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THE THEORY AND CALCULATION OF SCREENING CONSTANTS

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Abstract

It is shown that if H is the negative energy operator, and ϕ any function satisfying the boundary conditions of quantum dynamics and possessing the symmetry properties characteristic of a given spectral series, then $E=\int\phi^*H\phi d\tau$ is a lower limit to the term-value of the lowest level of that series. If the integral is evaluated for various ϕ's, the largest value obtained will be the best approximation to this term value. The method is applied to various electronic configurations with satisfactory results. The degree to which ϕ approximates the wave function of the state is not determined, but it is shown to be likely that the approximation is not good at large distances from the nucleus.

THE empirical interpretation of x-ray spectra has long been based on the idea that each electron of an inner shell screens the outer electrons from the field of the nucleus. The outer electrons are supposed to move in an approximately central field, much as though the inner electrons were not present and the nucleus had an effective charge less than its true charge. Millikan and Bowen have also shown that this idea is applicable to many optical spectra.

Quantum dynamics has furnished a qualitative justification for this idea, but the effective nuclear charges have never been deduced from first principles in any systematic way. It is true that L. Pauling[1] has obtained numerical values for them which are in excellent agreement with observation, but his calculation begins with the wave equation of a single electron moving in the field of an artificial distribution of charges on spherical surfaces. This amounts to assuming the general form of the result, and neglecting some of the finer features of the problem. J. Frenkel[2] has used the method which forms the subject of the present paper. He calculates the screening constant for the normal state of helium-like atoms, but assumes it to be applicable to any state. It was found empirically (cf. Section 5) that the method fails miserably when applied to $(1s)(2s)\ 2^1S$, but, remarkably enough, gives very good results for $(1s)(2s)2^3S$. This is shown to be a consequence of a definite limitation on the method, which is applicable only to the lowest state of any spectral series. (Section 1.).

The method is analogous to that first used by Ritz[3] to calculate characteristic numbers. The Ritz method has already been used to solve problems

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[1] L. Pauling Zeits. f. Physik **40,** 344 (1926).

[2] J. Frenkel, Einführung in die Wellenmechanik, p. 291. (Berlin, Julius Springer, 1929). Also Guillemin and Zener, Zeits. f. Physik **61,** 199 (1930).

[3] W. Ritz, Journ. f. reine u. angew. Math. **135,** 1 (1909).

of quantum dynamics,[4] but the investigators have not adhered very closely to the original procedure,[5] and it appears that the deviations are largely responsible for the success of the calculation. They are all in the direction indicated by the empirical theory of screening. In this paper, a theoretical justification for them is given and the original Ritz procedure is abandoned[6] entirely. This simplifies the calculations considerably without greatly reducing the accuracy of the result. If higher accuracy is required, however, the Ritz method may be superposed as was done by Kellner and Hylleraas.

It may be well to make a few general remarks about the various kinds of screening constants[7] (or effective nuclear charges). These numbers are essentially parameters determining an average value of the electrostatic field in which an electron moves, and there will be as many different ones as there are different ways of averaging. The present paper will be primarily concerned with that effective charge which is to be used in the wave function. The approximate value of the main energy term is also obtained, from which that screening constant called σ_1 by Pauling could be calculated if it were desirable. This latter is responsible for the "screening doublets"; the "spin" screening constant is not calculated.

1. The Direct Method of Calculating Characteristic Numbers

The fundamental equation of a characteristic value problem may be written

$$H\psi_n = W_n\psi_n, \tag{1}$$

which is normally a partial differential equation, H being an operator, W_n the characteristic number, and ψ_n a function of the coordinates. This equation is to be solved subject to certain boundary conditions, and possesses solutions satisfying these only for certain values of W_n, say

$$W_1 \geqq W_2 \geqq W_3 \geqq \cdots. \tag{2}$$

(In quantum dynamics there is always a greatest W if this letter denotes the negative energy or term value.) For the following, it will be convenient to use the letters ϕ, ϕ', ϕ'' $\cdots$ to denote functions which satisfy the boundary conditions just mentioned, but are otherwise arbitrary. If the operator H is hermitan the characteristic solutions ψ_n of Eq. (1) may be normallized so that

$$\int \psi_n\psi_m{}^* d\tau = \delta_{nm} \tag{4}$$

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[4] G. W. Kellner, Zeits. f. Physik **44,** 91, 110, (1927), E. Hylleraas, Zeits. f. Physik **48,** 469 (1927).

[5] Courant-Hilbert, Mathem. Methoden der Physik p. 157 (Berlin, J. Springer, 1924).

[6] This has also been done by V. Guillemin, Jr. and C. Zener, Zeits. f. Physik **61,** 199 (1930); C. Zener Phys. Rev. **36,** 51 (1930).

[7] For details, see L. Pauling and G. Goudsmit "Structure of Line Spectra," pp. 61, 180, 188 (McGraw-Hill, 1930).

and any of the functions ϕ may be expanded in a convergent series:

$$\phi = \Sigma a_n \psi_n, \text{ where } a_n = \int \phi \psi_n^* d\tau \tag{5}$$

If ϕ is itself normallized, i.e., if

$$\int | \phi |^2 d\tau = 1, \text{ or } \Sigma | a_n |^2 = 1 \tag{6}$$

then the integral

$$E = \int \phi^* H \phi d\tau \tag{7}$$

possesses certain important properties. For convenience, it will be called the variational integral and any normallized ϕ will be called a comparison function.

On substituting the expression (5) for ϕ into Eq. (7) and making use of Eqs. (1) and (4), it follows that

$$E = \Sigma | a_n |^2 W_n.$$

It is immediately seen that if all the a's are zero except one ($\phi \equiv \psi_m$) then $E = W_m$; if ϕ differs only little from ψ_m, E will approximate W_m. To investigate this approximation, it is necessary to study the difference

$$W_m - E = \sum_n | a_n |^2 (W_m - W_n). \tag{8}$$

Because of the inequalities (2) the difference $W_1 - E$ must always be positive, since $W_1 - W_n \geqq 0$, and W_1 is therefore the maximum value assumed by the variational integral for any comparison function whatever. If E has been evaluated for various comparison functions, then the largest of these values will be the best approximation to W_1.

This reasoning applies only to the largest characteristic number, but if the first $m-1$ coefficients of the expansion (5) are all zero, it will apply equally to W_m. It is often possible to find comparison functions satisfying this condition, even though the functions ψ_n are not known exactly. A simple example is afforded by an atomic system with two electrons. If x_1, x_2 be their cartesian coordinates (the spin variables are entirely neglected) it is known that

$$\psi_1(x_1, x_2) = \psi_1(x_2, x_1)$$

and hence if

$$\phi(x_1, x_2) = - \phi(x_2, x_1)$$

it follows from Eq. (5) that $a_1 = 0$. Any antisymmetric comparison function will thus furnish a lower limit to the second characteristic number.

Similarly, if $\boldsymbol{M}$ be the operator associated to the angular momentum of the system and the comparison function be restricted by the equation

$$\boldsymbol{M}^2\phi = L(L+1)\phi$$

where $L=0, 1, 2, \cdots$, then the value of E obtained will be a lower limit to the lowest (largest W) $S, P, D, \cdots$, term, respectively.

These results afford a basis for a direct method of calculating those characteristic values to which they apply. If comparison functions $\phi, \phi', \phi'' \cdots$ are known, which result in values $E \leqq E' \leqq E'' \leqq \cdots$, it may be presumed that this sequence of numbers will converge toward the corresponding W_n. The proof of this convergence will usually be difficult, and no attempt will be made to construct one in this paper. Instead, a mode of reasoning will be adopted which is much simpler.

It depends on the fact that there exists one comparison function which has a certain theoretical justification:[8] if the operator H be written $H'+H''$, it is known from perturbation theory that

$$\begin{aligned} \psi_n &= \phi_n + \cdots \\ W_n &= W_n' + W_n'' + \cdots \end{aligned} \tag{9}$$

where

$$H'\phi_n = W_n'\phi_n \tag{10}$$

and

$$W_n'' = \int \phi_n^* H'' \phi_n d\tau. \tag{11}$$

The function ϕ_n is the first term of an infinite series and is generally accepted as a "zeroth" approximation ot ψ_n, while $W_n'+W_n''$ is the "first" approximation to W_n. For physical purposes, they may therefore be taken as standards by which other approximations are to be judged—if $|W_n - E| < |W_n - W_n' - W_n''|$ then E will be a good approximation according to this criterion. The direct method immediately enables us to find a good approximation whenever it is available and ϕ_n is known.

The operator H' and the function ϕ_n will usually depend on a numerical parameter Z (say the nuclear charge); if this parameter, whose true value is a part of the given data, be allowed to assume arbitrary values α in ϕ_n, then

$$E(Z, \alpha) = \int \phi_n^*(\alpha) H''(Z) \phi_n(\alpha) d\tau \tag{12}$$

will certainly be a lower limit to W_n. If $E(Z,\alpha)$ possesses a maximum for $\alpha = Z_e$ then it immediately follows that

$$W_n - E(Z, Z_e) \leqq W_n - E(Z, Z) = W_n - W_n' - W_n''.$$

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[8] The mathematician might not agree to the soundness of the theory, but it has the general assent of physicists.

Hence $E(Z, Z_e)$ is a good approximation according to the criterion adopted above. This is the explanation of the recognised fact that the substitution of effective charges and quantum numbers in formulas deduced from perturbation theory usually improves their agreement with observational data. It goes farther, however, and indicates when the process will certainly be successful and when it is likely to fail; in the former case, the numerical value of the "effective" parameter is determinate. It should be noted that $E(Z,Z_e)$ depends on the true, as well as on the effective, value of the parameter. This affords a theoretical clue to the use of "inner" and "outer" effective charges.

In the previous paragraph, only one parameter has been treated, but there is no limit to the number which can be introduced into ϕ_n provided only that its symmetry properties be left undisturbed. Any degeneracy in the characteristic values of H' must be removed in determining ϕ_n by perturbation theory.

2. Application to the Configuration $(1s)^2$

The details of this method may most simply be illustrated by its application to the configuration $(1s)^2$ (normal state of helium), and this case will therefore be treated even though it has already been published by Frenkel.[2]

The operator H is

$$H = \nabla_1^2 + \nabla_2^2 + 2Z/r_1 + 2Z/r_2 - 2/r_{12} \qquad (13)$$

where the indices denote the coordinates of the two electrons, which are measured in units of $a_H = 0.528$A. The constant W is the negative energy, measured in units of Rh cm^{-1} = 13.53v., and Z is the true nuclear charge in units of e. These units and designations will be used throughout the following. The operator H' is taken to be

$$H' = \nabla_1^2 + \nabla_2^2 + 2Z/r_1 + 2Z/r_2$$

whose characteristic function for the $(1s)^2$ configuration is

$$\begin{aligned} \phi(Z) &= u(Z, 1)u(Z, 2) \\ u(Z, k) &= (Z^3/\pi)^{1/2} \exp(-Zr_k.) \end{aligned} \qquad (14)$$

A comparison function may be obtained from this in various ways, the simplest being

$$\phi(\alpha) = u(\alpha, 1)u(\alpha, 2); \qquad (15)$$

substituting this in the variational integral, one finds (cf. Section 7) that

$$E(Z, \alpha) = 2[2(Z - 5/16)\alpha - \alpha^2]. \qquad (16)$$

This expression has a maximum for $\alpha = Z_e = Z - 5/16$ so that

$$E(Z, Z_e) = 2Z_e^2$$

is independent of Z in this case. The ionizing potential of the $(1s)^2$ state may be calculated from this by subtracting Z^2, the energy of the hydrogen-like ion.

The values given by this formula are compared with those from other sources in Table I.

TABLE I. *Ionizing potentials of* $(1s)^2$.

Atom	$V=$ $2Z_e^2-Z_2$	V (Calc. §6)	V (Observ.)
He I	1.70		1.81
Li II	5.45	5.50	5.564*
Be III	11.20	11.26	11.315*
B IV	18.95	19.00	
C V	28.70	28.75	

* B. Elden and A. Ericson, Nature **124**, 688 (1929).

A somewhat better approximation would be obtained by using

$$\phi(\alpha, \beta) = [u(\alpha, 1)u(\beta, 2) + u(\alpha, 2)u(\beta, 1)]/[2(1 + c^2)]^{1/2} \tag{17}$$

$$c = \int u(\alpha, 1)u(\beta, 1)d\tau_1 = 8\alpha^{3/2}\beta^{3/2}/(\alpha + \beta)^3$$

as comparison function. The variational integral is then

$$E(Z, \alpha, \beta) = 2Z\alpha + 2(Z - \sigma)\beta - (\alpha^2 + 2\alpha\beta c^2 + \beta^2)/(1 + c^2)$$

where

$$\sigma\beta = \iint [\phi(\alpha, \beta)]^2/r_{12}d\tau_1 d\tau_2$$

$$= \frac{\beta}{1 + c^2}\left[1 - \frac{2x + 1}{(x + 1)^3} + \frac{20x^3}{(x + 1)^5}\right], \quad x = \alpha/\beta.$$

It is difficult to determine the maximum of this function analytically, but a numerical approximation method yields a value of 5.755 for $\alpha = 2.14$, $\beta = 1.19$ in the case of He I ($Z = 2$). This corresponds to 1.755 for the ionizing potential—a value as good as Kellner's fourth approximation.

The interest does not center on an accurate determination of this ionizing potential, however: in the case of He I, it has been calculated very accurately by Hylleraas (loc. cit.) and the others of this isoelectronic sequence may be calculated more accurately by the indirect method explained in Section 6. The comparison function of this configuration is of great interest, however, for it enters into many of the other configurations considered later. The relative simplicity of the function $\phi(\alpha)$, Eq (15), leads one to use it rather than the more elaborate one.

3. APPLICATION TO THE CONFIGURATIONS $(1s)(2p)$ AND $(1s)(3d)$

The wave equation for these configurations is that of Eq. (13); the comparison function is to be taken as

$$\phi(\alpha, \beta) = [u(\alpha, 1)v(\beta, 2) \pm u(\alpha, 2)v(\beta, 2)]/2^{1/2} \tag{18}$$

where u is the function defined by Eq. (14) and in the case of $(1s)(2p)$,

$$v(\beta,\, k) = Y_1 \cdot (\beta^3/6)^{1/2}(\beta r_k/2) \exp{(-\,\beta r_k/2)} \tag{19}$$

is the characteristic function of the $(2p)$ state of a hydrogen atom with nuclear charge β; Y_1 is a normallized surface spherical harmonic of order 1. The upper sign is to be taken for the ${}^1P$, the lower for the ${}^3P$ level. The value of the variational integral is found to be

$$E(Z,\alpha,\beta) = (2Z - \alpha)\alpha + [2(Z - \sigma) - \beta]\beta/4 \tag{21}$$

where

$$\sigma = I \pm J$$

and, with $x = \alpha/\beta$

$$\begin{aligned} I &= (4/\beta) \int\!\!\int \{ [u(\alpha,\, 1)v(\beta,\, 2)]^2/r_{12} \} d\tau_1 d\tau_2 \\ &= 1 - (6x + 1)/(2x + 1)^5 \end{aligned} \tag{22}$$

$$\begin{aligned} J &= (4/\beta) \int\!\!\int \{ u(\alpha,\, 1)v(\beta,\, 1)u(\alpha,\, 2)v(\beta,\, 2)/r_{12} \} d\tau_1 d\tau_2 \\ &= (7/3)64x^3/(2x + 1)^7. \end{aligned} \tag{23}$$

The function $E(Z,\alpha,\beta)$ has a maximum for the values of α and β which satisfy the equations $\partial E/\partial\alpha = 0$, $\partial E/\partial\beta = 0$, or

$$\begin{aligned} \alpha &= Z - (d\sigma/dx)/4 \\ \beta &= Z - \sigma - x d\sigma/dx. \end{aligned} \tag{24}$$

These are readily solved by a semi-graphical method of approximation: σ and $d\sigma/dx$ are plotted from the values of I, J, and their derivatives given in Table II. As a rough approximation, $(1-\sigma)$ and $d\sigma/dx$ may be neglected, whence $\alpha = Z$, $\beta = Z - 1$. The values of σ and $d\sigma/dx$ for these values are taken from the graphs and substituted in Eq. (24), giving a better approximation to α and β; continuing the process, the roots are soon found with sufficient accuracy, and the maximum value of E is then calculable. The results of such calculations are summarized in Table III, V being the ionizing poten-

TABLE II. *Values of I, J, and their derivatives.*

x	I	dI/dx	J	dJ/dx
1.3	0.9854	0.0302	0.0418	−0.0654
1.4	0.9881	0.0234	0.0358	−0.0556
1.5	0.9902	0.0182	0.0308	−0.0468
1.6	0.9919	0.0146	0.0265	−0.0396
1.7	0.9932	0.0118	0.0230	−0.0334
1.8	0.9943	0.0094	0.0200	−0.0292
1.9	0.9951	0.0077	0.0175	−0.0236
2.0	0.9958	0.0066	0.0153	−0.0204
2.1	0.9964	0.0051	0.0135	−0.0184

tial of the state in units of 13.53 v. The numbers in the last two columns are the roots of Eq. (24).

TABLE III. *Ionizing potentials of* $(1s)(2p)$.

Level	$V/(Z-1)_2$ Calc.	$V/(Z-1)_2$ Obs.	α	β
He I, 2^1P	0.245	0.2475	2.003	0.965
He I, 2^3P	0.262	0.2657	1.99	1.09
Li II, 2^1P	0.245	0.250	3.007	1.94
Li II, 2^3P	0.261	0.263	2.98	2.16

To treat the configuration $(1s)$ $(3d)$ only slight changes are necessary: the function u remains the same, while

$$\begin{aligned}
v(\beta, k) &= Y_2\cdot(8\beta^3/1215)^{1/2}(\beta r_k/3)^2\cdot\exp(-\beta r_k/3),\\
E(Z, \alpha, \beta) &= (2Z - \alpha)\alpha + [2(Z - \sigma) - \beta]\beta/9,\\
\sigma &= I' \pm J',\\
I' &= (9/\beta)\iint\{[u(\alpha, 1)v(\beta, 2)]^2/r_{12}\}d\tau_1 d\tau_2\\
&= 1 - (12x + 1)/(3x + 1)^7,\\
J' &= (9/\beta)\iint\{u(\alpha, 1)v(\beta, 1)u(\alpha, 2)v(\beta, 2)/r_{12}\}d\tau_1 d\tau_2\\
&= (4/5)\cdot 729x^3/(3x + 1)^9.
\end{aligned} \tag{25}$$

In this case, σ is so nearly unity that $\alpha = Z$ and $\beta = Z - 1$ is a sufficient approximation if only the center of gravity of the ^1D and ^3D terms is required. Their separation may be calculated from J': it is

$$\Delta W = 4(Z - 1)J'/9 = (6)^4Z^3(Z - 1)^7/[5(4Z - 1)^9].$$

The numerical values of this expression are compared with the observed values in Table IV.

TABLE IV. $3^3D - 3^1D$.

	Calc.	Obs.
He I	5.14×10^{-5}	3.68×10^{-5}
Li II	3.80×10^{-4}	2.68×10^{-4}

4. THE CONFIGURATION $(1s)^2$ $(2p)$

For this configuration, the energy operator is

$$H = \sum_{k=1}^{3}(\nabla_k^2 + 2Z/r_k) - \sum_{(k,j)}(2/r_{kj}). \tag{26}$$

Since two electrons are in the $1s$ state, the two ways of introducing variable parameters discussed under Eqs. (15) and (17) are available; the former is much the simplest, so that it may be chosen:

$$\phi(\alpha, \beta) = u(\alpha, 1)[u(\alpha, 2)v(\beta, 3) - u(\alpha, 3)v(\beta, 2)]/2^{1/2}, \tag{27}$$

v having the significance of Eq. (19). The variational integral reduces to

$$E(Z, \alpha, \beta) = 2[2(Z - 5/16) - \alpha]\alpha + [2(Z - \sigma) - \beta]\beta/4 \tag{28}$$

with (cf. Eqs. (22) and (23))

$$\sigma = 2I - J.$$

The maximum value of this expression may be determined as already described. The results are shown in Table V, the ionizing potential of the state being obtained by subtracting $2(Z-5/16)^2$ from the maximum value of E. There are systematic differences between the calculated and observed values of $V/(Z-2)^2$ but both sequences show a flat maximum near Be II. This indicates that the method is capable of giving information even regarding the finer features of the dependence of W_n on Z. The systematic deviations could undoubtedly be diminished if the more complex function (17) were used for $(1s)^2$.

TABLE V. *Ionizing potentials of* $(1s)^2(2p)$.

	$V/(Z-2)^2$			$Z-\beta$	
Atom	Calc.	Obs.*	$Z-\alpha$†	(Calc.)	(Obs.)*
Li I	0.255	0.2605	0.31	1.98	2.019
Be II	0.258	0.2620	0.32	1.95	1.937
B III	0.258	0.2609	0.32	1.93	1.884
C IV	0.257	0.2595	0.32_5	1.91	1.858
N V	0.257		0.33	1.89	1.838
O VI	0.256		0.33	1.88	1.816

* Millikan and Bowen, Phys. Rev. **27**, 144 (1926). The observed values of $Z-\beta$ are taken from the spin doublet separation, and are only qualitatively comparable with the calculated values.

† Cf. Guillemin and Zener, loc. cit.

5. THE CONFIGURATION (1s) (2s)

This electronic configuration gives rise to two levels, 2^3S, 2^1S, of which the former is the lowest, the latter is the second term of its series. The method may be expected to fail when applied to 2^1S, and does so.

The energy operator is that of Eq. (13), and the comparison function is

$$\phi = [u(\alpha, 1)v(\beta, 2) \pm u(\alpha, 2)v(\beta, 1)]/[2(1 \pm b^2)]^{1/2}, \tag{29}$$

u being given by Eq. (14) and

$$v(\beta, k) = (\beta^3/8\pi)^{1/2}(1 - \beta r_k/2) \exp(-\beta r_k/2), \tag{30}$$

$$b = \int u(\alpha, 1)v(\beta, 1)d\tau_1 = (2x)^{3/2}(x - 1)/(x + \tfrac{1}{2})^4. \tag{31}$$

The variational integral reduces to

$$E(Z, \alpha, \beta) = \left\{ [2(Z - \sigma_1) - \alpha]\alpha + [2(Z - \sigma_2) - \beta]\beta/4 \right\}/(1 \pm b^2)$$

with

$$\sigma_1 = \pm (Z - \beta)b^2x/(1 - x)$$

$$\sigma_2 = A \pm [B - (Z - \alpha)b^2/(1 - x)]$$

$$A = \frac{4}{\beta}\iint \frac{[u(1)v(2)]^2}{r_{12}} d\tau_1 d\tau_2 = 1 - \frac{1}{4}\left\{ \frac{4x + 1}{(x + \frac{1}{2})^3} - \frac{5x + 1}{(x + \frac{1}{2})^4} + \frac{3}{8}\,\frac{6x + 1}{(x + \frac{1}{2})^5} \right\}$$

$$B = \frac{4}{\beta}\iint \frac{u(1)v(1)u(2)v(2)}{r_{12}} d\tau_1 d\tau_2 = \frac{x^3}{2}\cdot\frac{20x^3 - 30x + 13}{(x + \frac{1}{2})^7}\,. \qquad (33)$$

The derivatives of the function E are too complex to be used in computation, and it is simpler to calculate E numerically for various values of α and x, the maximum value being determined by graphical interpolation. The numerical work was simplified considerably by first tabulating the values of A, B, and b^2 (Table VI); this was also a saving of time, since these functions also enter into the work on $(1s)^2$ $(2s)$ and other more complex configurations.

TABLE VI.

x	b^2	A	B	C
1.0	0.0000	0.8396	0.0876	0.00000
1.1	0.0025	0.8504	0.1044	0.00216
1.2	0.0079	0.8604	0.1220	379
1.3	0.0143	0.8692	0.1400	497
1.4	0.0205	0.8772	0.1564	582
1.5	0.0263	0.8848	0.1716	641
1.6	0.0312	0.8916	0.1844	681
1.7	0.0352	0.8980	0·1952	706
1.8	0.0381	0.9036	0.2040	719
1.9	0.0404	0.9092	0.2112	724
2.0	0.0419	0.9140	0.2164	723
2.1	0.0429	0.9184	0.2204	716
2.2	0.0434	0.9228	0.2232	707
2.3	0.0435	0.9268	0.2248	694
2.4	0.0433	0.9304	0.2252	680
2.5	0.0428	0.9336	0.2252	

The values of the ionizing potential and effective charges as calculated for 2^3S are given in Table VII. The ionizing potential calculated for 2^1S was in each case somewhat greater than that for 2^3S—in direct contradiction to observation. It was attempted to improve matters by chosing $\beta = Z - 5/16$

TABLE VII. *Ionizing potentials of* $(1s)(2s)2^3S$.

Atom	Calc.	Obs.	α	β
He I	0.334	0.350	2.01	1.53
Li II	1.21	1.22	3.03	2.56

which makes the ϕ of Eq. (29) orthogonal to the approximate wave function for 1^1S:

$$u(Z - 5/16, 1)u(Z - 5/16, 2).$$

This reduced the calculated ionizing potential too much. Perhaps a method of this sort might be worked out using the expression (17) for the wave function of 1^1S.

6. THE CONFIGURATION $(1s)^2$ $(2s)$.

The operator H is that of Eq. (26) and the comparison function is

$$\phi = u(\alpha, 1)[u(\alpha, 2)v(\beta, 3) - u(\alpha, 3)v(\beta, 2)]/[2(1 - b^2)]^{1/2} \tag{34}$$

with v defined by Eq. (30) and b^2 as in Table VI. The variational integral reduces to

$$E(Z, \alpha, \beta) = \{[(2 - b^2)(2Z - \alpha) - \tau]\alpha + [2(Z - \sigma) - \beta]\beta/4\}/(1 - b^2) \tag{35}$$

where

$$\begin{aligned} \sigma &= 2A - B + 8C - (z - 1 - \alpha)b^2/(x - 1) \\ \tau &= 5/4 - 2(z - 1 - \beta)b^2x/(1 - x). \end{aligned} \tag{36}$$

A and B have the values given in Table VI and

$$\begin{aligned} C &= \frac{b^2(\alpha^2 - \beta^2/4)}{2\beta(\alpha - \beta)} - (b/\beta)\iint\{[u(1)]^2u(2)v(2)/r_{12}\}d\tau_1 d\tau_2 \\ &= (2x^3)^{1/2}b(3x^2 + 2x - \tfrac{1}{4})/(3x + \tfrac{1}{2})^4 \end{aligned}$$

is also given in that table.

TABLE VIII. *Ionizing potentials of* $(1s)^2(2s)$.

Atom	V Calc.	V Obs.	$Z-\alpha$	$Z-\beta$
Li I	0.456	0.397	0.30	1.22
Be II	1.41	1.34	0.30	1.16
B III	2.85	2.79	0.28	1.07
C IV	4.80	4.745	0.29	1.04

The maximum value of this function was again determined by plotting it for various values of α and x. The resulting ionizing potentials are all too high, as is shown in Table V. This is because the value $2(Z-5/16)^2$ is consistently less than the energy of $(1s)^2$; a better comparison with observation is obtained if the observed ionizing potential be subtracted from the maximum value of E. The result should be a lower limit to the true energy of $(1s)^2$. The third column of Table I contains the values of the ionizing potential of helium-like ions calculated in this way; the agreement with observation is good. The values for B IV and C V are as good as any available, and are presumably about 0.05-0.06 units lower than the true values.

7. FORMULAE USED IN EVALUATING THE FOREGOING INTEGRALS

The following is a brief summary of formulae, most of them well-known, which were used in evaluating the integrals of the foregoing sections. The functions u and v satisfy the equations

$$\Delta^2 u + 2\alpha u/r = \alpha^2 u/n^2$$
$$\Delta^2 v + 2\beta v/r = \beta^2 v/m^2$$

n and m being integers. Each has the form $X(r)\ Y_l\ (\theta, \phi)$, Y_l being a normallized surface spherical harmonic of order l (l is the aziumthal quantum number). The X's are also supposed normallized. From these definitions, it follows that

$$\int u[\nabla^2 u + 2Zu/r]d\tau = (2Z - \alpha)\alpha/n^2$$

(u may of course be replaced by v if other appropriate changes are made);

$$\int [u\nabla^2 v + v\nabla^2 u + 4Zu/r]d\tau$$
$$= 2b\{[\alpha^2(Z - \beta)]/n^2 - [\beta(Z - \alpha)]/m^2\}/(\alpha - \beta),$$
$$b = \iint uv\ d\tau,$$

The quantity b will vanish unless the aziumthal quantum numbers of u and v are equal.

If f and g are any functions independent of ϕ and θ, it may be shown that

$$\begin{aligned}\iint &\{f(r_1)[Y_l(\theta_1, \phi_1)]^2 g(r_2)/r_{12}\}d\tau_1 d\tau_2 \\ &= \int_{r_1=0}^{\infty} f(r_1)r_1 \int_{r_2=0}^{r_1} g(r_2)r_2^2 dr_2 dr_1 \\ &+ \int_{r_1=0}^{\infty} f(r_1)r_1^2 \int_{r_2=r_1}^{\infty} g(r_2)r_2 dr_2 dr_1,\end{aligned} \tag{40}$$

and

$$\iint \{f(r_1)Y_l(\theta_1, \phi_1)g(r_2)Y_l(\theta_2, \phi_2)/r_{12}\}d\tau d\tau_2$$
$$= \left\{\int_{r_1=0}^{\infty} f(r_1)r_1^{1-l} \int_{r=0}^{r_1} g(r_2)r_2^{l+2} dr_2 dr_1 \right.$$
$$\left. + \int_{r_1=0}^{\infty} f(r_1)r_1^{2+l} \int_{r_2=0}^{r_1} g(r_2)r_2^{1-l} dr_2 dr_1\right\}/(2l + 1).$$

In evaluating the integrals with respect to r_1 and r_2 the following formula is useful:

$$\int_r^\infty r^n e^{-\alpha r} dr = (n!/\alpha^{n+1}) \sum_{k=0}^{n} (\alpha r)^k/k!. \tag{42}$$

8. Discussion of the Results

The primary object of all calculations like the foregoing must be to determine the functions ψ_n approximately, or at least to approximate the electron density which is defined by

$$D(1) = 2 \int | \psi_n(1, 2) |^2 d\tau_2$$

in the case of two electrons. It may be hoped that an approximation will be obtained if a comparison function is substituted in this integral and its parameters are given the values determined as described.

While this paper was being written, two others dealing with the same subject were published by C. Zener[9] and J. C. Slater.[10] These authors use comparison functions ϕ which are much simpler than those used in the present calculations. This is presumably justified, for Zener has shown that the first term of the parenthesis $(1-\beta r_k/2)$ in Eq. (30) has very little effect on D. If this is true only for that value of β which makes the variational integral a maximum, then it is significant in the matter discussed in the preceding paragraph: it indicates that the same D is obtained for two comparison functions. But if the same is true for a wider range of β, then the observation merely means that this term may be neglected in evaluating D(or E), but does not give any information regarding the invariance of D—the difference between the two comparison functions is then trivially slight.

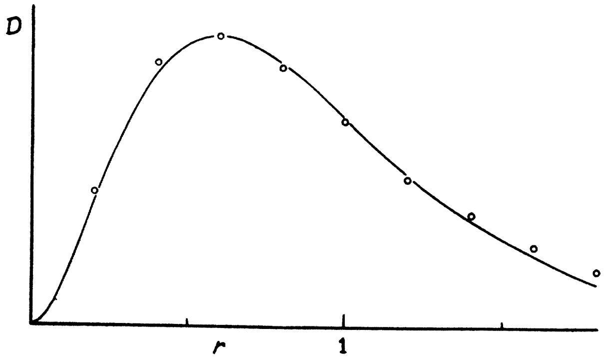

Fig. 1.

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[9] C. Zener, Phys. Rev. **36**, 51 (1930).

[10] J. C. Slater, Phys. Rev. **36**, 57 (1930).

The functions $\phi(\alpha)$, Eq. (15), and $\phi(\alpha, \beta)$, Eq. (17), may be compared in this respect. At first glance, they are widely different, but a closer examination shows that if r_1 and r_2 are of the same order of magnitude and not too large, $\phi(\alpha, \beta) \sim \exp[-(\alpha+\beta)(r_1+r_2)/2]$. In this region the two are not appreciably different, therefore, and the result of the comparison will be open to much the same doubt as Zener's. It is to be noted that the variational integral is a maximum for $2\alpha = 3.38$ if $\phi(\alpha)$ is used, and for $\alpha+\beta = 3.33$ if $\phi(\alpha, \beta)$. In Fig. 1, the curve represents the D obtained from $\phi(\alpha)$, the circles, the values of 1.56 D obtained from $\phi(\alpha, \beta)$. The relative values of D obtained from the two functions are thus nearly the same in the region $r < 1.5a_H$ but their absolute values differ by more than 50%. The reason for this becomes apparent on noting that $D[\phi(\alpha)]$ approaches zero like $\exp(-3.38r)$ for large values of r, while $D[\phi(\alpha, \beta)]$ approaches $\exp(-2.38r)$. The only rigorous conclusion is that the electron density calculated in this way may be quite inaccurate at infinity. It seems quite likely, however, that its behavior for small values of r is correctly given.

I wish to acknowledge my indebtedness to Mrs. Ardi's T. Monk, who performed many of the computations required for this work. Among other things not so easily enumerated, Tables II and VI are due to her.

Note added in proof: The following considerations afford a means of estimating the error introduced by the use of approximate wave functions. Let ψ_1 be the true wave function of the lowest state of a series and ϕ an approximation to ψ_1; both will be supposed real and normalized. The error introduced by using ϕ will generally be of the order of magnitude ϵ, where

$$\begin{aligned} \epsilon^2 &= \int(\psi_1-\phi)^2 d\tau \\ &= 2-2a_1 \qquad \text{by Eq. (5)} \end{aligned} \tag{43}$$

The expression for E (Eq. 7)) may be written

$$\begin{aligned} E &= a_1^2 W_1 + \Sigma_{n>1} a_n^2 W_n \\ &\leqq a_1^2 W_1 + W_2\, \Sigma_{n>1} a_n^2 \qquad \text{by Eq. (2),} \\ &= a_1^2 W_1 + W_2(1-a_1^2) \qquad \text{by Eq. (6);} \end{aligned}$$

hence

$$(W_1-E)/(W_1-W_2) \geqq 1-a_1^2 = 1-(1-\epsilon^2/2)^2.$$

If ϵ is not too great, this is equivalent to

$$\epsilon^2 \leqq (W_1-E)/(W_1-W_2). \tag{44}$$

The values of W_1 and W_2 are known from experiment so that an upper limit for ϵ may be calculated, which probably does not differ greatly from the true value.

Eq. (44) indicates that W_1-E is proportional to the second power of ϵ—a result which was obvious anyway—and that the factor of proportionality is not W_1 but $(W_1-W_2) < W_1$. These two facts explain the remarkably small values of W_1-E obtained above. They also show why the calculations of Section 6 yielded better values for the ionizing potentials of $(1s)^2$ than did those of Section 2.

In calculating other quantities than the energy, the error will be of first order in ϵ, which may therefore be taken as the probable fractional error. This should be the case in calculating the density function D; for $\phi(\alpha)$ Eq. (44) yields $\epsilon \leqq 0.27$ for $\phi(\alpha, \beta)$, $\epsilon \leqq 0.19$. The difference 50 percent in the values of D obtained from the two functions is thus no greater than might be expected.

In the case of Li II, 2^3P and Li I 2^2P, the values of ϵ for the functions given in Sections 3 and 4 are $\leqq 0.12$ and $\leqq 0.19$ respectively. These functions have been used elsewhere to calculate the relative displacements of Li (6) and Li (7) lines because of the motion of the nucleus.[11] The probable errors of these calculations can now be estimated:

Li II	λ5485	$\Delta\nu = 0.327 \pm 0.031$ cm^{-1}
Li I	λ6708	$\Delta\nu = 0.123 \pm 0.007$ cm^{-1}

The errors are small since only a part of the calculated value is affected by the error in the wave function.