origin of the slight discrepancy is not known, but it appears to be below the necessary accuracy requirements. The improved value of $\lambda_0^{(0)}$ is thus $-1.1354467+0.0000290=-1.135418$ to about 1 part in 10^{-6}.

A check on the function $\Phi_0^{(0)}$ was made using the virial theorem, according to which, a solution of the Schrödinger equation with potential energy homogeneous of degree -1 should give an average value of the potential energy equal to -2 times the average kinetic energy. To test φ_1 the ratio of the potential to the kinetic energy was computed for $\Phi_0^{(0)}$ and found to be $-2(1-2\times10^{-6})$. This check seems to confirm the order of accuracy of λ_0 which was quoted previously.

The desired accuracy was obtained by arranging the calculation in such a way that terms in $(\nabla\varphi_0)^2$ and φ_0^2 did not require numerical treatment by means of the net. Since φ_0 is the major part of Φ a relatively small accuracy in the cross product terms with φ_1 sufficed. Different methods were used in computing these terms and checked against each other. In these comparisons the way in which values of φ_1 between net points were made to depend on values at the net points was varied and it was found that although the individual cross terms were affected by such changes the final values of the potential and kinetic energies were not. Two main interpretations were used. In one Pearson's interpolation formulas[7] defined $\varphi_0\varphi_1$ between net points. In the other the interpolation surface of the numerical variational method defined φ_1.

IV. ANGULAR DEPENDENCE AND RESULTS

The angular terms Φ_l and the particular solution $\Phi_0^{(1)}$ of the inhomogeneous equation were next calculated according to the plan described previously. The function Φ_1 was computed first by relaxation methods using just $\Phi_0^{(0)}$ on the right side of Eq. (5). Then Φ_2 was calculated using $\Phi_0^{(0)}$ and Φ_1 on the right side of Eq. (5). A less accurate computation of Φ_3 was made using just $\Phi_0^{(0)}$ on the right side. The magnitudes of the first three angular terms were such that

$$g_1=2\times10^{-4}, \tag{21}$$

$$g_2=7\times10^{-6}, \tag{21.1}$$

$$g_3=0.7\times10^{-6}, \tag{21.2}$$

where

$$g_j=\int\int\Phi_j^2dr_1dr_2\bigg/\int\int\Phi^2dr_1dr_2. \tag{21.3}$$

TABLE I. Values of minimum f for different number of terms in φ_0.

Number of terms	f_{min}
1	1.1×10^{-2}
2	2.0×10^{-4}
3	5.0×10^{-6}

The function Φ_3 and functions with higher l thus seemed negligible for the purpose of energy and hyperfine structure calculation and were not considered further. The function Φ_1, however, was recomputed, using Φ_2 in addition to $\Phi_0^{(0)}$ by means of the numerical variational method. The final functional values were not greatly different from those obtained in the relaxation calculation. In obtaining Φ_1 and Φ_2, it was sufficiently accurate to use λ_0 in the differential equations in place of λ.

From Eq. (5), one sees that the differential equation for Φ_0 is of the form

$$[\mathcal{L}+(\lambda/4)]\Phi_0=R(r_1,r_2). \tag{22}$$

Utilizing the expansion of Φ_0 in the form of Eq. (9) one obtains

$$\Sigma_0^\infty(c_0^{(n)}/4)(\lambda-\lambda_0^{(n)})\chi_0^{(n)}=R. \tag{22.1}$$

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[7] K. Pearson, *Tracts for Computers* (Cambridge University Press, London, 1920), Vol. III, pp. 8–9, Eq. (IV).

The differential equation for $\Phi_0^{(1)}$ is found by subtracting Eq. (14) for $\Phi_0^{(0)}$ from Eq. (22), and is, writing Φ for $\Phi_0^{(0)}$,

$$[\mathfrak{L}+(\lambda/4)]\Phi_0^{(1)}=R-(1/4)(\lambda-\lambda_0^{(0)})\Phi. \quad (22.2)$$

Since $\Phi_0=c_0^{(0)}\chi_0^{(0)}$, the right side of Eq. (22.2) is, according to Eq. (22.1) orthogonal to Φ. This circumstance provides a means of calculating the value of λ to be used in Eq. (22.2) to obtain $\Phi_0^{(1)}$. It thus appears as though only routine numerical work remains at this stage in order to determine both λ and $\Phi_0^{(1)}$. It was found necessary, however, to exercise special care so as to avoid an instability in the calculation of $\Phi_0^{(1)}$ which can arise if Eq. (22.2) is not supplemented by an additional requirement. The difficulty became apparent when an attempt was made to calculate $\Phi_0^{(1)}$ by means of Eq. (22.2) starting with approximate values and employing a relaxation procedure without additional considerations. The sequencing process employed in this method kept on changing the values of $\Phi_0^{(1)}$ without any evidence of an approach to a limit. The origin of this phenomenon is the fact that Eq. (22.2) does not define $\Phi_0^{(1)}$ but only restricts it. In fact from any solution obtained for this function one can form an infinite number of other solutions by adding multiples of the solution of the homogeneous equation obtained by replacing the right side of the equation by zero. Since λ and $\lambda_0^{(0)}$ are very closely equal the function which may be added is a multiple of Φ within the limits of accuracy of the calculation. The addition of a multiple of Φ cannot be objected to in principle, but if it is made it becomes necessary to recalculate Φ_1, Φ_2, $\cdots$. Since any convention regarding the introduction of multiples of Φ at this stage is as good as any other the one requiring least work was chosen, *viz.*, the convention of having $\Phi_0^{(1)}$ orthogonal to Φ. As a result of enforcing this requirement the numerical treatment was made rapidly convergent. In order to have a further check on the values of $\Phi_0^{(1)}$ the direct calculations were supplemented by a variational calculation made as follows.

The differential equation for $\Phi_0^{(1)}$, Eq. (22), is of the form

$$(\Delta+U)g=R, \quad (23)$$

where U and R are functions of r_1 and r_2. It is supposed that an approximate solution g of this equation has been found and it is desired to find the multiplying factor A which will make the product Ag most nearly satisfy the equation. Thus the variation with respect to A of the quantity

$$I=\int\int[A(\Delta+U)g-R]^2 w dr_1 dr_2 \quad (24)$$

where w is a weighting factor, is set equal to zero. This leads to the following expression for A

$$A=\int\int R(\Delta+U)gwdr_1dr_2 \bigg/ \int\int(\Delta g+Ug)^2 wdr_1dr_2. \quad (25)$$

The weighting factors used in this work were unity and R^2. By means of this test a function with nearly the correct shape which has been determined by the relaxation method is being adjusted for the best over-all fit. If the relaxation procedure has been carried far enough the variational value of A should be close to unity. The writers are grateful to Professor G. Breit for pointing out the possibilities of this test as well as for pointing out the necessity of care regarding orthogonalization to Φ. They are indebted to Dr. R. Thaler for help in carrying out this stage of the calculation.

In calculating $\Phi_0^{(1)}$, two different sets of numerical values of the function obtained at different stages of the first calculations were used as starting values. The quantity A was computed for each set, and it was then multiplied by this factor. The new values were then relaxed once and the function made orthogonal to Φ by subtracting $(\Phi_0^{(1)},\Phi)\Phi$. The relaxing and orthogonalizing were repeated until the function had changed considerably. Then a new value of A was computed, and the whole process repeated until the functions obtained from the two starting points were in approximate agreement. The quantity A was computed for these two functions, and the values 0.985 and 0.982 were obtained when the weighting factor unity was used. For the weighting factor R^2, the values 1.018 and 1.011, respectively, were obtained. Over the part of the plane where $\Phi_0^{(1)}$ was as much as one-tenth its maximum value, the difference between the two functions was everywhere less than 10 percent and at most points less than 5 percent of either function.

With Φ_0, Φ_1, and Φ_2 calculated and the remaining terms of the expansion of φ negligible, the energy parameter λ may be computed. Substituting of φ in the Ritz integral leads to the expression

$$\lambda/4=\int\int_A \Sigma_l\{(\nabla\Phi_l)^2+[l(l+1)(r_1^{-2}+r_2^{-2}) -r_1^{-1}-r_2^{-1}]\Phi_l^2+(1/2Z)\Sigma_m M_{lm}\Phi_l\Phi_m\}dr_1dr_2 \Big/ \int\int_A \Sigma_l\Phi_l^2 dr_1dr_2. \quad (26)$$

In the numerator there occur contributions arising from one l at a time and also some cross terms arising from different l. The denominator contains no cross terms. The largest terms in both numerator and denominator are those for $l=0$. For purposes of calculation it is convenient to subtract Λ arranging the answer in terms of small quantities. One obtains

$$\lambda/4=\Lambda+(1/D)\int\int_A (T_1+T_2+T_3+T_4)dr_1dr_2 +(1/D)\int_C \Phi_0^{(1)}(\partial\varphi_0/\partial n)ds, \quad (26.1)$$

where

$$T_1 = 2[\nabla\varphi_1\cdot\nabla\Phi_0^{(1)} + (V-\Lambda)\varphi_1\Phi_0^{(1)}], \tag{26.2}$$

$$T_2 = (\nabla\Phi_0^{(1)})^2 + (V-\Lambda)(\Phi_0^{(1)})^2, \tag{26.3}$$

$$T_3 = \Phi_0\Sigma_{l>0}M_{0l}\Phi_l/(2Z), \tag{26.4}$$

$$T_4 = \Sigma_l\{(\nabla\Phi_l)^2 + [l(l+1)(r_1^{-2}+r_2^{-2}) - 1/r_1 - 1/r_2 + M_{ll}/(2Z)]\Phi_l^2 + \Sigma_{m\neq l}M_{lm}\Phi_l\Phi_m/(2Z)\}. \tag{26.5}$$

It is understood that the value of φ_0 corresponding to Λ rather than Λ_0 is used in the calculations. The last integral in Eq. (26.1) is zero provided $\Phi_0^{(1)}$ is zero on all of C as it is intended to be. It is not quite certain that the numerical work with the net has secured this condition with sufficient accuracy, but since there is no evidence to the contrary it was assumed that this integral may be neglected. The approximation made is perhaps more dangerous than other approximations because $\partial\varphi_0/\partial n$ is not a small quantity. The values of the integrals multiplying $1/D$ calculated by numerical methods are as follows due to $T_1 = -0.26\times10^{-6}$, due to $T_2 = 0.31\times10^{-6}$, due to $T_3 = (-67.71-4.68)\times10^{-6} = -72.39\times10^{-6}$, due to $T_4 = (-3.99-0.11)\times10^{-6} = -4.10\times10^{-6}$. In recording the contribution of T_3 the first contribution is for $l=1$, the second for $l=2$, and the same convention is used in recording T_4. The rapid decrease of contributions with increase in l is apparent. The sum of the terms multiplying $1/D$ is -76.4×10^{-6}. With the final values of the coefficients c_j, the integral $\int\int(\varphi_0)^2dr_1dr_2$ had the value 0.9998139. This number was not adjusted to be exactly 1 on account of technical detail which amounted to a time saving device. The remaining parts of the integral $\int\int(\Phi_0^{(0)})^2dr_1dr_2$ were computed in two ways. One method was to apply Pearson's scheme of integration to the integrands $\varphi_0\varphi_1$ and $(\varphi_1)^2$. The second utilized a Taylor expansion of φ_0 near the net points of φ_1 and the numerical variational interpolation formula for φ_1. Since $\Phi_0^{(1)}$ is orthogonal to $\Phi_0^{(0)}$ the only other term in $\int\int\Phi_0^2dr_1dr_2$ is $\int\int(\Phi_0^{(1)})^2dr_1dr_2$, which was evaluated by means of Pearson integration. The integrals $\int\int\Phi_1^2dr_1dr_2$ and $\int\int\Phi_2^2dr_1dr_2$ were also calculated both by Pearson's method and using the numerical variational interpolation formula. The values obtained for these integrals are given in Table II. Using the figures obtained by Pearson's method, the normalization integral $\Sigma_l\int\int\Phi_l^2dr_1dr_2$ has the value 0.999826, while the figures from the numerical variational interpolation yield 0.999832. As far as the computation of the energy is concerned, the difference between these is negligible. The term to be added to $\lambda_0^{(0)}$ in Eq. (26) is -277×10^{-6}, and λ is -1.135724.

TABLE II. Contributions to the normalization integral due to $\int\int x dr_1dr_2$.

x	Contribution evaluated by Pearson's formulas	Contribution according to numerical variational method
$2\varphi_0\varphi_1$	-206.9×10^{-6}	-192.9×10^{-6}
φ_1^2	5.6×10^{-6}	5.6×10^{-6}
$(\Phi_0^{(1)})^2$	0.9×10^{-6}	
Φ_1^2	205.2×10^{-6}	197.9×10^{-6}
Φ_2^2	7.2×10^{-6}	6.8×10^{-6}

This figure compares favorably with the experimental value of -1.135722 ± 0.000025 for the energy in units $RhcZ^2$. The latter value is obtained by adding the nonrelativistic energy of the inner electron to the difference in energy of the $1s2s\ {}^3S$ and $1s^2\ {}^1S$ levels given in the tables of the National Bureau of Standards.[8] In making the comparison consideration has been given to the possible presence of a relativistic energy correction. The importance of such a correction may be supposed to be small because the experimental value of the energy is obtained as the negative of the energy required to detach the $2s$ electron leaving one electron in the $1s$ state. Considering the problem in the central field approximation with effective central fields assumed independent of the degree of electron excitation the relativistic energy correction for the $1s$ electron is seen to enter experiment and theory in the same way. For the $2s$ electron the relativistic factor multiplying the nonrelativistic energy is $1+5Z^2\alpha^2/16$ where α is the fine structure constant. For $Z=3$ this factor minus unity is 1.5×10^{-4}. For a $2s$ electron in a field of $Z=3$ the expected addition to λ is, therefore, $-0.25\times1.5\times10^{-4} = -3.7\times10^{-5}$. However, the ionization energy of the $2s$ electron in units $RhcZ^2$ is 0.135 which is less than the 0.25 assumed in the preceding estimate. For this value the relativistic correction is only -2.0×10^{-5}. The value of Z used here is an overestimate, but the employment of the experimental energy largely compensates for this effect. An approximate way of taking into account the effect of screening is to use the picture of the effect of normalization employed by Fermi and Segrè[9] and by Breit.[10] In the notation of the latter reference one has

$$Z_0^2/n_0^2 = 0.135Z^2,$$

so that $n_0 = 1.81$ and

$$\psi^2(0)/\psi_0^2(0) = (2/3)^2(2/1.81)^3 = 0.58.$$

Here $\psi_0^2(0)$ refers to an hypothetical $2s$ electron in a field of $Z=3$ for which the correction was expected to be -3.7×10^{-5}. On this basis the correction may be expected to be $-0.58\times3.7\times10^{-5} = -2.2\times10^{-5}$. Both of the more careful estimates are on the limit of the experimental error. A correction for the nuclear motion is included in the use of the reduced electron mass for lithium in the Rydberg R. This correction had to be applied only to the difference between $-\lambda$ and unity because the experimental measurement, being concerned only with the ionization energy of the $2s$ electron has to do only with this difference.

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[8] Bureau of Standards Circular 467 (U. S. Government Printing Office, Washingon, D. C., 1949).

[9] E. Fermi and E. Segrè, Z. Physik **82**, 729 (1933).

[10] G. Breit, Phys. Rev. **42**, 348 (1932).

TABLE III. Contributions to $1+\epsilon$ due to $\int_0^\infty X dr_1$.

X	Contribution expressed in $\psi_{1s}^2(0)$
$\varphi_0'^2$	1.0632
$2\varphi_0'\varphi_1'$	−0.00035
$\varphi_1'^2$	0.00002
$\Phi_0^{(0)\prime}\Phi_0^{(1)\prime}$	−0.00026
$(\Phi_0^{(1)\prime})^2$	0.0000003

It is realized that the relativistic and reduced mass corrections should include additional effects taking into account the interaction between electrons. For the $1s2s$ configuration the Hughes-Eckart[11] effect gives no contribution if one neglects perturbations by other configurations, and one may expect the mass effect correction to be sufficiently reliable, therefore. Both corrections might need refinement, however, and only their approximate magnitude is relevant in the comparison with the experimental λ.

In terms of the functions Φ_l, the correction factor $1+\epsilon$ appearing in the expression of Breit and Doermann for the hyperfine splitting is

$$1+\epsilon=\Sigma_l\int_0^\infty(\partial\Phi_l/\partial r_2)^2{}_{r_2=0}dr_1/\psi_{1s}^2(0)\Sigma_l\int\int\Phi_l^2dr_1dr_2. \tag{27}$$

Computation of this quantity is simplified by the fact that for $l>0$, the function Φ_l must be of the order r_2^{l+1} near $r_2=0$, on account of the term $l(l+1)(1/r_1^2+1/r_2^2)$ in the differential equation. Consequently, only the term in Φ_0 enters the numerator of the expression in Eq. (27). Here one has

$$\partial\Phi_0/\partial r_2=\partial\varphi_0/\partial r_2+\partial\varphi_1/\partial r_2+\partial\Phi_0^{(1)}/\partial r_2, \tag{27.1}$$

and the derivative of $\varphi_0=\Sigma_1^3c_jw_j(r_1)v_j(r_2)$ is readily found. The functions v_j are normalized so as to have unit slope at $r_2=0$ so that

$$(\partial\varphi_0/\partial r_2)_{r_2=0}=\Sigma_1^3c_jw_j(r_1). \tag{27.2}$$

The derivative of φ_1 must be computed from the numerical tables of this function, and the tabular values are not supposed to be the actual values of the function at the net points. Instead they are considered to approximate the true surface in such a manner that, within the limitations of the interpolation formula used, the energy is made a minimum. It was considered desirable, therefore, to improve $\partial\varphi_1/\partial r_2$ by other means. One method consisted in fitting parabolas in r_2 to the tabular values near $r_2=0$ by least squares and computing the derivatives on the assumption that the parabolas represent φ_1. These derivatives were checked by fitting third-order curves to the same points. Later, the values obtained from the parabolas were improved in the following manner. For fixed r_1, the differential equation for φ_1 derived from Eqs. (14) and (14.1) was treated as an ordinary differential equation with approximate values of $\partial^2\varphi_1/\partial r_1^2$ obtained from the numerical tables of φ_1,

$$d^2\varphi_1/dr_2^2+(\chi+1/r_2)\varphi_1=R' \tag{28}$$

with $\chi=\lambda_0/4+(Z-1)/(Zr_1)$ and $R'(r_2)=(\Lambda_0-\Lambda)\varphi_0-\partial^2\varphi_1/\partial r_1^2$. If y is a solution of the homogeneous part of Eq. (28), the function yw will satisfy the inhomogeneous equation provided that

$$(d/dr_2)(y^2dw/dr_2)=yR. \tag{28.1}$$

The function y was computed by the method of Hartree[6] for about 9 representative values of r_1, taking starting values from a series expansion about $r_2=0$. Two quadratures then gave w. The function φ_1 was taken to be $yw+ay$ and the constant a determined in such a way as to join this function to the numerical tables of φ_1. The derivative $(\partial\varphi_1/\partial r_2)_{r_2=0}$ computed from $yw+ay$ was used to correct the previously determined values.

A similar method was employed in the case of $\Phi_0^{(1)}$. A third degree curve was fitted to the net point values near $r_2=0$ and the derivatives obtained from this were subsequently corrected by means of Hartree type integrations. In Table III are the integrals, aside from the normalization integrals, which make up the quantity $1+\epsilon$. In Table III a prime indicates differentiation with respect to r_2. The values in Table III together with the value 0.99983 of the normalization integral obtained from Table II give

$$1+\epsilon=1.06191\pm0.00003.$$

The uncertainty here is principally because of inability to evaluate the integral in $\Phi_0^{(1)}$ accurately. Relativistic corrections are not included in the calculation of $1+\epsilon$.

The authors would like to thank Professor G. Breit for his continued help and encouragement in the work. They would also like to acknowledge the help of Dr. S. Share, then at the University of Wisconsin, in making preliminary trials of the method, Dr. R. Thaler of the Sloane Physics Laboratory for help in the calculation for $\Phi_0^{(1)}$, and Mr. S. Geltman in the early phases of the work at Yale.

APPENDIX A

In order to obtain a check on the function φ_1, a perturbation calculation was made as follows. Let $\mathcal{L}$ be the operator given by

$$\mathcal{L}=\partial^2/\partial r_1^2+\partial^2/\partial r_2^2+[1-(1/Z)]/r_1+1/r_2 \quad r_1>r_2,$$
$$\mathcal{L}=\partial^2/\partial r_1^2+\partial^2/\partial r_2^2+1/r_1+[1-(1/Z)]/r_2 \quad r_2>r_1. \tag{A-1}$$

This operator defines the complete, orthonormal set of functions v_ν through the equation

$$(\mathcal{L}-\Lambda_\nu)v_\nu=0, \tag{A-2}$$

where $\nu=1, 2, 3\cdots$ and $\Lambda_1<\Lambda_2<\Lambda_3\cdots$. The function Φ

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[11] D. S. Hughes and C. Eckart, Phys. Rev. 36, 694 (1930).

is taken to be

$$\begin{aligned} \Phi &= \varphi_0(r_1, r_2) \qquad r_1 > r_2 \\ \Phi &= -\varphi_0(r_2, r_1) \qquad r_2 > r_1. \end{aligned} \tag{A-3}$$

Along the line $r_2 = r_1$, Φ is taken to be zero. The function Φ satisfies the differential equation

$$(\mathfrak{L} - \Lambda)\Phi = -2\varphi_0(r_1, r_2)\delta'(r_2 - r_1) \equiv U(r_1, r_2) \tag{A-4}$$

where δ' is the derivative of the Dirac δ-function. It is desired to find the function $\delta\varphi$, corresponding to φ_1, such that

$$\delta\varphi = v_1 - \Phi. \tag{A-5}$$

The function $\delta\varphi$ may be expanded in terms of the set of functions v_v, *viz.*,

$$\delta\varphi = \Sigma_v a_v v_v. \tag{A-6}$$

The coefficients a_v are found with the aid of (A-4) and (A-5) to be

$$\begin{aligned} a_1 &= 1 + [1/(\Lambda - \Lambda_1)] \int\int U v_1 dr_1 dr_2, \\ a_n &= [1/(\Lambda - \Lambda_n)] \int\int U v_n dr_1 dr_2, \end{aligned} \tag{A-7}$$

where $n = 2, 3, 4 \cdots$. As a_1 is an inconvenient quantity to work with, it is better to eliminate it from the calculation by utilizing the normalization condition

$$(\Phi, \Phi) = 1. \tag{A-8}$$

This, together with (A-5), gives for v_1 the expression

$$v_1 = (\Phi + \Sigma_n a_n v_n)/(1 - \Sigma_n a_n^2)^{\frac{1}{2}}. \tag{A-9}$$

In order to approximate the functions v_n without excessive labor, antisymmetrized products of hydrogen-like wave functions were used, e.g.,

$$\begin{aligned} v_2 \approx (2)^{-\frac{1}{2}}[&w_1^{(Z)}(r_2) w_3^{(Z-1)}(r_1) \\ &- w_1^{(Z)}(r_1) w_3^{(Z-1)}(r_2)]. \end{aligned} \tag{A-10}$$

Here $w_1^{(Z)}$ is the S-state hydrogen function for atomic number Z and principal quantum number 1, corresponding to the inner electron, while $w_3^{(Z-1)}$ is the S-state hydrogen function for atomic number $Z-1$ and principal quantum number 3, corresponding to the outer electron, which is assumed to be completely screened by the inner one. Using the subscript j for the principal quantum number of the hydrogen function for the inner electron and k for the outer electron, coefficients were computed for the functions v_{jk} in the cases of $v_{13} \equiv v_2$, v_{14}, v_{15}, v_{16}, v_{23}, v_{24}, v_{25}, v_{34}, and v_{45}. The coefficients were found to become markedly smaller as j and k increased, as would be expected. Coefficients for functions of the type v_{1n} where n refers to the continuum were also computed. The contributions of the continuum energy spectrum were found to be not limited to the low energy end but were appreciable up to an energy equal to about 14 times the ionization energy of ionized lithium. It was impracticable to extend the calculation further, especially since there was no assurance that the higher energy contributions would be negligible. Consequently, the calculation was stopped at this point.

Estimates of the effect of $\delta\varphi$ on the hyperfine structure integral were made. The main contribution of $\delta\varphi$ to $1+\epsilon$ is the term

$$\begin{aligned} &\left[2/(1 - \Sigma_n a_n^2)\psi_{1s}^2(0)\Sigma_l \int\int \Phi_l^2 dr_1 dr_2\right] \\ &\qquad \times \left[\int_0^\infty \{(\partial\varphi_0/\partial r_2)(\partial(\delta\varphi)/\partial r_2\}_{r_2=0} dr_1\right]. \end{aligned} \tag{A-11}$$

The discrete states contributed the amount -0.00013 to this term and the continuum, as far as computed, contributed the amount $+0.00009$. This last figure is not very significant, however, as the contribution of the continuum at the highest energy calculated was more than half the magnitude of the maximum continuum contribution and no estimate could be made of the contributions of higher energies. The continuum contributions were oscillatory as a function of energy, and the positive and negative parts nearly canceled each other, leaving the 0.00009 value as a residue. The perturbation calculation values are to be compared with that obtained using φ_1, which was -0.00035. It is seen that the perturbation values confirm the general order of magnitude of that obtained with the more accurate φ_1 which was obtained by the numerical relaxation procedure. They are not felt to be in conflict with the φ_1 value both because the perturbation calculation was incomplete and because the functions used in the expansion were only approximate. The reason for the large contributions caused by high energy lies in the fact that very short wavelengths are needed to smooth the discontinuity in the function Φ.