

related to each other, so that we can expect elliptically polarized radiations for the side components. The predicted elliptical polarization mode of the longer wavelength side component is illustrated in Fig. 8. The central component is linearly polarized along the $[\bar{1}\bar{1}0]$ axis ($H \parallel [\bar{1}\bar{1}0]$) when the magnetic field is applied along the $[\bar{1}10]$ axis.

The longitudinal Zeeman effect with $H_0 \parallel [111]$ is obtained from the results given in Table IV. The Zeeman patterns are visualized in Fig. 6. The characteristic feature of this result is such that the central component is linearly polarized in the (111) plane while the side components are circularly polarized in the opposite sense to each other in the same plane.

The agreement of these calculated longitudinal Zeeman patterns with the experimental ones is very good in all cases as expected.

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Thomas-Fermi Technique for Determining Wave Functions for Alkali Atoms with Excited Valence Electrons*

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A technique has been developed for the calculation of excited state, one-electron wave functions based on the Thomas-Fermi statistical theory of the atom. This technique is applied to heavy alkali atoms for which Hartree-type solutions are complex and difficult to obtain. The Thomas-Fermi differential system for the alkali positive ions is accurately solved utilizing Milne's method, and the results are summarized. This Thomas-Fermi core potential is then used as a central field in the Schrödinger equation together with the Heisenberg type of polarization energy correction. Angular dependence is assumed to be capable of separation, and two basic techniques for solving the radial Schrödinger equation are discussed, one due to Ridley, the other to Biermann and Lübeck. The general approach permits correction for penetration of the excited electron's orbital. The Biermann and Lübeck type solution also allows for the inclusion of a qualitative correction for exchange. The techniques are applied to the potassium atom with an excited valence electron in the $6s$ state. The results are encouraging when compared with a Biermann and Lübeck type calculation using a Hartree central potential done by Villars. The $7s$ state of the cesium atom which has not been obtained by Hartree central potential is also computed.

I. INTRODUCTION

THE only systematic approach to the calculation of atomic structure and properties is via the Hartree¹ or Hartree-Fock² approximation. However, there are limitations to these calculations. Their numerical complexity makes it difficult to obtain an overall physical picture of the atom. Only isolated solutions are possible in these approximations and for heavier atoms the numerical complexity of the self-consistent iterations makes the calculations for atomic structure all but impossible.

There are additional complications which arise when attempting to calculate the structure of excited states since one requires that the wave functions used be orthogonal to all lower states, and it is sometimes impossible to obtain solutions with this requirement.

For those states for which Hartree or Hartree-Fock one-electron wave functions cannot be obtained, one can use a somewhat cruder approximation which has the advantage of simplicity, namely the Thomas-Fermi model.^{3,4} The basic assumptions in this model, however, require that we investigate only the ground-state configurations. Some attempts have been made by Latter⁵ to investigate the excited states of an electron in the Thomas-Fermi central potential. This is of course an approximation to the description of excited states

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¹ D. R. Hartree, Proc. Cambridge Phil. Soc. **23**, 542 (1926).

² V. Fock, Z. Physik **61**, 126 (1930).

³ L. H. Thomas, Proc. Cambridge Phil. Soc. **23**, 542 (1926).

⁴ E. Fermi, Rend. accad. nazl. Lincei **6**, 602 (1927); Z. Physik **48**, 73 (1928).

⁵ R. Latter, Phys. Rev. **90**, 510 (1955).

of atoms since, for example, some self-force on the electron is included and there is no correction for interaction effects. The procedure described in this paper is a combination of the Thomas-Fermi technique and a self-consistent procedure. It is easiest to apply to cases where there are several closed shells and the excitations being discussed are those of electrons outside of these closed shells. We consider the excited electron to move in the Thomas-Fermi field of the remaining electrons, and we use a self-consistent procedure to account for the distortion of the Thomas-Fermi field due to the penetration of the charge cloud by the excited electron.

In this paper, we first treat the $6s$ state of the potassium ion. Potassium was chosen since it represents the heaviest alkali which has been treated by a Hartree method, so that our method can be compared with the Hartree result. An s state was chosen because we felt that the effects of the penetration of the ion core would be most prominent. Since the results with potassium were practically identical to those previously obtained by the Hartree central field method, we were emboldened to attempt the calculation of the $7s$ state of cesium, an element too heavy to be treated by the Hartree method.

The proposed technique is mainly outlined in Sec. II. Section III discusses the accurate solution of the Thomas-Fermi equation for pure ions, and Sec. IV discusses the solution of the Schrödinger equation with the effective central potential. The self-consistency features are in Sec. V, results are presented in Sec. VII, and conclusions in Sec. VIII. It should be noted that our object is to find reasonable and relatively simple wave functions to describe an atomic system, and much of the analysis we make is to be regarded as heuristic rather than rigorous.

II. THE GENERAL TECHNIQUE

For an alkali atom, we first neglect the interaction of the excited electron with the remaining ion core. The ion core can then be treated by the Thomas-Fermi technique since the remaining core electrons are all in the ground state, and for a heavy ion, well approximated by a continuous distribution. Such an ionic system obeys the following differential system⁶:

$$\phi''(x) = \phi^{\frac{3}{2}}(x)/x^{\frac{3}{2}}, \quad (2.1)$$

with

$$\phi(0) = 1, \quad (2.2)$$

$$\phi(x_0) = 0, \quad (2.3)$$

$$x_0\phi'(x_0) = -(Z-N)/Z, \quad (2.4)$$

where

$$\phi(r) = r[V(r) - V_0]/Ze, \quad (2.5)$$

$$x = r/a_0(9\pi^2/128Z)^{\frac{1}{3}} = rZ^{\frac{1}{3}}/0.885341a_0, \quad (2.6)$$

⁶ P. Gombas, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, Germany, 1956), Vol. 36, Part II, p. 125.

with $V(r)$, the radially symmetric potential; a_0 , the first Bohr radius; Z , the nuclear charge; N , the number of electrons in the ion core; and r_0 , the effective radius of the ion, being defined such that for $r > r_0$, $V(r) = (Z-N)e/r$. Solving this set of equations yields a potential distribution for the core which will be called $V_{\text{ion core}}$. The solution of the Thomas-Fermi ion will be considered in the next section.

This potential will not be exactly the one that the excited electron moves in. We first include polarization effects. Even for a completely nonpenetrating outer electron, which might be expected to move in a completely hydrogen-like Coulomb field, there is produced a resultant asymmetry or polarization which leads to a slightly greater binding energy for the nonpenetrating electron than for the hydrogenic electron. For our analysis, the effect of polarization by the outer electron can be treated by a technique suggested by Born and Heisenberg.⁷ The argument is as follows: in those regions where the effective radius r of the electron's orbit exceeds the dimensions of the core, the electron exerts a sensibly homogeneous field, $-e/r^2$, on the core, and so induces a dipole moment $-\alpha_p e/r^2$ in the core, where α_p is the latter's specific polarizability. The dipole will always be oriented so that the excited electron lies along the dipole axis; thus the dipole will react on the excited electron with an attractive force

$$F(r) = 2\alpha_p e^2/r^5, \quad (2.7)$$

since a dipole of strength μ yields a field $2\mu/r^3$ along its axis. The potential energy contribution due to polarization of the ion core is then

$$\int F(r)dr = -\alpha_p e^2/2r^4 = U_{\text{pol}}. \quad (2.8)$$

The value of the polarizability of the ion core can be determined by a number of theoretical and experimental methods. It can be obtained from the index of refraction of the ion in solutions,^{8,9} or in crystals,¹⁰ or by theoretical techniques of Mayer and Mayer,¹¹ Pauling,¹² and Sternheimer.¹³ The polarizability values which were chosen for the present calculation are those obtained from the second-order Stark effect. In general the energy of interaction between an atom and an applied field may be represented by the series

$$\Delta T = AF + BF^2 + CF^3 + \dots \text{ cm}^{-1}, \quad (2.9)$$

where ΔT is the correction to the term value of the atom, F is the applied field strength (volts/cm) and A , B , and C are constants referred to as the first-order,

⁷ M. Born and W. Heisenberg, *Z. Physik* **23**, 388 (1924).

⁸ A. Heydweiller, *Z. Physik* **26**, 526 (1925).

⁹ K. Fajans and G. Joos, *Z. Physik* **23**, 1 (1924).

¹⁰ I. Tessman, A. Kahn, and W. Shockley, *Phys. Rev.* **92**, 890 (1953).

¹¹ J. E. Mayer and M. G. Mayer, *Phys. Rev.* **43**, 605 (1933).

¹² L. Pauling, *Proc. Royal Soc. (London)* **A114**, 181 (1927).

¹³ R. Sternheimer, *Phys. Rev.* **96**, 951 (1954).

second-order, and third-order coefficients. The hydrogen atom alone has a nonzero value for A . The second order Stark effect is essentially the energy contribution due to the induced electric moment. This amounts to $-\frac{1}{2}\alpha_p F^2$,¹⁴ thus $\alpha_p = -2Bhc$. The polarizabilities of the alkali ions as obtained in this way are presented in Table I.¹⁵

It is seen from the above discussion that the polarization energy is one that should be included mainly in the region outside the ion core; however, it is intuitively obvious that there is no discontinuity in the polarization potential at the core boundary and some polarization effect can be expected in the outer regions of the core itself. How the transition can be made is discussed further in Sec. IV.

III. THE THOMAS-FERMI IONS

For free positive ions, the Thomas-Fermi system is given by Eqs. (2.1) through (2.5). Solutions for positive ions are in the form indicated in Fig. 1. From the boundary relation given as Eq. (2.4), it is to be noted that $(Z-N)/Z$ signifies the segment of the ordinate axis which the tangent to the ϕ curve at the crossing point $(x_0, 0)$, cuts off from the ordinate axis when extended backwards. From this geometrical observation,

TABLE I. Polarizabilities of alkali ions.

Ion	α_p (10^{-24} unit)
Li ⁺	0.0292
Na ⁺	0.180
K ⁺	0.835
Rb ⁺	1.41
Cs ⁺	2.42

it can easily be seen that x_0 becomes smaller as the degree of ionization increases. This result is explained by the fact that for greater positive charge excess, the electron cloud is more tightly pulled together.

It is not trivial to obtain accurate solutions for particular Thomas-Fermi positive ions since the equation is nonlinear and has nonstandard boundary conditions. The technique most commonly used to solve nonlinear equations is a cut and try process where one integrates in from the first point and back from the second, checking the solution for continuity in value and slope at some matching point. In the case of the Thomas-Fermi ions, we know the starting point $(0, 1)$, but we only know the termination point $(x_0, 0)$ through a condition on the value of the slope that the desired solution is to have at x_0 [Eq. (2.4)]. Accurate solutions for positive alkali ions have been given by Kobayashi¹⁶ by the Thomas-Fermi-Amaldi¹⁷ method, and by one of

¹⁴ D. Bohm, *Quantum Theory* (Prentice-Hall, New York, 1951), p. 461.

¹⁵ J. Rand McNally, Jr., in *Handbook of Physics*, edited by E. U. Condon and H. Odishaw (McGraw-Hill Book Company, Inc., New York, 1957), pp. 7-34.

¹⁶ S. Kobayashi, *J. Phys. Soc. (Japan)* **14**, 1039 (1959).

¹⁷ E. Fermi and E. Amaldi, *Mem. accad. Italia* **6**, 117 (1934).

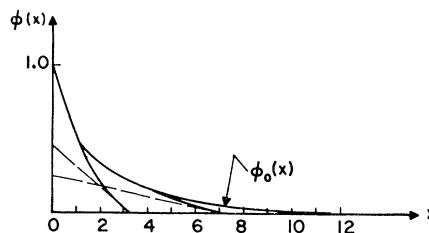


FIG. 1. The form of the Thomas-Fermi solutions for positive ions.

the authors¹⁸ in a report. These calculations will not be presented in detail, but some indication will be given as to how the results are obtained and what the difficulties are. The technique used in this study involved graphically interpolating approximate values of x_0 obtained by Fermi¹⁷ for various hypothetical degree of ionization values to provide an approximate $x_0^{(1)}$ starting value for the particular $(Z-N)/Z$ value under consideration. Then using the $x_0^{(1)}\phi'(x_0^{(1)}) = -(Z-N)/Z$ relation, the slope at the assumed termination point is determined. From the Thomas-Fermi equation, the second derivative of ϕ is seen to vanish at this point; differentiation of the equation provides higher derivatives. Using a Taylor expansion it is thus possible to determine an initial set of values for a backwards numerical integration. If this is carried out, the solution will be found to cross the ordinate axis at some value which can be represented as $1+\beta^{(1)}$ where $\beta^{(1)}$ would be zero if the Fermi values were exact. A small assumed correction is then made to give another starting value, $x_0^{(2)}$, and the procedure is repeated yielding a $\beta^{(2)}$ value. By interpolating for a $\beta=0$ value, a new improved value of x_0 , $x_0^{(3)}$, is obtained. By repeating the process accurate solutions to the Thomas-Fermi equation were obtained for the alkali ions. The details of the solutions can be found in reference 18. In Table II we list the values of x_0 obtained in this study, together with the corresponding values obtained by Kobayashi¹⁶ in the Thomas-Fermi-Amaldi approximation. Converting back to ordinary dimensions, it is found that the effective radii of the alkali ions, according to Thomas-Fermi theory are given by the values indicated in Table III. Graphs of the Thomas-Fermi $\phi(x)$ distributions for the

TABLE II. Values of x_0 for the Thomas-Fermi and Thomas-Fermi Amaldi equations.

Ion	x_0 (TF Eq.) (Brudner)	x_0 (TFA Eq.) (Kobayashi)
Li ⁺	4.589060	...
Na ⁺	11.60870	11.604
K ⁺	15.68552	15.678
Rb ⁺	21.87429	21.857
Cs ⁺	26.31931	...

¹⁸ H. J. Brudner, New York University Research Division Technical Report No. 3, Electron Scattering Project, June 15, 1959 (unpublished).

TABLE III. Effective radii of the alkali ions according to Thomas-Fermi theory.

Ion	r_0 (Å)	r_0 (atomic units)
Li ⁺	1.49070	2.81705
Na ⁺	2.44545	4.62129
K ⁺	2.75394	5.20425
Rb ⁺	3.07544	5.81180
Cs ⁺	3.24235	6.12723

alkali ions are given in Fig. 2. Reference 18 has tabulated values of $\phi(x)$ and $\phi''(x)$ accurate to six significant figures.

The charge distribution $\rho(r)$ of the alkali ions can be determined as follows: From Poisson's equation

$$-\nabla^2 V(r) = 4\pi\rho(r). \quad (3.1)$$

In spherical coordinates with radial symmetry

$$-\frac{1}{r} \frac{d^2(rV)}{dr^2} = 4\pi\rho(r). \quad (3.2)$$

But $r(V - V_0) = Ze\phi(x)$ from Eq. (2.5), and $r = \mu x$ from Eq. (2.6); thus the radial charge distribution is given by

$$-\rho(r) = (Ze/4\pi\mu^3)(\phi''/x). \quad (3.3)$$

Accurate values of the parameters determining the charge distribution are presented in reference 18.

IV. SOLUTION OF THE SCHRÖDINGER EQUATION

The charge distribution and consequently the potential of the ion can now be used as a central field in which the valence electron moves. The calculated excited and/or ground state one-electron wave functions will give the charge distribution of the valence electron for the states considered. This statement is only approximately true for several reasons, the most important of which is that we have calculated a charge distribution for the core which is good only in the Thomas-Fermi approximation. Other approximations which will have to be made concern the partial shielding of the core due to the penetration of the valence electron's charge distribution, the exchange effects, and the dynamical aspects of the problem which include the deformation of the core due to the presence of the penetrating electron. It will be seen that these last three effects can be included approximately in our calculation.

If we consider a separable, product-type wave function, and make the further assumption that angular dependence can be separated out, the one-electron wave function of the i th electron is given by

$$\psi_i = R(r)Y_{l,m}(\theta,\phi) = [\chi(r)/r]Y_{l,m}(\theta,\phi), \quad (4.1)$$

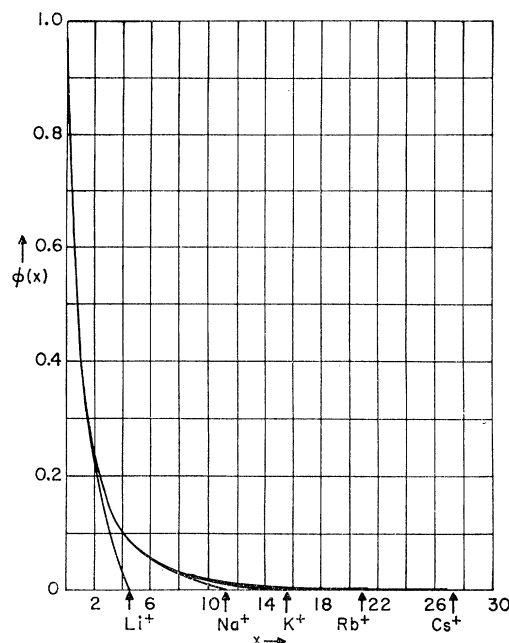
and the wave equation for the valence electron moving in the field of the Thomas-Fermi potential of the ion is

$$\chi_i''(r) - [(2m\epsilon_i/\hbar^2) - (2meV_{TF}(r)/\hbar^2) + (l(l+1)/r^2)]\chi_i(r) = 0, \quad (4.2)$$

where $Y_{l,m}(\theta,\phi)$ are the spherical harmonic functions, $V_{TF}(r)$ the core potential, l the angular momentum quantum number, and ϵ_i the corresponding eigenvalue. In accordance with normalization we further require that

$$\int_0^\infty r^2 R(r)R^*(r)dr = \int_0^\infty \chi(r)\chi^*(r)dr = 1. \quad (4.3)$$

It is seen from the above that after angular dependence is separated out, the remaining second-order equation can be put into a form that does not contain the first derivative by introducing the $\chi(r)$ function. It is then amenable to numerical integration by the Milne¹⁹ method which was also used in the solution of the pure Thomas-Fermi ion. The equation can also be integrated by standard numerical techniques due to Hartree,²⁰ Gauss-Jackson-Numerov,^{21,22} and Blanch.²³ The trouble with these methods of solving a differential equation with two point boundary conditions is that there is no systematic way of improving one's guesses. A method due to Ridley²⁴ does allow for improvement especially in cases such as these where excellent preliminary knowledge of the eigenvalues exists. The technique considers a general, homogeneous, second order equation with homogeneous boundary conditions,

FIG. 2. Thomas-Fermi ϕ distributions for the alkali ions.

¹⁹ W. E. Milne, *Am. Math. Monthly* **40**, 322 (1933).

²⁰ D. R. Hartree, *Mem. Proc. Manchester Lit. & Phil. Soc.* **77**, 130 (1932).

²¹ H. Jeffreys and B. S. Jeffreys, *Methods of Mathematical Physics* (Cambridge University Press, Cambridge, 1950), pp. 276, 665.

²² B. Numerov, *Publ. l'Obs. Astrophys. Russie* **2**, 637 (1933).

²³ G. Blanch, *Mathematical Tables and Other Aids to Computation* **6**, 219 (1952).

²⁴ E. C. Ridley, *Proc. Cambridge Phil. Soc.* **51**, 702 (1955).

of the form

$$y'' + [\lambda + f(x)]y = 0, \quad (4.4)$$

with λ an adjustable parameter, and with boundary conditions

$$y(a) = y(b) = 0. \quad (4.5)$$

The determination of the characteristic values and functions utilizes a process similar to the one used for normal two-point boundary condition problems, namely, by carrying out an outward integration from $x=a$ and an inward integration from $x=b$, and matching them at an intermediate point, say $x=X$. The results of these two integrations are written as y_{out} and y_{in} . Ridley's technique uses the degree of mismatch between the results of inward and outward integration, as measured by the difference between the values of $y'(x)/y(x)$ for the two integrations, to estimate an improved trial value. It is shown²⁴ to first order in $\Delta\lambda$,

$$\left[\frac{\int_a^X y_{\text{out}}^2 dx}{y_{\text{out}}^2(X)} + \frac{\int_X^b y_{\text{in}}^2 dx}{y_{\text{in}}^2(X)} \right] \Delta\lambda = \left[\frac{y'(X)}{y(X)} \right]_{\text{out}} - \left[\frac{y'(X)}{y(X)} \right]_{\text{in}}. \quad (4.6)$$

If we consider the $\chi(r)$ solution at the nucleus, it would be expected that the potential can be represented by the Coulomb form and the wave function would start off as a hydrogenlike solution with charge Ze . This information is not accurate enough for obtaining starting values for numerical integration. The potential is Coulomb-like if the Thomas-Fermi potential, ϕ , were equal to one near the nucleus. Checking the potassium solution determined in Sec. III indicates that at $r=0.004$ A, ϕ has already fallen off to 0.969, and at $r=0.014$ A, $\phi=0.903$. The departure from the Coulomb potential is seen to begin immediately, and with a high rate as we move away from the nucleus. To obtain accurate starting values, the solution in the region near the nucleus must be numerically evaluated by determining a power series solution to the general equation, treating $\phi(r)$ as a parameter. The details of this calculation can be found in a report by one of us.²⁵

In order to start the backward integration, it is convenient to go out so far that the wave function has an exponential decay (to one part in 10^6), and compute the back starting points using the asymptotic form of the solution, $\chi(r) = k \exp\{-[(2m\epsilon_i)^{3/2}/\hbar]r\}$.

The Polarization Contribution

As indicated in Sec. II, the Heisenberg form for the polarization potential energy is $-\alpha_p e^2/2r^4$, where the

argument for its determination holds only in the region outside the core. If this term were added only in the outer region, there would be a discontinuity at the core boundary. Following Biermann and Harting²⁶ we will add a polarization term of the form

$$(\alpha_p e^2/2r^4)\{1 - \exp[-(r/fr_0)^8]\}$$

for the inner region as well. Here f is a fraction which was taken as 0.4 for most of the calculations. Although the exponent can be raised to any power greater than four, eight was found to give the best fit with optical term values.²⁶ The addition of this term has the effect of eliminating the polarization term in the core until $r=fr_0$. It then goes smoothly into the $1/r^4$ behavior at the core boundary. Although strictly speaking this is an empirical correction, it will be seen to be a small one, and too much concern need not be given to the exact form of the correction.

There are various computational difficulties associated with the Ridley scheme outlined above, and although these can be and were overcome, it is desirable to also discuss another scheme for solving Eq. (4.2).

The Biermann-Lübeck Method

A useful method for computing wave functions is that developed by Biermann and Lübeck.²⁷ In addition to including the polarization contribution, and being adaptable to the Thomas-Fermi potential, the method also allows for the inclusion of a semiempirical exchange correction. Introduction of the latter correction has the effect of introducing a nonexperimentally determined parameter into a system which is already determined without redundancy. In order to compensate for this while calculating the best possible wave function for the assumed potential (originally taken as a Hartree central potential), Biermann and Lübeck solve the wave equation utilizing the experimentally determined term value. Accurate listings of these values can presently be found in a circular of the National Bureau of Standards.²⁸ Starting with the experimental term values is not necessarily an unfair approach since both Hartree and Thomas-Fermi central potentials do lead to term values which are very close to the experimentally determined ones.

The exchange correction made by Biermann and Lübeck can be applied here by multiplying the Thomas-Fermi central potential distribution by the function

$$B(r) = \{1 + \beta r \exp[-(r/fr_0)^8]\};$$

for the computation it is convenient to express the r and β coefficients of the exponential in A and 1/A units, respectively. In their work, Biermann and Lübeck take the fr_0 value as the radial distance of the last inflection

²⁶ L. Biermann and H. Harting, *Z. Astrophys.* **22**, 87 (1942).

²⁷ L. Biermann and K. Lübeck, *Z. Astrophys.* **22**, 157 (1943).

²⁵ H. J. Brudner, New York University Research Division Technical Report No. 4, Electron Scattering Project, July 1, 1959, (unpublished), Appendix E.

²⁸ *Atomic Energy Levels*, edited by C. E. Moore, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C. 1947).

point of the outermost one-electron wave function of the core as given by the Hartree potential. This is felt to be a somewhat sophisticated definition for an intuitively determined distance, and in the present calculation f was simply taken as 0.4 and the r_0 value as that of the Thomas-Fermi ion. With this approach the radial wave equation to be solved is now

$$\chi'' - \left[\frac{2m\epsilon_{\text{exp}}}{\hbar^2} - \frac{2meV(r)}{\hbar^2} + \frac{l(l+1)}{r^2} - \frac{\alpha_p e^2}{2r^4} \{1 - \exp[-(r/fr_0)^8]\} \right] \chi = 0, \quad (4.7)$$

where

$$V(r) = [Ze\phi(r)/r + e/r_0] \times \{1 + \beta r \exp[-(r/fr_0)^8]\}; \quad 0 \leq r \leq r_0 \quad (4.8)$$

and

$$V(r) = (e/r) \{1 + \beta r \exp[-(r/fr_0)^8]\}; \quad r > r_0. \quad (4.9)$$

The solution of the equation for large values of r is once again given as $\chi(r) = k \exp[\pm(2m\epsilon_i)^{1/2}r/\hbar]$. Varying β for a particular eigenvalue and angular momentum state leads to solutions such that all diverge as $\pm e^{+ar}$ except the one associated with the desired value of β ; in this case we have the physically required exponential decay.

Since this procedure takes advantage of the experimentally determined term value, and makes at least partial correction for almost all other effects, it can be expected to yield fairly accurate wave functions, even for excited states. Indeed this is the case, and Biermann and Lübeck find that oscillator strengths for the states in the principal series agree well with those obtained from experimental measurements. A more detailed description and evaluation of the Biermann and Lübeck procedure, as used with Hartree potentials, has been given by Villars.²⁹ The Biermann and Lübeck procedure neglects, however, the effect of the penetration of the excited electron into the core, and the modification of the core potential due to this penetration. While this is a small correction in the case of the more highly excited levels, it can be significant for the first few excited states. It is possible to include the effect of this penetration by utilizing a self-consistent iterative process which we now describe.

V. A SELF-CONSISTENT TECHNIQUE

The effect of the penetration of the valence electron into the core is partially to shield the nuclear charge and consequently to increase the size of the ion core. The form of the core charge distribution also changes, and with it, the effective potential in which the valence electron moves changes. Since the effective potential depends on the charge distribution, and this in turn depends on the effective potential, we have in principle the ingredients of a self-consistent procedure.

²⁹ D. S. Villars, J. Opt. Soc. Am. 42, 522 (1952).

We first solve the problem neglecting penetration of the core. If the portion of the computed excited electron's charge distribution penetrating the core is α , the core size increases somewhat, and the potential at the edge of the core becomes $(Z-N-\alpha)e/r'_0$, where r'_0 is the new core radius. This new core potential combined with the polarization contribution is used to solve the Schrödinger equation for the new charge distribution until the solution is self-consistent.

There are complications in carrying out this procedure. The penetration not only leads to a modified set of boundary conditions, but strictly speaking, to a modified Thomas-Fermi equation as well.

The Thomas-Fermi potential distribution for the pure ion represents a zeroth order approximation to the ion core. We use this potential with a polarization correction in the Schrödinger equation to calculate an energy eigenvalue and a wave function for the excited electron e^* which is in some state characterized by specific principal and azimuthal quantum numbers. From the one-electron wave function, ψ_{e^*} , so determined, we can calculate a number density for the excited electron:

$$n_{e^*} = |\psi_{e^*}|^2. \quad (5.1)$$

We can also define a dimensionless potential, that is calculated from the potential V_{e^*} as determined by Poisson's equation,

$$\nabla^2 V_{e^*} = 4\pi n_{e^*} e; \quad (5.2)$$

$$\phi_{e^*} = rV_{e^*}(r)/Ze. \quad (5.3)$$

An ion core and excited electron potential are illustrated in Fig. 3 with $|\phi|$ as the ordinate since ϕ_{e^*} is actually negative.

It is important to note that even though we are dealing with a $V_{\text{TF}}(r)$ potential for the ion core, and a $V_{e^*}(r)$ potential for the excited electron, since the distribution has some *temporary equilibrium form*, there must be some maximum value of the total energy of the electrons at each point, $-eV_0$, where V_0 is a positive constant. This follows from the argument that if this quantity were not constant, the electrons would move from points with smaller V_0 to those of greater V_0 value. If we assume that within the imaginary sphere defined by r_0 , the fraction α of the excited electron's charge

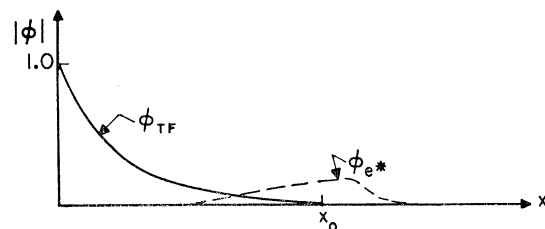


FIG. 3. Thomas-Fermi ion core and excited electron dimensionless potential distributions.

distribution penetrates, since $V_0 = V(r_0)$ we must have

$$V_0 = [Z - N - \alpha(r_0)]e/r_0. \quad (5.4)$$

The V_0 value determines the total energy of the core electrons at any distance r since

$$(1/2m)p_0^2 - eV_{\text{tot}} = -eV_0. \quad (5.5)$$

Since the Thomas-Fermi core electrons are still assumed to be in the lowest permissible energy states,

$$n_{\text{TF}} = (8\pi/3h^3)[2me(V_{\text{tot}}(r) - V_0)]^{3/2} \quad (5.6)$$

in accordance with the usual Thomas-Fermi density-potential relation. The Poisson equation for the total charge requires

$$\nabla^2 V_{\text{tot}} = 4\pi n_{\text{tot}} e, \quad (5.7)$$

where since

$$n_{\text{tot}} = n_{\text{TF}} + n_{e^*}, \quad (5.8)$$

we must have

$$V_{\text{tot}} = V_{\text{TF}} + V_{e^*}. \quad (5.9)$$

Substituting (5.8) into (5.7) and using the expressions given in Eqs. (5.6) and (5.2), we obtain a generalized Thomas-Fermi equation:

$$\nabla^2 V_{\text{tot}} = 4\pi e \left\{ (8\pi/3h^3)[2me(V_{\text{tot}}(r) - V_0)]^{3/2} + (\nabla^2 V_{e^*}/4\pi e) \right\},$$

or

$$\nabla^2 (V_{\text{tot}} - V_{e^*} - V_0) = 4\pi \sigma_0 e (V_{\text{tot}} - V_0)^{3/2}. \quad (5.10)$$

In order to convert this equation to the dimensionless form, and still to retain as much of the original Thomas-Fermi formalism as is possible, we define

$$\phi_{\text{TF}} = r(V_{\text{tot}} - V_0)/Ze, \quad (5.11)$$

and using (5.3) we obtain a generalized dimensionless equation

$$\phi_{\text{TF}}''(x) - \phi_{e^*}''(x) = \phi_{\text{TF}}^{3/2}(x)/x^{3/2}. \quad (5.12)$$

As in the case of the pure ion, the boundary conditions at the nucleus and limiting radius are

$$\phi_{\text{TF}}(0) = 1; \quad \phi_{\text{TF}}(x_0) = 0. \quad (5.13)$$

It will now be shown that in defining the potentials as above, we have also preserved the content of the relationship between x_0 and $\phi_{\text{TF}}'(x_0)$. This relation is determined by application of Gauss's theorem. Since spherical symmetry exists, the total charge inside a sphere of radius r is given by

$$-r^2 \partial V_{\text{tot}} / \partial r = -r^2 (\partial / \partial r) (V_{\text{TF}} + V_{e^*}),$$

and using Eq. (5.11),

$$\begin{aligned} &= -r^2 (\partial x / \partial r) (\partial / \partial x) (Ze \phi_{\text{TF}} / r + V_0) \\ &= -Ze [\phi_{\text{TF}}(x) - x \phi_{\text{TF}}'(x)]. \end{aligned} \quad (5.14)$$

The detail of this third boundary relation alters at this point since the total charge enclosed by the sphere of radius x_0 is now $(Z - N - \alpha)e$. It thus becomes

$$-(Z - N - \alpha)/Z = x_0 \phi_{\text{TF}}'(x_0). \quad (5.15)$$

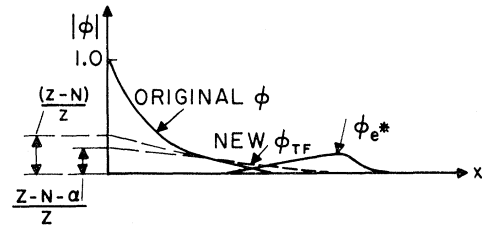


FIG. 4. Modification of the pure ion core Thomas-Fermi distribution by the excited electron.

It will be seen that the small penetration charge, $\alpha(x_0)$, serves to extend the pure ion x_0 value via shielding effect since it lowers the intercept on the $\phi_{\text{TF}}(x)$ ordinate axis by an amount α/Z ; it does this partly by decreasing the positive curvature of the potential falloff (which is about equal to ϕ'' in the outer region of the core) as indicated in Eq. (5.12). However, $\phi_{\text{TF}}(x_0)$ can still be defined as zero, and identified as the boundary of the disturbed pure ion core, if we solve the generalized differential system instead of the ordinary Thomas-Fermi equation. In order to solve Eq. (5.12), we must know the original distribution of $\phi_{e^*}''(x)$ for all $x < x_0$, since the excited electron's orbital slightly modifies the pure ion core Thomas-Fermi distribution. The effect is indicated in Fig. 4.

It is seen that for rigor the solution of the differential system, Eqs. (5.12), (5.13), and (5.14), for a given $\phi_{e^*}''(x)$ distribution requires an iterative approach in itself, within the more general self-consistent approach. This comes about since solution of the modified Thomas-Fermi ion leads to a second $x_0^{(2)}$ value which is slightly larger than the original x_0 value, and will therefore include more of the excited electron's charge distribution. This contribution will be seen to be a second order one, however, as the ion radius occurs in the region of a node in the excited electron's charge distribution. In this respect the present approach partly implies the atomic shells which ordinary Thomas-Fermi theory lacks. If a very accurate calculation were desired, the Thomas-Fermi modified ion equation could be resolved with a new value $\alpha^{(2)}(x_0^{(2)})$, and the process repeated to yield a final $x_0^{(j)}$ value accurate to a high degree. This iteration on x_0 , however, would not be worthwhile except in the final potential determining step in the more complete self consistent approach. The latter can be summarized as:

(1) Solve for the potential distribution of the ion core, $V_{\text{TF}}(r)$, and r_0 via the ordinary Thomas-Fermi equation and the pure ion boundary conditions.

(2) Use this potential with a polarization and if desired, an exchange correction as the effective field to determine an excited state (n, l) wave function and energy eigenvalue via the Schrödinger equation.

(3) Determine the excited state's charge distribution.

(4) Determine $\phi_{e^*}''(x)$ for all values of x . It will be seen that this can be done without utilizing Poisson's

equation each time since a general relation exists between the dimensionless potential and the radial wave function.

(5) Use the generalized Thomas-Fermi equation, and the iterative x_0 process if desired, to redetermine $\phi_{\text{TF}}(x)$ and $\alpha(x_0)$.

(6) Use the new $\phi_{\text{TF}}(x)$ function with a polarization, and if desired an exchange correction as the effective potential to redetermine an improved excited state wave function and energy eigenvalue via the Schrödinger equation.

(7) Repeat the process starting with step (3). The process is stopped when the energy eigenvalue of the excited electron is regenerated within a stated accuracy, if exchange is neglected, or when the wave functions converge to some limiting form if exchange is included and the experimental term value used. In the former case the Ridley approach can be used to solve the wave equation; in the latter the Biermann-Lübeck technique can be used.

It should be pointed out that while the introduction of the dimensionless variable x is useful in demonstrating the characteristic length property of neutral atoms, this change in scale from the ordinary r variable is not necessary for ions. One can still introduce a function

$$\omega(r) = r(V - V_0)/Ze, \quad (5.16)$$

which satisfies the Thomas-Fermi equation, now in the form

$$d^2\omega/dr^2 = b(\omega^3/r^3), \quad (5.17)$$

where

$$b = 32\pi^2(2m)^{3/2}e^3Z^{1/2}/3h^3, \quad (5.18)$$

and for free positive ions

$$\omega(0) = 1, \quad \omega(r_0) = 0, \quad (5.19)$$

and

$$r_0(d\omega/dr)_r = -(Z - N)/Z.$$

Ordinarily, this is not convenient since the b value is large and irrational. For instance, for potassium $b_K = 1.35934 \times 10^{12}$. However, it is convenient to partly work in the $\omega(r)$ system for the above type of procedure since this facilitates both the solution of the Schrödinger equation and any later conversion to atomic units. The generalized Thomas-Fermi equation is then

$$\omega_{\text{TF}}''(r) - \omega_{e^*}''(r) = b(\omega^3(r)/r^3), \quad (5.20)$$

with the same boundary conditions as in Eq. (5.19) except for replacing $(Z - N)$ by $(Z - N - \alpha)$. Instead of resolving the pure ion for the $\omega(r)$ function, it is simple to convert a $\phi(x)$ table into an $\omega(r)$ table by interpolation on a computer.

Then, as mentioned, the $\omega_{e^*}''(r)$ distribution can be directly determined from the excited electron's wave function. We have defined

$$\omega_{e^*}(r) = rV_{e^*}(r)/Ze, \quad (5.21)$$

where $V_{e^*}(r)$ is determined from Poisson's equation. Thus

$$\nabla^2 V_{e^*}(r) = -4\pi\rho_{e^*}, \quad (5.22)$$

or

$$(1/r)(d^2(rV_{e^*}/dr^2)) = -4\pi\rho_{e^*}(r).$$

Therefore

$$(Ze/r)(d^2\omega_{e^*}/dr^2) = -4\pi\rho_{e^*}(r). \quad (5.23)$$

If we consider the total amount of the excited electron's charge enclosed by a sphere of radius r , this quantity is given by

$$q = \int_0^r \rho_{e^*} dv = 4\pi \int_0^r r^2 \rho_{e^*}(r) dr = -e \int_0^r \chi^2(r) dr.$$

Since this is so for any value of r ,

$$\rho_{e^*}(r) = -e\chi^2/4\pi r^2. \quad (5.24)$$

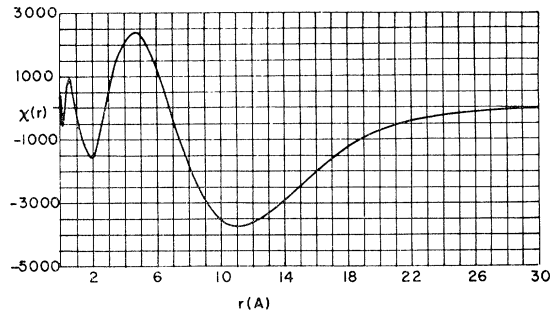


FIG. 5. Ridley type solution for the 6s state of potassium.

Substituting (5.24) into (5.23), it is seen that

$$d^2\omega_{e^*}/dr^2 = +\chi^2(r)/Zr, \quad (5.25)$$

relating the second derivative of the excited electron's $\omega_{e^*}(r)$ distribution to the radial wave function $\chi(r)$.

VI. STARTING VALUES

As indicated the inner region starting values can be obtained by expanding $\chi(r)$ as a power series in r , substituting into the differential equation and setting the collected coefficients of the r powers to zero. If exchange effect near the origin is neglected, we can write the Schrödinger equation as

$$\chi''(r) - [\sigma + s_1/r^2 - s_2\phi(r)/r]\chi(r) = 0, \quad (6.1)$$

where

$$\sigma = (2m/\hbar^2)(\epsilon - eV_0), \quad s_1 = (l)(l+1), \quad (6.2)$$

and

$$s_2 = 2me^2Z/\hbar^2.$$

Expressing the wave function in power series form

$$\chi(r) = \sum_{n=0}^{\infty} a_n r^n, \quad (6.3)$$

and the collected coefficient of the general term r^m is $(m+1)(m+2)a_{m-2} - \sigma a_m + s_2\phi(r)a_{m-1} - s_1a_{m-2} = 0$. (6.4)

The $\phi(r)$ function varies between zero and unity through the entire inner region and is treated as a parameter in the expansion. The series must be evaluated from $m = -2$ since there is an inverse square term. Combining the above results for the various angular momenta yields the following expansion for the s state:

$$\begin{aligned} \chi_{s\text{-state}}(r) &= a_1[r - (s_2\phi(r)/2)r^2 + (1/6)[(\sigma + s_2^2\phi^2(r)/2)]r^3 \\ &\quad - (1/12)(s_2\phi(r)/2)[\sigma + (1/3)(\sigma + s_2^2\phi^2(r)/2)]r^4 \\ &\quad + (1/20)\{(\sigma/6)(\sigma + s_2^2\phi^2(r)/2) - s_2^2\phi^2(r)/(24) \\ &\quad \times [\sigma - (1/3)(\sigma + s_2^2\phi^2(r)/2)]\}r^5 - \dots \end{aligned} \quad (6.5)$$

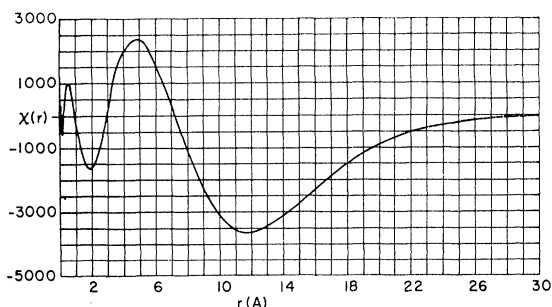


FIG. 6. Biermann-Lübeck type solution for the 6s state of potassium.

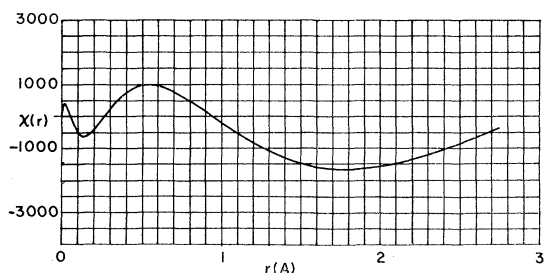


FIG. 7. Biermann-Lübeck type solution for the 6s state of potassium-inner region expanded.

Even neglecting the exchange correction term, the coefficients are seen to become complex as higher powers are needed. Unfortunately it will be seen that heavy atom wave functions are rapidly changing in the strong Coulomb field near the nucleus, and even if a fairly small interval is taken for the $\chi(r)$ tabulation, using the Milne method of integration the starting value calculation becomes tedious. Although the present calculation was carried out in this manner, the authors recommend the Gauss-Jackson-Numerov^{21,22} method for future work. In this case the initial interval can be made extremely small and changed as needed further out. This being the case, only two or three terms of the expansion in (6.5) are needed. This approach requires that the Thomas-Fermi potential be determined at

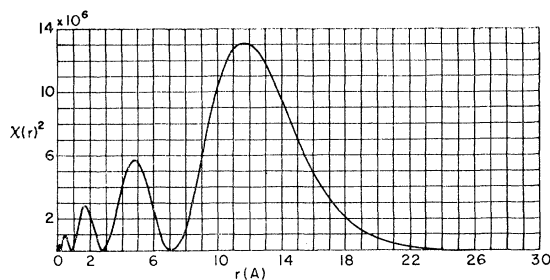


FIG. 8. Charge density distribution for the 6s potassium state.

irregular intervals near the origin, but that is less cumbersome than determining starting values using a fifth or sixth degree polynomial.

It can also now be pointed out that the β parameter involved in the Biermann and Lübeck scheme must be known with ever greater accuracy as heavier atoms are studied. In their original work, Biermann and Lübeck required only three significant figures for convergence. Villars²⁹ noted that five significant figures were required for his work with potassium. Unfortunately, for the 55 electron cesium atom, eight significant figures were found to be necessary. This begins to exhaust the capabilities of even advanced computers, and the authors suggest that for heavier atoms, the Ridley scheme be used since the exchange correction is smaller.

VII. RESULTS

For the evaluation of the procedures described above, the potassium atom with valence electron in the 6s excited state was first chosen. According to reference 28, this atom is characterized by a ground state, $4s^2S_{1/2}$ at $35\,009.78\text{ cm}^{-1}$. Its 6s configuration, $3p^6(^1S)6s$ is at a level $27\,450.65\text{ cm}^{-1}$. Thus the energy above the ground state of the 6s level corresponds to 7559.13 cm^{-1} or an energy, W , of $-1.501385 \times 10^{-12}$ erg.

The 6s state as determined by the above Thomas-Fermi technique using Ridley's method, on first iteration was found to have the proper $\chi'(r_0)/\chi(r_0)$ continuity for an eigenvalue of $\epsilon = -W = 1.55389 \times 10^{-12}$ erg. This is about 3.5% in error compared with the experimental term value. It was found that a second iteration, providing for penetration, improved the

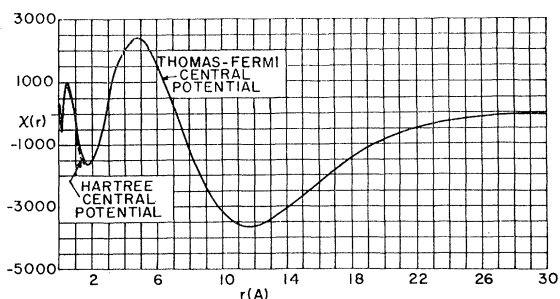


FIG. 9. Comparison of Biermann-Lübeck type solutions with Thomas-Fermi and Hartree potentials.

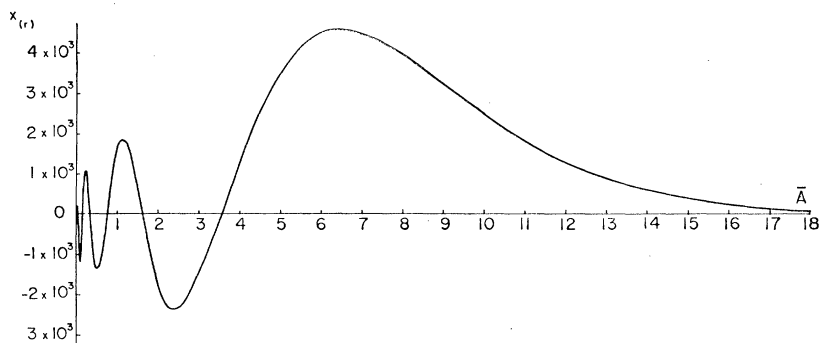


FIG. 10. The 7s state of cesium.

eigenvalue to 1.54442×10^{-12} erg, still leaving a residual error of some 2.8%. It will be seen that r_0 is in the region of one of the wave function nodes and so further iteration would not produce any significant change since there is virtually no change in the α value.

In order to produce a more accurate wave function for the 6s state, the experimental term value was used in the Biermann and Lübeck procedure. It is interesting to note that the wave function took on the proper asymptotic exponential decay value for a $\beta=0.17020$ value in $(1/A)$ units; converting to atomic units indicates a smaller exchange parameter than that required in the Biermann and Lübeck calculation using a Hartree potential as a central field.³⁰

The solution obtained using the Ridley type integration procedure is presented in Fig. 5. Figure 6 presents the more accurate Biermann and Lübeck type solution utilizing the experimental term value and allowing for some exchange energy correction. Since the wave function is changing very rapidly in the region of the nucleus, the inner region of the solution is presented on an expanded scale in Fig. 7. The radial probability density is presented in Fig. 8.

The nodes for the Ridley-type solution come at 0.064, 0.283, 1.0234, 2.80, and 6.95 Å. The nodes for the Biermann and Lübeck type procedure occur at 0.058, 0.275, 0.944, 2.92, and 7.24 Å. Similarly, the maxima and minima for the Ridley type solution come at 0.0239, 0.144, 0.564, 2.08, 4.654, and 11.2 Å, whereas those for the Biermann and Lübeck scheme occur at

0.239, 0.144, 0.544, 1.80, 4.85, and 11.6 Å. It is seen that the two solutions compare fairly well with each other indicating that the form of the wave function is not too sensitive to the small error in the theoretically determined Ridley-type solution eigenvalue.

From the wave functions and probability distribution, it is seen that almost exactly four full shells of electrons are in the ion core; while this may seem surprising at first, it simply confirms the fact that the atom would be in the ground state if the 6s electron were in the 4s state.

The above Biermann-Lübeck type solution is compared in Fig. 9 with a similar solution using a Hartree ion core potential that has been determined by Villars.^{29,30} The latter wave function was presented in atomic units; it has been converted for comparison in Fig. 9. The outer regions agree nearly exactly as should be the case since the boundary conditions and potentials in the outer region correspond. In the inner region, some differences are to be expected since the Thomas-Fermi potential corresponds to something approaching a mean Hartree potential distribution. It is seen in Fig. 9 that the differences between the two solutions are small. It is not worthwhile to evaluate these differences critically since the main point in calculating the present Thomas-Fermi central field wave functions is for use in cases where regular Hartree or even Hartree central field solutions are not practical to calculate.

To further evaluate this situation, the 7s state of the

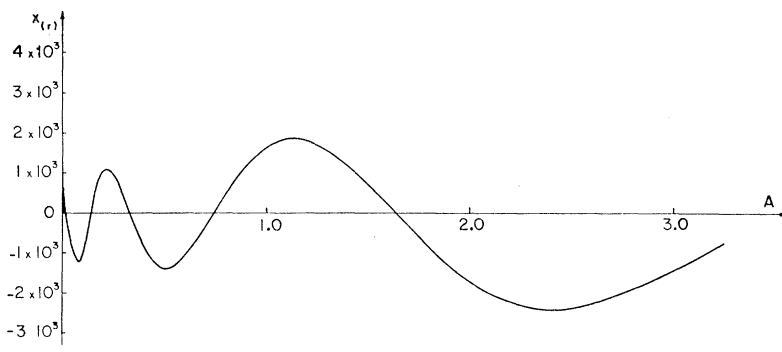


FIG. 11. The 7s state of cesium, inner region expanded.

³⁰ D. S. Villars, NavOrd Report 1923; Library of Congress ADI Document No. 3655, 1951.

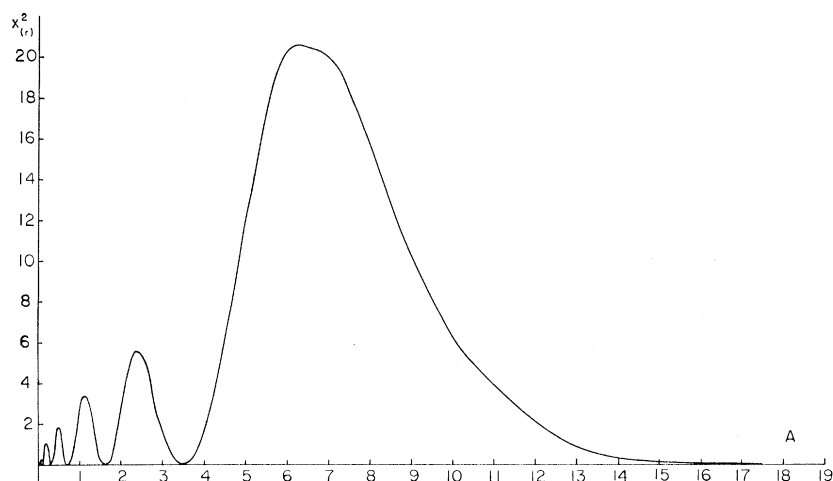


Fig. 12. Charge density distribution for the $7s$ state of cesium.

relatively heavy cesium atom was calculated. This state is only one excited level above its ground state and therefore shows a greater degree of penetration. Using the Biermann-Lübeck approach, with the experimental term value of 2.556439×10^{-12} erg, a degree of penetration, α , was determined as 7.07%. Figure 10 presents the determined wave function, Fig. 11 shows the inner region expanded, and Fig. 12 illustrates the probability distribution. Reference 31 presents a summary of the solution for the cesium $7s$ state.

VIII. CONCLUSIONS

It has been seen that the ordinary Thomas-Fermi theory for a pure ion can be modified to allow for penetration by an external charge distribution, and that the resulting potential distribution can be used in a central field approximation to calculate excited state wave functions.

³¹ H. J. Brudner, New York University, Institute of Mathematical Sciences, Research Report CX-51, October, 1960 (unpublished).

The pure ion distribution yields an energy eigenvalue which differs only by a few percent from the experimental term value; including the penetration effect of the excited electron tends to reduce the discrepancy. It was further seen that polarization and exchange effects can be included on a semiempirical basis utilizing techniques developed by Biermann and Harting and Biermann and Lübeck. The results compare very well with Hartree central field calculations. As indicated, an effective technique for calculating excited state wave functions for heavy atoms with complete cores, where Hartree solutions are not available, is to use the Thomas-Fermi self-consistent central field corrected for polarization and exchange effects.

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