orthogonality correction, may be readily obtained by using the results (A–D). The calculations for the 6- and 8-electron problems are, of course, more tedious, but proceed along similar lines[10] after calculation of the additional requisite character operators for the higher order classes.

In this more physical approach the presence of additional elements of (space) symmetry in a given problem is also recognized by noting that **V** commutes with a certain *subgroup* of the symmetric group involved, the character operators of which therefore furnish additional commuting constants of the motion whose values may be simultaneously assigned, leading to a further significant classification of energy levels and a simplification of the problem. Group-theoretically this, of course, corresponds to recognizing that the rotation-reflection group of **V** (under which **V** is invariant) in such cases is realizable in terms of an appropriate subgroup of the symmetric group, i.e., with which it is abstractly identical. Thus, one finds *six* additional commuting constants of the motion in the 6-electron problem with hexagonal symmetry, *five* for octahedral symmetry, *ten* in the 8-electron problem with (extended) cubic symmetry, etc.[11] Needless to say, the more formal treatment, as given by Serber, is in many respects simpler since it is guided by the more definite prescription of group theory proper, but the present viewpoint shows again that following Dirac's program the formal group methods can, in effect, be avoided.

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[10] This method may be compared with the equivalent treatment given by R. Serber, J. Chem. Phys. **2**, 697 (1934), along more matrical (group-theoretical) lines, which comparison also serves to show the relation between the symbolic and formal group methods. It may be mentioned that the iterations in the latter method give sums of eigenvalues rather than averages, for obvious reasons. Cf. Eq. (3).

[11] R. Serber, see reference 10.

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On the Rydberg-Ritz Formula in Quantum Mechanics

ROBERT JASTROW
Columbia University, New York, New York

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A derivation is given of the Rydberg-Ritz formula for series spectra. Simple expressions are obtained for the Rydberg and Ritz coefficients. It is shown that the Ritz coefficient is proportional to the difference between the radial period of the electron and the period of the hypothetical orbit, with the same energy which would exist if the atomic core were to contract to zero radius.

The derivation necessitates a study of the confluent hypergeometric function. An expansion in powers of the energy is obtained for this function. The coefficients in the expansion are found to be simple combinations of Bessel functions.

Calculations of the Rydberg and Ritz coefficients are carried out for the S series of Na, K, and Cs and show satisfactory agreement with observation. The comparison with experiment yields information concerning the relative accuracy of different types of central fields employed to approximate the effect of the atomic core upon the valence electron. It is concluded that the Hartree-Fock field is not a convenient starting point for this purpose.

I. INTRODUCTION

IT is known that in many cases the terms of series spectra obey the empirical Rydberg-Ritz formula,

$$E=-\frac{1}{2}\frac{1}{(\mathbf{n}+\alpha+\beta E)^2}, \tag{1.1}$$

where E is the energy expressed in atomic units, n is the principal quantum number, and α and β are the Rydberg and Ritz coefficients, respectively. For a given atom these coefficients depend only upon l, the azimuthal quantum number.

Bohr, considering the electron as moving in the static central field arising from the nucleus and the core electrons, gave an ingenious derivation of (1.1) on the basis of the old quantum theory.[1] Bohr's theory contained an interesting physical interpretation for the Ritz coefficient, β. He found that β should be proportional to the difference between the actual radial period of the electron and the period of the hypothetical orbit, with the same energy, which the electron would traverse if the core were to shrink to zero radius. Calling these periods t and t^*, Bohr's formula runs

$$\beta = R(t - t^*).$$

In a series of papers on atoms with non-Coulomb central fields,[2] Hartree showed that wave mechanics leads naturally to the following general expression for the effective quantum number, n,

$$n = (-2E)^{-\frac{1}{2}} = \mathbf{n} + \alpha + \beta E + \gamma E^2 + \cdots, \quad (1.2)$$

which is identical with (1.1) if the development is broken off after the second term. Some formulae pertaining to the calculation of the Ritz coefficient were subsequently derived by Hargreaves[3] but no applications were given.

In the present paper we will investigate in detail the nature of the Rydberg and Ritz coefficients. Particular attention will be paid to the latter, since it offers the problem of determining the wave mechanical justification for the formula of Bohr. It will be shown that our expression can be brought into a form which corresponds to the Bohr interpretation.

The formula will be applied to the calculation of β for the S series of Na, K, and Cs. The agreement with experiment is satisfactory.

The numerical results depend upon the type of central field used in the calculation. Comparison of these results with experiment thus gives information concerning the validity, for use in a central field approximation, of various methods for finding the effective core distribution. The matter is discussed in Section 4, but we note here the conclusion that the Hartree-Fock field does not seem to be suitable for this purpose.

The general energy level formula is determined by the condition that the wave function inside the atomic core must join smoothly, at some intermediate point, with the wave function valid at large distances from the nucleus. The latter function satisfies the hydrogen wave equation, since a Coulomb field prevails outside the core.

For this hydrogenic solution, known to be the confluent hypergeometric function, an expansion in powers of the energy will be required. The problem of obtaining this expansion in a simple way has been partially treated by Wannier.[4] The complete expansion is obtained in Section 2 of this paper, and is of some interest apart from its application to our problem. As will be seen, the coefficients in the expansion are simple combinations of Bessel functions.

Notation

In what follows we will use Hartree atomic units. If R is the radial part of the wave function for the valence electron, we define P by

$$P = rR.$$

P satisfies the equation

$$P'' + 2\left(E - V - \frac{l(l+1)}{2r^2}\right)P = 0. \quad (1.3)$$

Here E is the energy of the electron, $V(r)$ is the central field in which it is assumed to move, and l is the azimuthal quantum number. The effective quantum number, n, and the energy parameter, ϵ, are defined by: $\epsilon = 1/n^2 = -2E$.

All quantities which refer to the region of the atomic core will be distinguished by a superscript "i" standing for interior, while quantities referring to the region exterior to the core will have attached a superscript "e." E.g., the radial solution valid inside the core will be denoted by ^iP and the exterior solution in the Coulomb region by ^eP.

2. THE EXTERIOR SOLUTION (COULOMB REGION)

An Integral Representation

The solution of the hydrogenic wave equation which vanishes at infinity is a confluent hypergeometric function, $W_{n,\,l+\frac{1}{2}}(2r/n)$, in the nota-

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[1] M. Born, *Vorlesungen Über Atommechanik* (Verlag Julius Springer, Berlin, 1925), pp. 185–187.

[2] D. R. Hartree, Proc. Camb. Phil. Soc., **24**, 426 (1928); **25**, 310 (1929).

[3] J. Hargreaves, Proc. Camb. Phil. Soc. **25**, 315 (1929).

[4] G. H. Wannier, Phys. Rev. **64**, 358 (1943).

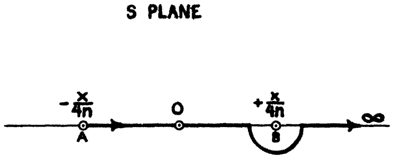

FIG. 1. The contour C which defines ${}^eP$, the confluent hypergeometric function vanishing at infinity.

tion of Whittaker and Watson.[5] We rewrite (1.3) for a Coulomb field,

$$ {}^eP''+\left(-\frac{1}{n^2}+\frac{2}{r}-\frac{l(l+1)}{r^2}\right){}^eP=0. \tag{2.1}$$

It is possible to write the required solution to (2.1) in the form of the following integral,

$$ {}^eP(x)=x^{-2l-1} \times Re\left\{\frac{1}{2\pi i}\int_c e^{-\frac{1}{2}xs}\frac{\left(1+\dfrac{4ns}{x}\right)^{n-l-1}}{\left(1-\dfrac{4ns}{x}\right)^{n+l+1}}ds\right\}, \tag{2.2}$$

where the independent variable is now $x=(8r)^{\frac{1}{2}}$. Constant multiplicative factors have been disregarded.

The left side of (2.2) satisfies (2.1) if the contour C fulfills the following condition:

$$ \left.\frac{e^{-\frac{1}{2}xs}}{x^2}\left(\frac{1+\dfrac{4ns}{x}}{1-\dfrac{4ns}{x}}\right)^n\right|_c=0 \tag{2.3}$$

The integrand in (2.2) has branch points at $s=\pm x/4n$, consequently a cut is drawn between these two points.

In Fig. 1 is shown a contour which satisfies (2.3). The arguments of both $[1+(4ns/x)]$ and $[1-(4ns/x)]$ are zero along the stretch AB. Therefore the part of the integral from the negative half of the s plane, which becomes infinite as x approaches infinity, is purely real and does not contribute to ${}^eP$. The remainder goes to zero as $x\rightarrow\infty$, hence ${}^eP$ vanishes at infinity. Thus (2.2) gives the desired solution.

In the region $B\rightarrow\infty$ the argument of $[1+(4ns/x)]$ remains zero, but that of $[1-(4ns/x)]$ has increased to πi. We may therefore write (2.2) in the form

$$ {}^eP=Re\left\{\frac{e^{-n\pi i}}{2\pi i}\int_c e^{-\frac{1}{2}xs}\frac{\left(1+\dfrac{4ns}{x}\right)^{n-l-1}}{\left(1-\dfrac{4ns}{x}\right)^{n+l+1}}s^{-2l-2}ds\right\}, \tag{2.4}$$

provided the arguments of both $[1+(4ns/x)]$ and $[1-(4ns/x)]$ are taken as zero along $B\rightarrow\infty$. This form is convenient for comparison with the Bessel functions, since for $n\rightarrow\infty$ the integral in (2.4) will converge to the well known Schläfli representation for the Hankel function of the first kind.

We denote the integral in (2.4) by $H_l{}^n$, and its real and imaginary parts by $J_l{}^n$ and $N_l{}^n$, so that

$$H_l{}^n=J_l{}^n+iN_l{}^n.$$

Using these definitions,[6]

$$ \begin{aligned} {}^eP&=xRe\{e^{-n\pi i}H_l{}^n\} \\ &=xJ_l{}^n\cos\pi n+xN_l{}^n\sin\pi n. \end{aligned} \tag{2.5}$$

The integral in (2.4) has been labeled $H_l{}^n$ with the intention of indicating that it has the nature of an extended Hankel function. Similarly, $J_l{}^n$ and $N_l{}^n$ are related to the Bessel and Neumann functions. It will be shown below that $H_l{}^n$ may be expanded in powers of the energy, i.e., of $1|n^2$, the coefficients in the expansion being linear combinations of Hankel functions.

We note that the approximately sinusoidal dependence upon n, expressed in (2.5), agrees with the results of Hartree and of Wannier.

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[5] Whittaker and Watson, *Modern Analysis* (The Cambridge University Press, 1927), §16.12 (example).

[6] It is of interest to note that as n approaches infinity the solution to the limiting form of the equation for ${}^eP$ differs from the limiting form of the solution, since the latter never loses its sinusoidal dependence upon n. This anomaly arises from the fact that ${}^eP$ is subject to a boundary condition at infinity. The effect of the infinite interval of integration is clarified by making the transformation, $r=1/u$ upon the independent variable in (2.1). The transformed equation is

$$\frac{d^{2e}P}{du^2}+\frac{2}{u}\frac{d^eP}{du}+\left(-\frac{1}{n^2u}+\frac{2}{u^2}-l(l+1)\right){}^eP=0.$$

We see from this equation that in the neighborhood of $u=0$, i.e., for large r, the term involving n becomes important no matter how large n may be. We are indebted to Professor F. J. Murray for this point.

Expansion in Powers of the Energy

We wish to show the relation of $H_l{}^n$ to the ordinary Hankel function of the first kind, defined by

$$H_l{}^{(1)}(x)=(-1)^{l+1}\frac{1}{\pi i}\int_0^\infty e^{-\frac{1}{2}x(s-1/s)}s^{-l-1}ds, \qquad (2.6)$$

where the contour is as in Fig. 2. To do this we write the integrand in (2.4) in the form[7]

$$e^{-\frac{1}{2}x(s-1/s)}s^{-2l-2}a\left(\frac{x}{4ns}\right), \qquad (2.7)$$

where

$$\begin{aligned} a(v)&=e^{-2vn}\left(\frac{1+v}{1-v}\right)^n(1-v^2)^{-l-1}\\ &=1+(l+1)v^2+\tfrac{2}{3}nv^3+\cdots\\ &=1+\left[(l+1)\frac{x^2}{16s^2}+\frac{2}{3}\frac{x^3}{64s^3}\right]\frac{1}{n^2}+\cdots. \qquad (2.8)\end{aligned}$$

The expansion of $a(v)$ in powers of v or of $1/s$ is possible if s is always large enough so that $|v|=|x/4ns|<1$. In Fig. 3 we have redrawn the contour of Fig. 1 so as to satisfy this condition.

If the result of the expansion of $a(v)$ is substituted in (2.7), the latter becomes a series each of whose terms has the form of the integrand in (2.6). More important, it is readily seen from (2.8) that $a(v)$ contains n only in powers of $1/n^2$. Hence the expansion of $a(v)$ is a power series in ϵ.

Substituting the expansion of (2.7) into (2.4), we obtain the desired formal expansion of $H_l{}^n$ in powers of ϵ. The functions which constitute the expansion coefficients are integrals whose integrands are identical with those defining the Hankel functions, but whose contours differ from the Hankel contours in that one terminus is at $s=-x/4n$, rather than at $s=0$. (Compare Figs. 2 and 3.) However, this difference is not an essential one, because the contour in Fig. 3 may be broken into two parts,

$$\int_{-x/4n}^\infty=\int_0^\infty-\int_0^{-x/4n},$$

of which the first is the Hankel contour, and the second, from $s=0$ to $s=-x/4n$, may easily be shown to behave as e^{-2n} and consequently may be neglected beside any power of $1/n^2$.

Using (2.6), (2.7), and (2.8) together with the definition of $H_l{}^n$ in (2.4), and neglecting the terms behaving as e^{-2n}, we have

$$\begin{aligned} &H_l{}^n=F_0+F_1\epsilon+F_2\epsilon^2+\cdots;\\ &F_0=xH^{(1)}{}_{2l+1},\\ &F_1=\left[(l+1)\frac{x^3}{16}H^{(1)}{}_{2l+3}-\frac{x^4}{96}H^{(1)}{}_{2l+4}\right],\text{ etc.}\end{aligned} \qquad (2.9)$$

For reference below we combine (2.5) and (2.9) into the final result for the series expansion of ${}^eP$,

$$\begin{aligned}{}^eP=Re\Bigg\{e^{-n\pi i}\Bigg[xH^{(1)}{}_{2l+1}+\Bigg((l+1)\frac{x^3}{16}H^{(1)}{}_{2l+3}\\ -\frac{x^4}{96}H^{(1)}{}_{2l+4}\Bigg)\epsilon+\cdots\Bigg]\Bigg\}. \qquad (2.10)\end{aligned}$$

3. THE INTERIOR WAVE FUNCTION

In the preceding section we have determined the dependence upon n of the exterior solution to the radial wave equation in a Coulomb field. We will now consider certain features of the solution which obtains in the neighborhood of the nucleus. We assume for this solution an expansion in powers of $\epsilon=1/n^2$. Let

$${}^iP={}^iP_0+{}^iP_1\epsilon+{}^iP_2\epsilon^2+\cdots={}^iP_0(1+{}^iT_\epsilon). \qquad (3.1)$$

${}^iT$ is defined by the two relations in (3.1).

In order that the interior and exterior solutions should join smoothly, their logarithmic derivatives must be equal at any intermediate point. Consequently, it is the energy dependence of $\varphi=P'/P$ in which we are interested, rather than in that of P itself. We have, using (3.1),

$${}^i\varphi={}^i\varphi_0+{}^i\varphi_1\epsilon;\quad {}^i\varphi_0={}^iP_0'/{}^iP_0,\quad {}^i\varphi_1={}^iT'. \qquad (3.2)$$

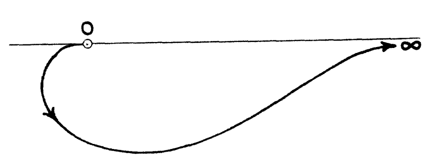

FIG. 2. The contour which defines the Hankel function of the first kind.

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[7] The manipulation of the integrand herein performed is identical with that carried out by Wannier for $J_l{}^n$.

We now determine ${}^iT'$ from the differential equation satisfied by P. Let ${}^iP_0$ be a solution of the equation

$$ {}^iP_0''+\left(-2V-\frac{l(l+1)}{r^2}\right){}^iP_0=0, \qquad (3.3)$$

and let ${}^iP$ be a solution of

$$ {}^iP''+\left(-\epsilon-2V-\frac{l(l+1)}{r^2}\right){}^iP=0. \qquad (3.4)$$

Substituting (3.1) into (3.4) and making use of (3.3), we obtain

$$2{}^iP_0{}^iT'+{}^iP_0T''={}^iP.$$

Integrating,

$${}^iP_0^2{}^iT')_r-{}^iP_0^2{}^iT')_a=\int_a^r {}^iP_0^2dr+0(\epsilon).$$

For the interior wave function, P_0^2T' is clearly zero at the origin. Hence

$${}^iT'(r)=\frac{1}{{}^iP_0^2}\int_0^r {}^iP_0^2dr. \qquad (3.5)$$

It is clear that a similar analysis can be applied to the exterior wave function, so that writing

$${}^eP={}^eP_0(1+{}^eT\epsilon),$$

one has, in analogy with (5),

$${}^eT'(r)=\frac{1}{{}^eP_0^2}\int_{r_p}^r {}^eP_0^2dr. \qquad (3.6)$$

Here the lower limit, r_p, is the value of r for which ${}^eT'$ vanishes. It may be shown, by using the formulae of Section 2, that ${}^eT'$ changes sign in the neighborhood of the classical perihelion of the electron's orbit. Hence, r_p is approximately equal to the perihelion distance.

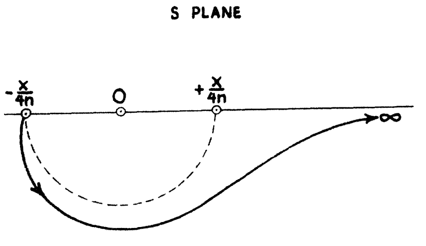

FIG. 3. The contour of Fig. 1 has been redrawn so as to have $|s|>x/4n$. This is necessary for the expansion of the integrand in powers of $x/4ns$.

4. THE ENERGY LEVEL FORMULA

The matching condition determining the energy levels is

$${}^i\varphi={}^e\varphi,$$

or

$${}^i\varphi=\frac{F'+G'\tan\pi n}{F+G\tan\pi n}, \quad \begin{Bmatrix} F=xJ_l{}^n \\ G=xN_l{}^n \end{Bmatrix}, \qquad (4.1)$$

where (2.5) has been substituted for ${}^e\varphi$. Solving for n,

$$\pi n=\pi\mathbf{n}-\tan^{-1}\gamma; \quad (\mathbf{n}=\text{positive integer}) \qquad (4.2)$$

$$\gamma=\frac{F'-{}^i\varphi F}{G'-{}^i\varphi G}.$$

The Rydberg Coefficient

The Rydberg and Ritz coefficients, α and β, respectively, are defined by the expansion of the effective quantum number in powers of ϵ,

$$n=\mathbf{n}+\alpha+\beta\epsilon+\cdots. \qquad (4.3)$$

From (4.2) and (4.3) we have for α,

$$\alpha=\left.\frac{1}{\pi}\tan^{-1}\gamma\right)_{\epsilon=0}$$

$$=\frac{1}{\pi}\tan^{-1}\gamma_0, \quad \gamma_0=\frac{F_0'-{}^i\varphi_0F_0}{G_0'-{}^i\varphi_0G_0}. \qquad (4.4)$$

The quantity γ_0 is to be evaluated at any point sufficiently far outside the core so that the field is Coulombian.

The expression for α becomes particularly simple if the matching is effected at a zero of ${}^iP_0$. Then

$$\gamma_0=\frac{F_0}{G_0}=\frac{J_{2l+1}(x)}{N_{2l+1}(x)}. \qquad (4.5)$$

The matching condition expressed by (4.1) must be imposed well outside the atomic core. It was found that at any such point x is large enough to justify the use of the asymptotic expressions for the Bessel functions,

$$J_{2l+1}=\left(\frac{2}{\pi x}\right)^{\frac{1}{2}}\left\{\cos\left[x-(2l+\tfrac{3}{2})\frac{\pi}{2}\right]+0\left(\frac{1}{x}\right)\right\}, \qquad (4.6)$$

$$N_{2l+1}=\left(\frac{2}{\pi x}\right)^{\frac{1}{2}}\left\{\sin\left[x-(2l+\tfrac{3}{2})\frac{\pi}{2}\right]+0\left(\frac{1}{x}\right)\right\}. \quad (4.7)$$

Combining (4.4), (4.5), (4.6), and (4.7), we arrive at the simple result

$$\left.\alpha\right)_{ni}=\frac{\left.x_0\right)_{ni}}{\pi}-\tfrac{1}{4}, \quad (4.8)$$

where x_0 is any zero of ${}^iP_0$ outside the core, and the subscript "*ni*" means "non-integral part of."

The Ritz Coefficient

From (4.3) we see that the Ritz coefficient is determined by

$$\beta=\left.\frac{dn}{d\epsilon}\right)_{\epsilon=0} \quad (4.9)$$

Inserting (4.2) in (4.9),

$$\begin{aligned}\pi\beta&=-\frac{1}{(1+\gamma_0^2)}\left.\frac{d\gamma}{d\epsilon}\right)_{\epsilon=0}\\&=-\frac{1}{1+\gamma_0^2}\left[\frac{F_0{}^i\varphi_1+F_1{}^i\varphi_0-F_1'}{G_0{}^i\varphi_0-G_0'}\right.\\&\qquad\left.-\frac{G_0{}^i\varphi_1+G_1{}^i\varphi_0-G_1'}{(G_0{}^i\varphi_0-G_0')^2}(F_0{}^i\varphi_0-F_0')\right]. \quad (4.10)\end{aligned}$$

As with α, this expression may be made to assume a simple and rather elegant form at a zero of ${}^iP_0$. At such a point, using (3.2) and (3.5), (4.10) becomes

$$\pi\beta=\frac{1}{1+(F_0/G_0)^2}\times\left[\frac{d}{d\epsilon}\left.\left(\frac{G}{F}\right)\right)_{\epsilon=0}+\frac{{}^i\varphi_1}{{}^i\varphi_0^2}\frac{d}{dr}\left(\frac{G_0}{F_0}\right)\right]. \quad (4.11)$$

It is clearly indicated by (4.11) that in place of F and G we should define two new variables, θ and ρ:

$$\theta=\tan^{-1}(G/F), \quad \rho=(F^2+G^2)^{\frac{1}{2}}. \quad (4.12)$$

When stated in terms of θ and ρ, the wave function is

$${}^eP=F\cos\pi n+G\sin\pi n=\rho\cos(\pi n-\theta). \quad (4.13)$$

From (4.11), (4.12), and (3.5), the Ritz coefficient is now given by

$$\pi\beta=\left.d\theta/d\epsilon\right)_{\epsilon=0}+\frac{\theta_0'}{{}^iP_0'^2}\int_0^r {}^iP_0^2dr, \quad (4.14)$$

where θ_0 indicates θ evaluated at $\epsilon=0$.

The Bohr Formula

We show next that

$$\left.\frac{d\theta}{d\epsilon}\right)_{\epsilon=0}\propto {}^eP_0^2{}^eT'=-\int_{r_p}^r {}^eP_0^2dr. \quad (4.15)$$

This result will lead us to our desired interpretation of β as a certain difference in orbital periods, since

$$\int_{r_1}^{r_2} P^2dr$$

is proportional to the time the electron spends in the region between r_1 and r_2.

To achieve this we recall first from Section 3 that if ${}^e\varphi$ is written in the form

$${}^e\varphi={}^e\varphi_0+{}^e\varphi_1\epsilon,$$

then ${}^e\varphi_1={}^eT'$. For our purposes we need ${}^e\varphi$ in terms of θ and ρ rather than F and G. Using (4.13),

$${}^e\varphi={}^eP'/{}^eP=\eta+\theta'\tan(\pi n-\theta); \quad (\eta=\rho'/\rho)$$

$${}^e\varphi_1=\left.d\varphi/d\epsilon\right)_{\epsilon=0}=\left.d\eta/d\epsilon\right)_{\epsilon=0}+\left.d\theta'/d\epsilon\right)_{\epsilon=0}\times\tan(\pi n-\theta_0)-\theta_0'\left.\frac{d\theta}{d\epsilon}\right)_{\epsilon=0}\sec^2(\pi n-\theta_0).$$

We remember that the matching point has been assumed to be a zero of P_0[8] and therefore of $\cos(\pi n-\theta_0)$. Hence the last term in the expression above dominates the others and we have

$${}^e\varphi_1=-\frac{\theta_0'\left.\frac{d\theta}{d\epsilon}\right)_{\epsilon=0}}{\cos^2(\pi n-\theta_0)}. \quad (4.16)$$

The various derivatives of θ occurring in (4.14) and (4.16) may be expressed in terms of x by referring to (2.10) in order to determine the relation of θ to the Bessel functions, and then employing the asymptotic formulae (4.6) and

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[8] The superscripts may be dropped outside the core since the two functions are identical in that region.

(4.7). We also use the following expression for P_0 which is obtained from (4.13) by means of (4.6) and (4.7):

$$^{e}P_0 = x^{\frac{1}{2}} \cos(\pi n - \theta_0). \qquad (4.17)$$

It is found in this way that (4.16) reduces to

$$^{e}\varphi_1 = -\frac{4}{^{e}P_0^2}\frac{d\theta}{d\epsilon}\Big)_{\epsilon=0}.$$

Hence, since $^{e}\varphi_1 = {}^{e}T'$,

$$d\theta/d\epsilon)_0 = -\tfrac{1}{4}P_0^{2e}T' = -\frac{1}{4}\int_{r_p}^{r} {}^{e}P_0^2 dr.$$

Referring again to (4.14), we find by a similar procedure that the coefficient therein occurring is given by

$$\theta_0'/{}^{i}P_0'^2 = 1/4.$$

Substituting these results in (4.14), the Ritz coefficient becomes

$$\pi\beta = \frac{1}{4}\left\{\int_0^r {}^{i}P_0^2 dr - \int_{r_p}^{r} {}^{e}P_0^2 dr\right\}. \qquad (4.18)$$

The first integral on the right in (4.18) represents the time t which the electron spends within the radius r.[9] The second integral represents the time which the electron would spend in this region if it were traversing a hypothetical orbit with the same energy, but in a field which was Coulombian all the way down to the nucleus, i.e., assuming the radius of the core were to shrink to zero. Calling this hypothetical time t^*, we have from (4.18),

$$\beta = (1/4\pi)(t - t^*). \qquad (4.19)$$

The time in (4.18) is expressed in atomic units. (A.u./sec. $= h^3/8\pi^3 m e^4$.) If t and t^* are expressed in seconds, we arrive at precisely the formula of Bohr,

$$\beta = R(t - t^*).$$

TABLE I. Sodium.

	α	β	Ionization pot'l.
Observed	0.652	−0.07	4.145×10⁴ cm⁻¹
Effective field	0.648	−0.06	4.155
Hartree-Fock field	0.780	−0.05	3.387

TABLE II. Potassium.

	α	β	Ionization pot'l.
Observed	0.822	−0.16	3.501×10⁴ cm⁻¹
Hartree-Fock field	1.020	−0.11	2.766
Hartree-Fock field expanded 20%	0.860	−0.13	3.309

TABLE III. Casium.

	α	β	Ionization pot'l.
Observed	0.953	−0.29	3.114×10⁴ cm⁻¹
Effective field	0.940	−0.27	3.162
Bohr Theory		−0.18	

5. COMPARISON WITH EXPERIMENT

The application of the formulae (4.8) and (4.14) for α and β requires a knowledge of $^{i}P_0$, the unbound or zero energy solution to the wave equation in the core region. This solution is obtained by numerical integration[10] of (3.4) out from the origin past the core, using a suitable potential $V(r)$.

In the course of carrying out these integrations, it was found that all factors which would be expected to affect $^{i}P_0$, such as small numerical errors, refinement of interval of integration, etc., left unchanged the positions of the zeros of $^{i}P_0$ although they did alter its amplitude. Now this means that the calculated value of α is largely independent of minor numerical mistakes or poor integration techniques, since (3.7) indicates that α depends only upon the position of these zeros. Unfortunately, β depends upon the amplitude of $^{i}P_0$ as well as upon the location of its zeros and consequently will be affected by integration errors.

In order to determine $^{i}P_0$ one must have a central field, $V(r)$, to use in the integration of the wave equation. One possible field for this purpose is the Hartree-Fock field of the core combined with the Coulomb field of the nucleus. Another possibility is an effective field so constructed to have the x-ray levels of an electron in this field match the observed levels, to a WKB approximation, for about twenty levels beginning with the K shell. For purposes of

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[9] We have $t/T = \int_0^r p^2 dr / \int_0^\infty p^2 dr$, where T is the radial period of the electron. But when P is so normalized as to fit the relation (4.17), then it is found that $T = \int_0^\infty p^2 dr$. Hence directly $t = \int_0^r p^2 dr$.

[10] The integration method employed is described by L. Feinstein and M. Schwarzschild, Rev. Sci. Inst. 12, 405 (1941), although carried out by hand rather than with the punched card methods therein reported.

comparison, calculations were carried out for Na both with the Hartree-Fock field[11] and with an effective field determined in the second manner by Prokofjew.[12] Potassium was treated with a Hartree-Fock field,[13] and also with the same field after it had been uniformly expanded by 20 percent. Caesium was calculated with an effective field.[14] The Ritz coefficient for Cs was also computed from Bohr's formula directly as a difference in times, using half-integral angular momentum on the orbital model. The latter calculation is of interest because of the demonstration by Kramers[15] that the Bohr theory with half-integral angular momentum should provide a good approximation to the central field problem.

The results of these calculations are compared with the experimental values of α and β in Tables I, II, and III and are discussed below. The observed and calculated values for the first ionization potential are also included.

Comparison of the Two Types of Central Fields

The results for K and Na indicate that the uncorrected Hartree-Fock field does not provide a good approximation to a central field for the motion of the valence electron. From Table II it may be seen that a uniform expansion of the Hartree core distribution by 20 percent almost suffices to remove the discrepancy. A field expanded by 25 percent probably would produce quite good results.

The unsuitability of the unadjusted Hartree-Fock field for calculating optical energy levels also indicates that it should not be used for determining the valence electron wave functions. One may, of course, modify the field by adding to it fictitious polarization potentials, etc.,[16] and then adjusting various parameters in these added terms so as to have the calculated energy levels agree with the observed values. Biermann[16] has calculated the intensities of certain lines in the alkali spectra, using a Hartree field so modified by the introduction of fictitious potentials. He finds that the results show good agreement with the experimental values. However, even assuming one has available the Hartree-Fock field for a given atom, the additional labor required for the modification of this field to obtain good energy levels, and therefore good wave functions, is of the same order as the labor necessary for the entire construction of the effective field. For the heavier atoms the latter field is the only one possible since the Hartree-Fock calculations for these atoms are prohibitively long.

Tables I and III show good agreement between the experimental values of α and β and the values calculated from the effective fields on our theory. Because of the nature of the effective field, agreement as regards α is probably to be expected. However, our interest in the calculation was directed primarily toward the Ritz coefficient.

It is also indicated by Table III that the calculation based upon the Bohr theory, while of the right order of magnitude, compares rather unfavorably with the more exact result.

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