

Simple, Analytic, Atomic Wave Functions*

ARNOLD RUSSEK, CHARLES H. SHERMAN, AND DAVID E. FLINCHBAUGH
The University of Connecticut, Storrs, Connecticut

(Received September 5, 1961)

A method is presented for the determination, with relatively small effort, of analytic one-electron wave functions for an electron in an approximately self-consistent screened Coulomb field. The method enables one to avoid direct numerical solution of the Schrödinger equation. Instead, for each state one has to adjust two parameters to make a certain expression for the screening function reasonably approximate that which follows from the Thomas-Fermi ion for the atom in question. When this is done, one has automatically a simple, analytic expression for the eigenfunction and the corresponding energy eigenvalue for that state. In particular, pairs of parameters have been obtained for states of

several alkali atoms, including all of the normally filled states of sodium, the 6s state of potassium and most of the important excited states of cesium. The analytic wave functions thus obtained are simple enough so that the expectation values of many quantities can be easily calculated by analytic methods, a few of which are illustrated. Thus, the normalization constants are calculated for three of the states of cesium. Moreover, calculations for the fine structure and hyperfine structure energy splittings of cesium are carried out as a test of the goodness of the wave functions. Good agreement is obtained with experiment and with previous calculations.

I. INTRODUCTION

IT is well known that the Hartree-Fock procedure gives good approximations to the atomic wave functions. It is also well known that, although this method can always be carried out in principle, it is limited by practical considerations to the lighter atoms. Consequently, several workers have simplified the approach by replacing the potential, which, in the Hartree-Fock method, is derived in a self-consistent manner, by an approximately self-consistent potential obtained from the Thomas-Fermi statistical model. Of course, this simplification is achieved at the expense of accuracy, but the results are still good enough for many applications. The most recent attempt along these lines is that of Brudner and Borowitz,¹ who use the Thomas-Fermi ion potential to calculate wave functions for the 6s state of potassium and the 7s state of cesium. (The use of the potential for the ion instead of the neutral atom insures that an electron far away from the nucleus "sees" the potential produced by a single positive charge).

The present work proceeds along the lines followed by the paper of Brudner and Borowitz. (Consequently the introductory material and bibliography will here be kept to a minimum.²) The principal contribution made here is to develop *simple, analytic*, approximate wave functions that can be quickly obtained. For the expenditure of approximately an hour of time, with the aid of a slide rule, an analytic expression for the wave function for a given single particle state can be written down which yields only slightly poorer accuracy than was obtained by Brudner and Borowitz. It is simple enough that the expectation values for many quantities can be calculated analytically. Thus, with the wave functions obtained in Sec. II, normalization constants as well as fine structure and hyperfine structure split-

tings are obtained in Sec. III for some states of cesium, to illustrate the method. These are compared with the experimental values and yield relatively good agreement.

It should be pointed out that none of the sophisticated effects mentioned or taken into account by Brudner and Borowitz (penetration and polarization of the core by the outer electron, as well as exchange effects), are incorporated in this work. The two parameters used here do not permit sufficient flexibility in the screening function to warrant the inclusion of these small effects.

II. THE SIMPLEST APPROXIMATION

A. Wave Functions

In line with the principal objective of this paper, that of practical utility, the most useful results will be stated directly. Proofs will be relegated to Sec. IV along with methods for improving the accuracy. Thus, it will be shown in Sec. IV that the radial wave function for the n, l electronic state in an approximately self-consistent approximation is given by

$$\chi_{nl}(r) = [(1 + \beta_{nl}\gamma_{nl}r)/(1 + \alpha_{nl}\beta_{nl}\gamma_{nl}r)]^{\frac{1}{2}} \times \chi_{nl}^H[\zeta_{nl}(r)]. \quad (1a)$$

Here, α_{nl} and β_{nl} are two constants which will be determined later, $\chi_{nl}^H[\zeta_{nl}(r)]$ is the radial wave function for the n, l state of *ordinary hydrogen* and $\zeta_{nl}(r)$ is given by

$$\zeta_{nl}(r) = [(1 - \alpha_{nl})/\beta_{nl}] \ln(1 + \beta_{nl}\gamma_{nl}r) + \alpha_{nl}\gamma_{nl}r, \quad (1b)$$

and

$$\gamma_{nl} = Z/[1 + \frac{1}{2}l(l+1)\beta_{nl}(1 - \alpha_{nl})]. \quad (1c)$$

For convenience we also write down the functional form of χ_{nl}^H :

$$\chi_{nl}^H(\zeta) = (2\zeta/n)^{l+1} e^{-\zeta/n} L_{n+l-1}^{2l+1}(2\zeta/n), \quad (1d)$$

where the L_{n+l-1}^{2l+1} are the associated Laguerre polynomials. The functions (1d) are not normalized, inasmuch as each of the functions (1a) must be normalized separately.

* This research has been supported by the National Science Foundation.

¹ H. J. Brudner and S. Borowitz, Phys. Rev. **120**, 2053 (1960).

² See also E. H. Kerner, Phys. Rev. **83**, 71 (1951); T. Tietz, J. Chem. Phys. **25**, 789 (1956); **29**, 684 (1958).

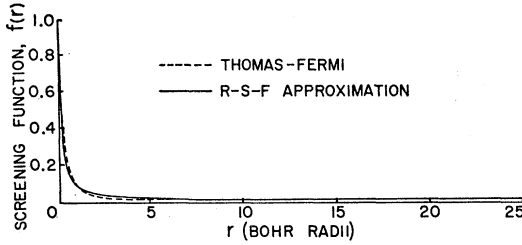


FIG. 1. A typical screening function (6s state of cesium) compared with the screening function derived from the Thomas-Fermi potential for the cesium ion.

Strictly speaking, the wave function given by Eqs. (1) is an exact eigenfunction of the differential equation:

$$\frac{d^2\chi}{dr^2} + \left[-\frac{l(l+1)}{r^2} + \frac{2Z}{r}f(r) + 2E \right] \chi = 0, \quad (2a)$$

with the energy eigenvalue given by

$$E = -\alpha^2\gamma^2/2n^2, \quad (2b)$$

in atomic units. This is the radial equation, in a.u., for an electron in a screened Coulomb potential, subject to the usual boundary condition at $r = \infty$, where the screening function is given by the formidable expression

$$f(r) = \frac{1}{Z} \left\{ \frac{r}{\xi} \gamma^2 \left(\frac{1+\alpha\beta\gamma r}{1+\beta\gamma r} \right)^2 + \frac{l(l+1)}{2r} \left[1 - \gamma^2 \frac{r^2}{\xi^2} \left(\frac{1+\alpha\beta\gamma r}{1+\beta\gamma r} \right)^2 \right] - \frac{\gamma^2}{2n^2} r \left[\left(\frac{1+\alpha\beta\gamma r}{1+\beta\gamma r} \right)^2 - \alpha^2 \right] + \frac{\gamma^2\beta^2(1-\alpha)}{8} \frac{(1+3\alpha)r + 4\alpha\beta\gamma r^2}{(1+\alpha\beta\gamma r)^2(1+\beta\gamma r)^2} \right\}. \quad (3)$$

For simplicity, we will omit the subscripts n and l on α , β , and γ whenever possible. Equation (3) reduces, in the near and far limits to

$$f \rightarrow 1 + \frac{\gamma^2}{Z} (1-\alpha)r \left\{ \frac{1}{2}l(l+1) \left[\frac{5}{8}\beta^2(1-\alpha) - \frac{4}{3}\beta^2 \right] - \frac{3}{2}\beta + \frac{1}{8}\beta^2(1+3\alpha) - \frac{1}{2n^2}(1+\alpha) \right\} + \dots, \quad r \rightarrow 0; \quad (4a)$$

$$f \rightarrow \frac{\alpha\gamma}{Z} \left[1 - \frac{1-\alpha}{n^2\beta} \right], \quad r \rightarrow \infty. \quad (4b)$$

Complicated as it may look, the expression (3) for the screening function can, for any given n and l , be made to fit quite closely to the screening function which follows from the Thomas-Fermi ion by suitably adjusting the

two parameters α and β . [Once this is done, γ is fixed by Eq. (1c).] The screening function (3) has the following properties: (1) At zero radius the screening function is unity, corresponding to the completely unscreened nuclear field. (2) As r increases, the screening function decreases to a broad, shallow minimum at around 15 Bohr radii, and then rises slightly as $r \rightarrow \infty$. These properties are illustrated in Fig. 1, which shows a typical screening function. The scale, however, is here too small to show the upturn beyond the minimum. The range in which the decrease to the minimum of f occurs is primarily determined by the parameter β , while the height of the minimum is primarily determined by the parameter α . The parameters α and β must both be positive in order to avoid singularities. Moreover, α will always be less than unity.

The method of adjusting α and β depends somewhat on the type of problem being considered. For the excited states of alkali atoms the best adjustment is achieved by requiring that (1) the screening function be equal to that which follows from the Thomas-Fermi ion at some radius in the neighborhood of unit radius, and that (2) the minimum value of the screening function be equal to Z^{-1} . The slight rise in the value of the screening function as $r \rightarrow \infty$ is inconsequential, inasmuch as the minimum is so broad, that often the ultimate rise is not apparent out to 25 Bohr radii.

It should be pointed out that the screening function given by (3) will be slightly different for different values of n and l . Therefore, the usual orthogonality relations that obtain will be only approximately fulfilled by the radial wave functions given by Eqs. (1). Figure 2 shows, by way of illustration, the screening functions for several excited states of cesium obtained by optimum adjustment of α and β as described above. For comparison,

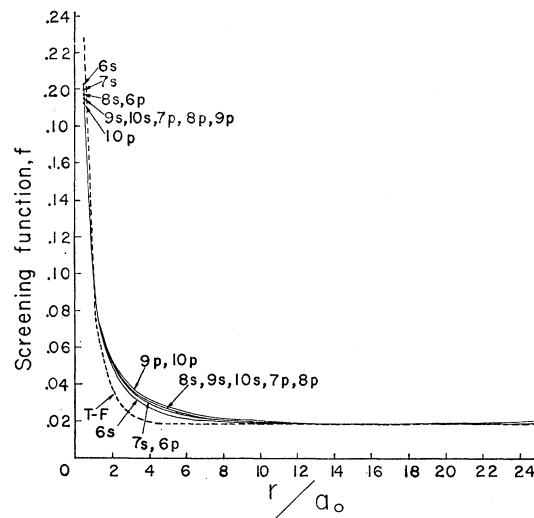


FIG. 2. Screening functions for the excited states of cesium compared with the Thomas-Fermi (T-F) screening function. The parameters α , β , and γ corresponding to these screening functions are given in Table I.

TABLE I. Parameters for excited states of cesium.

State	α	β	γ	Percentage error in energy
6s	0.058	0.066	55	-2%
7s	0.043	0.071	55	-2%
8s	0.037	0.075	55	1%
9s	0.034	0.078	55	6%
10s	0.032	0.079	55	11%
6p	0.051	0.079	51.2	3%
7p	0.041	0.085	50.9	1%
8p	0.036	0.089	50.6	3%
9p	0.034	0.091	50.5	6%
10p	0.032	0.093	50.4	11%
6d	0.043	0.132	39.9	3%
7d	0.040	0.139	39.3	5%
8d	0.038	0.143	38.9	6%
9d	0.037	0.145	38.8	11%

the screening function appropriate to the Thomas-Fermi cesium ion³ is also shown. All functions in Fig. 2 go to unity at zero radius. However, in order to make the differences between them visible, it was necessary to use an expanded vertical scale which only shows part of this range. It should be noted, nevertheless, that the percentage deviation between our screening functions and the Thomas-Fermi screening functions, is appreciable for small radii. Therefore, our approximation is poorest for the inner, or core electrons which have the greatest probability of being in this region. For those interested in the excited states of cesium, the parameters α and β are listed in Table I. These parameters make $f(1)=0.102$, which is the value derived from the Thomas-Fermi potential, and they make the minimum value of f equal to 0.0182, which is $1/Z$. Also listed in Table I, are the percentage errors in the calculated energy levels [from Eq. (2b)] for these states, as compared with the experimentally determined energy levels.

B. Properties of the Wave Function

In order to visualize the behavior of the wave function set down in Eqs. (1), it is necessary first to examine the behavior of ζ . A simple series expansion of (1b) yields

$$\zeta \rightarrow \gamma r, \quad r \rightarrow 0, \quad (5a)$$

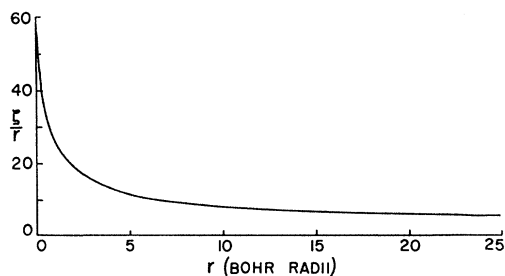


FIG. 3. A typical curve showing the dependence of ζ on r (6s state of cesium).

³ S. Kobayashi, Mem. Fac. Liberal Arts Educ. Kagawa Univ. 2, 62 (1958); see also J. Phys. Soc. Japan 14, 1039 (1959).

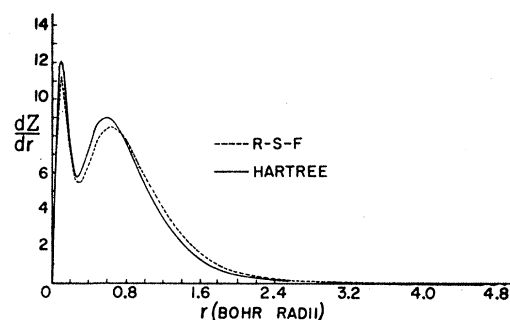


FIG. 4. Radial charge distribution ($-dZ/dr$) for singly ionized sodium as calculated by the present method and by Hartree.

while for large distances the logarithmic term is negligible compared to the linear term, so that

$$\zeta \rightarrow \alpha \gamma r, \quad r \rightarrow \infty. \quad (5b)$$

As has been mentioned previously, the parameter α is always less than one, so that the ratio ζ/r decreases as r goes from zero to infinity; more than that, it decreases monotonically. Figure 3 illustrates this behavior for the 6s state of cesium.

Now, from Eq. (1a) χ_{nl} is given as the product of two factors. The first factor increases monotonically from unity at $r=0$ to α^{-1} at $r=\infty$ (remember that $0 < \alpha < 1$). The second factor is the hydrogenic wave function, Eq. (1d), with ζ as the independent variable.

It is clear then that this wave function will look similar to the corresponding hydrogenic wave function, e.g., it will have the same number of nodes, but there will be two important differences. First, the scale factor relating ζ and r , which determines the distance between nodes, varies with r from γ to $\alpha\gamma$. Thus, the first node occurs approximately at γ^{-1} (Z^{-1} for s states) times the radius at which this node occurs in the same state of hydrogen. With increasing radius, the distance between nodes increases as compared to the distances between the corresponding nodes in hydrogen. The second difference between this wave function and the corresponding hydrogen wave function is due to the first factor which causes successive maxima and minima to increase monotonically in magnitude, relative to the corresponding magnitudes in hydrogen. Thus, we have the picture of a hydrogenic-type wave function with small, tight oscillations near the nucleus which widen out, as well as increase in amplitude as the radial coordinate increases. Of course, these are the expected qualitative features of the radial wave functions. But the present method is clearly able to supply quantitative details as well.

C. Comparison of the Wave Functions

Some of the wave functions obtained by the present method will be compared with those obtained by other means, in order to give some idea of the accuracy of the approximation. Figure 4 shows the radial charge distribution here obtained for singly ionized, sodium com-

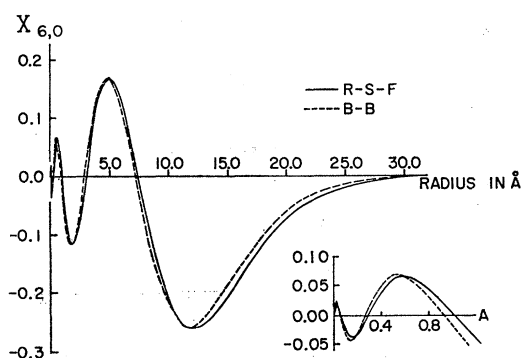


FIG. 5. The 6s state of potassium compared with that obtained by Brudner and Borowitz (B-B). Here both wave functions are normalized.

pared to the corresponding Hartree distribution.⁴ The parameters for these states were calculated, even though, as pointed out previously, the method should not be expected to have high accuracy for the inner electrons. The parameters α and β for this atom are listed in Table II. These were obtained by adjusting the value of the screening function to the Thomas-Fermi value at $r=1$ and to $1/Z$ at $r=\infty$ instead of at the minimum of the screening function. [For the smaller values of Z , the difference between the values of the screening function at the minimum, and at infinity is relatively small, so that it was not necessary to hunt for the minimum here. Thus, for slightly poorer accuracy than could otherwise be obtained, the work involved in finding α and β was reduced, inasmuch as $f(\infty)$ is directly given by Eq. (4b).]

Finally, Figs. (5) and (6) show the comparisons of the 6s state of potassium (for which $\alpha=0.083$ and $\beta=0.17$) and the 7s state of cesium with those obtained by Brudner and Borowitz.

III. CALCULATIONS USING THE WAVE FUNCTIONS

We now turn to the calculation of a few quantities related to the atomic structure of cesium to show the

$$\int_0^\infty e^{-\lambda \zeta} \zeta^q [\chi_{nl}^H(\zeta)]^2 d\zeta = [(n+l)!]^4 \left(\frac{n}{2}\right)^{q+1} \sum_{k,p=0}^{n-l-1} \frac{(-1)^{k+p} (2l+2+q+k+p)!}{(n-l-1-k)!(n-l-1-p)!(2l+1+k)!(2l+1+p)!k!p!} \left(\frac{1}{1+n\lambda/2}\right)^{2l+3+q+k+p} \quad (8)$$

where λ is a constant, and q is an integer such that $q > -3-2l$. Although computation of this integral for given n, l, q for a range of values of λ is somewhat tedious, the values obtained can be tabulated and used in other calculations involving different atoms. With this brief indication of the general method for carrying out calculations, we turn to the calculation of some specific quantities.

⁴ D. R. Hartree, Proc. Cambridge Phil. Soc. 24, 89, 111 (1928).

TABLE II. Parameters for the ground state of sodium.

State	α	β	γ
1s	0.72	0.32	11
2s	0.38	0.20	11
2p	0.32	0.25	9.4
3s	0.17	0.19	11

ease with which calculations using these wave functions can be carried out. At the same time, the accuracy of these wave functions can be tested by comparing the calculations with experimental data and with other calculations.

The normalized one-electron wave function is

$$\psi_{nlm}(r, \theta, \varphi) = N_{nl}(\chi_{nl}(r)/r)Y_{lm}(\theta, \varphi), \quad (6)$$

where N_{nl} is the normalization constant for the radial function, and Y_{lm} is the normalized spherical harmonic. In calculating the expectation value of some quantity $g(r)$, in the state characterized by the quantum numbers n, l we must evaluate the integral

$$\langle g(r) \rangle = N_{nl}^2 \int_0^\infty g(r) \chi_{nl}^2(r) dr = \frac{N_{nl}^2}{\gamma} \int_0^\infty g(r) \left(\frac{1+\beta\gamma r}{1+\alpha\beta\gamma r}\right)^2 [\chi_{nl}^H(\zeta)]^2 d\zeta. \quad (7)$$

A good approximate method of evaluating such integrals is to approximate that part of the integrand in (7) which is explicitly exhibited as a function of r as a function of ζ , by using an analytical expression consisting of products of powers of ζ and exponentials. When such an expression is inserted in Eq. (7), and the explicit expression for the hydrogenic function is used, we obtain integrals which can be evaluated in terms of factorials. Thus we have

A. Normalization Constants

We first consider calculation of the normalization constants. These are obtained by setting $g(r)=1$, so that

$$N_{nl}^{-2} = \frac{1}{\gamma} \int_0^\infty \left(\frac{1+\beta\gamma r}{1+\alpha\beta\gamma r}\right)^2 [\chi_{nl}^H(\zeta)]^2 d\zeta. \quad (9)$$

By making a semilogarithmic plot of $(1+\beta\gamma r)/(1+\alpha\beta\gamma r)$

TABLE III. Values of $I_{nl}(\lambda)/I_{nl}(0)$.

λ	6s	6p	6d
0.001	0.948	0.948	0.950
0.003	0.852	0.854	0.860
0.01	0.593	0.599	0.617
0.02	0.365	0.372	0.411
0.0374	0.177	0.184	0.196
0.0594	0.0851	0.0899	0.0983
0.0834	0.0465	0.0501	0.0556
0.143	0.0189	0.0212	0.0234

as a function of ζ , it is easy to find the desired type of approximate expression. For example, for the cesium 6s state (where the values of α , β , γ were given previously) we find that

$$\frac{1+\beta\gamma r}{1+\alpha\beta\gamma r} \approx -\frac{1}{\alpha} \left(1 - \frac{1}{\alpha}\right) \times [0.4e^{-0.0065\zeta} + 1.5e^{-0.085\zeta} - 0.9e^{-0.063\zeta}]. \quad (10)$$

This expression has the correct behavior both for large and small values of r , and it reproduces the actual values to within about 10% at worst, and much better than this over most of the range of r . If desired, a more accurate approximation of the same kind could be obtained by using more terms in Eq. (10). When Eqs. (9) and (10) are combined, we use Eq. (8) with $q=0$. Using the notation

$$I_{nl}(\lambda) = \int_0^\infty e^{-\lambda\zeta} [\chi_{nl}^H(\zeta)]^2 d\zeta, \quad (11a)$$

it follows that

$$I_{nl}(0) = n^2 [(n+l)!]^3 / (n-l-1)!, \quad (11b)$$

from the well-known integral for the hydrogen normalization constant. We give in Table III a brief tabulation of $I_{nl}(\lambda)/I_{nl}(0)$ computed from Eq. (8) for the range of λ needed for evaluating normalization constants. From Eqs. (9) and (10) we obtain the normalization constant in terms of $I_{nl}(\lambda)$ for several values of λ , and then, using Table III, get its numerical value. The result is given in Table V in two forms: as the actual numerical value of the normalization constant and as the ratio of this to the corresponding normalization constant for hydrogen, here denoted by H_{nl} , where

$$H_{nl} = [a_0 I_{nl}(0)]^{-\frac{1}{2}}, \quad (12)$$

and a_0 is the Bohr radius. The normalization constants for the cesium 6p and 6d states were calculated in the same way, and are also given in Table V.

B. Fine Structure

We next calculate the doublet separation due to spin-orbit interaction. Here we have

$$g(r) = \xi(r) = \frac{1}{2m^2c^2} \frac{1}{r} \frac{\partial V}{\partial r} = \frac{Ze^2}{2m^2c^2r^3} \left(f - r \frac{df}{dr} \right), \quad (13)$$

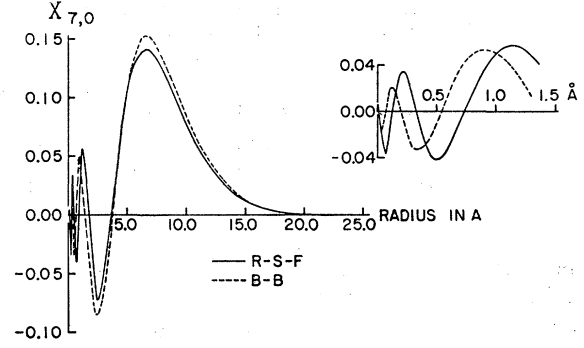


FIG. 6. The 7s state of cesium compared with that obtained by Brudner and Borowitz (B-B). Here both wave functions are normalized.

and the doublet separation given by first order perturbation theory⁵ is, in wave numbers,

$$\begin{aligned} \Delta\sigma_{nl} &= (N_{nl}^2/hc) (l+\frac{1}{2}) \hbar^2 \int_0^\infty \xi(r) \chi_{nl}^2(r) dr \\ &= \frac{N_{nl}^2}{hc} (l+\frac{1}{2}) \hbar^2 \int_0^\infty \xi(r) \\ &\quad \times \left(\frac{1+\beta\gamma r}{1+\alpha\beta\gamma r} \right)^2 [\chi_{nl}^H(\zeta)]^2 d\zeta. \end{aligned} \quad (14)$$

The approximation

$$\xi(r) \left(\frac{1+\beta\gamma r}{1+\alpha\beta\gamma r} \right)^2 \approx \frac{Ze^2\gamma^3}{2m^2c^2} \frac{1}{\zeta^3} (1.4e^{-0.065\zeta} - 0.4e^{-0.22\zeta}), \quad (15)$$

for the cesium 6p state is easily found graphically, and is adequate for this calculation [the values of α , β , γ and the function $f(r)$, have been given previously]. We now need the integrals

$$J_{nl}(\lambda) = \int_0^\infty \zeta^{-3} e^{-\lambda\zeta} [\chi_{nl}^H(\zeta)]^2 d\zeta.$$

These were evaluated by use of Eq. (8) with $q=-3$, and values of $J_{nl}(\lambda)/I_{nl}(0)$ are given in Table IV. Combining Eqs. (14) and (15) and using Table IV, we obtain

TABLE IV. Values of $J_{nl}(\lambda)/I_{nl}(0)$.

λ	6p	6d
0.0594	0.00139	0.000229
0.0834	0.00134	0.000205
0.143	0.00122	0.000160
0.223	0.00109	0.000118
0.333	0.000945	0.0000793

⁵ E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1951), p. 122, 423.

TABLE V. Normalization constants (N_{nl}) and doublet separation ($\Delta\sigma_{nl}$) for cesium.

State	N_{nl}/a_0	N_{nl}/H_{nl}	Calc. $\Delta\sigma_{nl}$ (cm^{-1})	Expt. $\Delta\sigma_{nl}$ (cm^{-1})
6s	724×10^{-7}	0.765
6p	14.9×10^{-7}	0.655	800	554
6d	0.197×10^{-7}	0.393	45	43

the doublet separation for the cesium 6p state. The doublet separation for the cesium 6d state was calculated in the same way. Both results are given in Table V along with the experimental values⁶ for comparison. The agreement between the calculated and experimental values is reasonably good, indicating the approximate validity of both the screening functions and the wave functions involved in the calculation. To our knowledge, no other theoretical calculation of the doublet separation for cesium is given in the literature.

C. Hyperfine Structure

As a final example, we consider the hyperfine structure of the cesium energy levels. An s state is split into two energy levels, (due to interaction with the nuclear magnetic moment) with separation in wave numbers given, according to Fermi's formula,⁷ by

$$\delta\sigma = (8/3hc)\mu_0\mu\pi\psi^2(0)[(2I+1)/I]. \quad (16)$$

μ_0 is the Bohr magneton, μ is the nuclear magnetic moment, I is the nuclear angular momentum quantum number, and $\psi(0)$ is the value of the normalized s -state wave function at the origin. Since this formula is known to require corrections,^{8,9} we first compare the value of $\psi^2(0)$ obtained by the present method with a previously calculated value. From Eq. (6) we find

$$\psi^2(0) = (N_{n0}n!Z)^2/\pi a_0^2, \quad (17)$$

and, using the normalization constant in Table V, we obtain $\psi^2(0) = 1.78 \times 10^{25} \text{ cm}^{-3}$ for the 6s state of cesium. Apparently the best previous calculation was made by Nile⁹ and is given by Breit.⁸ Nile's value is $1.7(5) \times 10^{25} \text{ cm}^{-3}$ in good agreement with our value. With this value of $\psi^2(0)$ and using $\mu = 2.577$ nuclear magnetons and $I = \frac{7}{2}$ we find the hyperfine separation of the cesium 6s state to be about 0.2 cm^{-1} , the observed value⁶ is 0.3 cm^{-1} .

The hyperfine separations for a p state are given by a formula similar to Eq. (16) but with $\pi\psi^2(0)$ replaced by $\langle r^{-3} \rangle$. We have calculated $\langle r^{-3} \rangle$ for the cesium 6p state by the methods described above [it requires the integrals $J_{nl}(\lambda)$ which were already evaluated for the fine structure calculations]. The value obtained is $\langle r^{-3} \rangle = 1.85 a_0^{-3}$. It is worth while noting, that in this

case one can obtain a good approximation to $\langle r^{-3} \rangle$ by using the small r approximation for ζ ($\zeta \approx \gamma r$). Then we have

$$\langle r^{-3} \rangle \approx N_{nl}^2 \gamma^2 \int_0^\infty \zeta^{-3} [\chi_{nl}^H(\zeta)]^2 d\zeta = N_{nl}^2 \gamma^2 \langle r^{-3} \rangle_H / H_{nl}^2, \quad (18a)$$

where

$$\langle r^{-3} \rangle_H = \frac{[(n+l)!]^3}{H_{nl}^2 a_0^2 (n-l-1)! n! (l+1)! (l+\frac{1}{2})}. \quad (18b)$$

Thus, in this approximation the value of $\langle r^{-3} \rangle$ differs from that for hydrogen, mainly through the different normalization constant. The result obtained this way is $\langle r^{-3} \rangle = 1.73 a_0^{-3}$, which shows that in certain cases approximate calculations can be done very easily with these wave functions once the normalization constants have been calculated. An approximate value of $\langle r^{-3} \rangle \mathcal{H}$ (where \mathcal{H} is a small relativistic correction) was determined for the cesium 6p state from fine structure data by Barnes and Smith.¹⁰ They found $\langle r^{-3} \rangle \mathcal{H} = 1.29 a_0^{-3}$.

For the hyperfine structure of the 6p state, we give only the separation of the two levels into which the $^2P_{\frac{3}{2}}$ state is split. This separation in wave numbers is given by⁵

$$\delta\sigma = (8/3hc)\mu_0\mu\langle r^{-3} \rangle [(2I+1)/I], \quad (18)$$

and, using $\langle r^{-3} \rangle = 1.85 a_0^{-3}$, we get $\delta\sigma = 0.046 \text{ cm}^{-1}$. The measured value¹¹ of this splitting is 0.037 cm^{-1} .

IV. MATHEMATICAL DERIVATIONS

In this section, the assertions made in Sec. II will be justified. In addition, it will be pointed out how the present approach can be generalized to obtain screened Coulomb wave functions for screening functions that have greater flexibility than those presented in Sec. II.

We wish to find the eigenfunctions and energy eigenvalues of the eigenvalue equation,

$$\frac{d^2\chi}{d\rho^2} + \left[-\frac{l(l+1)}{\rho^2} + \frac{2Z}{\gamma} \frac{f(\rho)}{\rho} + \frac{2E}{\gamma^2} \right] \chi = 0, \quad (19)$$

subject to the usual condition of finiteness at infinity. Here, f is the screening function and, for later convenience, we have introduced the radial coordinate

$$\rho = \gamma r, \quad (20)$$

where r is measured in Bohr radii. Note that the special case of Eq. (19) in which $\gamma = Z = f = 1$ is just the eigenvalue equation for ordinary hydrogen. Using the notation of Sec. II, we have

$$\frac{d^2\chi^H}{d\zeta^2} + \left[-\frac{l(l+1)}{\zeta^2} + \frac{2}{\zeta} - \frac{1}{n^2} \right] \chi^H = 0. \quad (21)$$

⁶ R. F. Bacher and S. A. Goudsmit, *Atomic Energy States* (McGraw-Hill Book Company, New York, 1932), p. 171.

⁷ E. Fermi, *Z. Physik* **60**, 320 (1931).

⁸ G. Breit, *Phys. Rev.* **42**, 348 (1931).

⁹ S. W. Nile, *Phys. Rev.* **38**, 375 (1931).

¹⁰ R. G. Barnes and W. V. Smith, *Phys. Rev.* **93**, 95 (1954).

¹¹ H. Kopfermann, *Nuclear Moments* (Academic Press, Inc., New York, 1958), p. 101.

In Eq. (21) we have substituted the known energy levels for hydrogen and have called the radial coordinate ζ , since this quantity is, for our purposes, merely an auxiliary mathematical variable.

Let us now consider the function:

$$\chi(\rho) = \chi^H(\zeta) (d\zeta/d\rho)^{-\frac{1}{2}}, \quad (22)$$

where ζ is an, as yet, unspecified function of ρ . Differentiating Eq. (22) with respect to ρ gives

$$\begin{aligned} \frac{d\chi}{d\rho} &= \frac{d\chi^H}{d\rho} \left(\frac{d\zeta}{d\rho}\right)^{-\frac{1}{2}} + \chi^H \frac{d}{d\rho} \left(\frac{d\zeta}{d\rho}\right)^{-\frac{1}{2}} \\ &= \frac{d\chi^H}{d\zeta} \left(\frac{d\zeta}{d\rho}\right)^{\frac{1}{2}} + \chi^H \frac{d}{d\rho} \left(\frac{d\zeta}{d\rho}\right)^{-\frac{1}{2}}, \end{aligned} \quad (23)$$

where we have substituted

$$\frac{d\chi^H}{d\rho} = \frac{d\chi^H}{d\zeta} \frac{d\zeta}{d\rho}. \quad (24)$$

Taking, now, the second derivative, we have, upon simplification

$$\frac{d^2\chi}{d\rho^2} = \frac{d^2\chi^H}{d\zeta^2} \left(\frac{d\zeta}{d\rho}\right)^{\frac{3}{2}} + \chi^H \frac{d^2}{d\rho^2} \left(\frac{d\zeta}{d\rho}\right)^{-\frac{1}{2}}. \quad (25)$$

When (25) and (22) are substituted into (19) and the whole equation is divided through by $(d\zeta/d\rho)^{\frac{3}{2}}$, we get

$$\begin{aligned} \frac{d^2\chi^H}{d\zeta^2} + \left[-\frac{l(l+1)}{\rho^2} + \frac{2Z}{\gamma} \frac{f(\rho)}{\rho} + \frac{2E}{\gamma^2} \right. \\ \left. + \left(\frac{d\zeta}{d\rho}\right)^{\frac{1}{2}} \frac{d^2}{d\rho^2} \left(\frac{d\zeta}{d\rho}\right)^{-\frac{1}{2}} \right] \chi^H \left(\frac{d\zeta}{d\rho}\right)^{-2} = 0. \end{aligned} \quad (26)$$

However, the function $\chi^H(\zeta)$ must also satisfy the equation (21) which defines it. Subtracting (21) from (26) and solving the resulting equation for f yields

$$\begin{aligned} \frac{Z}{\gamma} f(\rho) &= -\frac{\rho}{\zeta} \left(\frac{d\zeta}{d\rho}\right)^2 + \frac{l(l+1)}{2\rho} \left[1 - \frac{\rho^2}{\zeta^2} \left(\frac{d\zeta}{d\rho}\right)^2 \right] \\ &\quad - \rho \left[\frac{E}{\gamma^2} + \frac{1}{2n^2} \left(\frac{d\zeta}{d\rho}\right)^2 \right] - \frac{\rho}{2} \left(\frac{d\zeta}{d\rho}\right)^{\frac{1}{2}} \frac{d^2}{d\rho^2} \left(\frac{d\zeta}{d\rho}\right)^{-\frac{1}{2}}, \end{aligned} \quad (27)$$

where ζ is an arbitrary function of ρ with the sole requirement that its derivative is never zero in the entire range $0 \leq \rho \leq \infty$, [since we have divided by $(d\zeta/d\rho)^{\frac{3}{2}}$ in obtaining (27)].

If we insisted that we find the transformation $\zeta(\rho)$ that takes us from the hydrogenic eigenfunction to the screened Coulomb eigenfunction for a given function $f(\rho)$, we would have the hopeless nonlinear differential

equation (27) to solve. However, the whole philosophy of the present approach is to find a screening function f which is close in shape to a reasonable screening function, and which yields simple eigenfunctions. We do not care how complicated is the functional form of f we use. Picking a reasonable function ζ to meet these requirements is, as yet, still an art. The simplest acceptable transformation with the constants chosen to give the proper behavior for both large and small ρ , used in Sec. II, is

$$\zeta = [(1-\alpha)/\beta] \ln(1+\beta\rho) + \alpha\rho, \quad (28)$$

the derivative of which is

$$d\zeta/d\rho = (1+\alpha\beta\rho)/(1+\beta\rho). \quad (29)$$

As a first step toward making $f(\rho)$ a reasonable screening function, we insist that $f(0)=1$. It then follows from (27), using (28) and (29), that

$$2Z/\gamma = 2 + l(l+1)\beta(1-\alpha), \quad (30)$$

from which Eq. (1c) follows immediately. We also find from (27) that as ρ approaches infinity

$$(2Z/\gamma)f(\rho) \rightarrow 2\alpha \left[1 - \frac{1-\alpha}{n^2\beta} \right] - \rho \left[\frac{2E}{\gamma^2} + \frac{\alpha^2}{n^2} \right], \quad (31)$$

and to keep $f(\infty)$ finite, we must have

$$E = -\alpha^2\gamma^2/2n^2, \quad (32)$$

which is Eq. (2b). The screening function is obtained in the form given in Eq. (3) when (32) and (29) are used with (27). We then have the screening function expressed in terms of the two parameters α and β , which can be determined as described in Sec. II.

Greater flexibility in fitting to a given screening function can be achieved by using a functional form for ζ

$$\zeta = \frac{1-\alpha}{\beta} \ln(1+\beta\rho) + \frac{1}{1+b\rho^2} - 1 + \alpha\rho \frac{1+c\rho}{1+c\rho}. \quad (33)$$

If a and c are much less than α and β , then the factor $(1+ac\rho)/(1+c\rho)$ can give flexibility in determining the behavior of f for large ρ without much changing the shape of f at small ρ . On the other hand, the term $(1+b\rho^2)^{-1} - 1$ gives greater flexibility in determining the behavior at small ρ without much changing the shape at large ρ .

ACKNOWLEDGMENTS

The authors wish to express their appreciation to the United Aircraft Corporation Research Laboratory for the use of their computational facilities in obtaining the data for plotting the final graphs as well as all the preliminary graphs which assisted in optimizing the method.