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ANALYTIC ATOMIC WAVE FUNCTIONS

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Abstract

The wave functions for the atoms Be, B, C, N, O, F, Ne, are written as simple analytic expressions with several parameters. The best values of these parameters are then determined by the variation method. In the final wave functions the effective quantum number is very nearly two, the radial node is so small as to have little effect upon the charge distribution, the coefficient in the exponential is related to an empirical "mean effective charge."

Introduction and Results

SEVERAL methods may be used to obtain approximate solutions of the wave equation for a many electron atom. Any one method cannot claim superiority in every respect. One naturally wants that type of solution which can be used to the best advantage. If he wants information derivable from a graphical $\psi\bar{\psi}$ distribution, then the Hartree[1] functions will be the best. In fact, the graphical method of integration, modified in the manner suggested by Slater[2] and Fock[3] to include resonance, will give the best approximation in which the total ψ is built from functions of only one electron, and in which magnetic forces are neglected.

If all questions could be answered by graphical functions without an undue amount of labor, we would not be justified in finding a less correct analytical ψ. But the integrals representing the mutual potential energy of two atoms are of a type which can be readily evaluated only when the wave functions are given by analytic expressions. Moreover, these integrals become increasingly laborious as the complexity of the atomic functions increases. Hence it is desirable to know the best possible functions which can be represented by simple analytic expressions.

Such atomic functions may be obtained starting from the hydrogenic solutions, exact when the interaction between the electrons is neglected, then partially taking care of this interaction by putting parameters into the function wherever flexibility may be obtained without increased complexity. This method has been used to obtain an approximate eigenfunction for Li by Guillemin and Zener.[4] In this paper the same method is applied to the normal states of the remaining elements in the first row of the periodic table.

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[1] D. R. Hartree, Proc. Camb. Phil. Soc. **24**, 89–132 and 426–437 (1928).

[2] J. C. Slater, Phys. Rev. **35**, 210 (1930).

[3] V. Fock, Zeits. f. Physik **61**, 126, (1930).

[4] V. Guillemin Jr. and C. Zener, Zeits. f. Physik **61**, 199, (1930).

Slater[5] has shown how to write the wave function of a many electron system without the use of the group theory. Since the normal states here considered are states of highest multiplicity, the complete ψ may be written

$$\psi = \frac{1}{n!^{1/2}} \sum_P (-1)^{\sigma_P} P u(1/x_1) u(1/x_2) u(s/x_3) \cdots$$
$$\delta(-\tfrac{1}{2}/m_{s_1}) \delta(\tfrac{1}{2}/m_{s_2}) \delta(-\tfrac{1}{2}/m_{s_3}) \cdots$$

n is the number of electrons; P is an operator which permutes the electron numbers; σ_p is the order of the permutation P; $u(r/x_i)$ is a space coordinate function of the i^{th} electron in the r^{th} quantum state; $\delta(m_s/m_{s_i})$ is the spin function of the i^{th} electron in a state with spin component m_s. The summation is over all permutations.

We shall denote the states (100), (200), (21–1), (210), (211) by 1, s, a, b, c respectively. The normalised u's which have been generalised from their hydrogenic form are

$$\begin{aligned} u(1/x) &= g_1 e^{-\gamma r} \\ u(s/x) &= g_2 r^{n^*-1}(1 - \alpha r^{-1}) e^{-\delta r} \\ u(b/x) &= g_3 \cos \theta r^{n^*-1} e^{-\delta r} \\ \left(\begin{smallmatrix} a \\ c \end{smallmatrix}/x\right) &= g_4 \sin \theta e^{\pm i\phi} r^{n^*-1} e^{-\delta r} \end{aligned}$$

where r is written in units of a_H. In every atom the four parameters n^* α, γ, δ are to be determined by finding that set which makes

$$J = \frac{\sum\limits_{m_{s_i}} \int \psi H \bar{\psi} d\tau}{\sum\limits_{m_{s_i}} \int \psi \bar{\psi} d\tau} \tag{1}$$

a minimum. H is the Hamiltonian operator without magnetic interactions.

It is found that γ changes little from its value

$$\gamma = (N - 5/16)$$

in helium-like ions[6] (N equals atomic number). In Ne, where interpenetration is the largest, the change is from 9.69 to 9.64. This variation in γ does not affect the minimal value of δ in the significant figures used. It is of interest to note that the resonance of the two 2s electrons counterbalances their interpenetration to give a net negative shielding of the K shell.

The minimal values of the remaining parameters are in Table I.

The small effect of α upon the charge distribution is shown in Fig. 1 for Be. Here the quantity

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[5] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

[6] J. Frenkel, Einfuhrung in die Wellenmechanik, p. 291, Berlin, J. Springer, 1929.

$$D(x_1) = r_1^2 \sum_{m_{s_1}} \int \psi\bar{\psi} dx_2 dx_3 dx_4 \sin\theta_1 d\theta_1 d\phi_1$$

in Be is plotted with $\alpha=0$, and its value for $\alpha=0.15$ is indicated by crosses.

TABLE I.

	Li[x]	*Be*	*B*	*C*	*N*	*O*	*F*	*Ne*
$n^*(\pm.04)$	2.0	2.0	—	—	—	—	—	—
$\alpha(\pm.02)$	.18†	.15	.10	.07	.05	—	—	—
$\delta(\pm.01)$	.63	.96	1.26	1.59	1.92	2.24	2.56	2.88

[x] Taken from Guillemin and Zener, reference 4.

† ±0.01

n^* has been varied only in Li and Be. Since in both atoms it has its hydrogenic value, it is to be expected to retain this value in the remaining atoms.

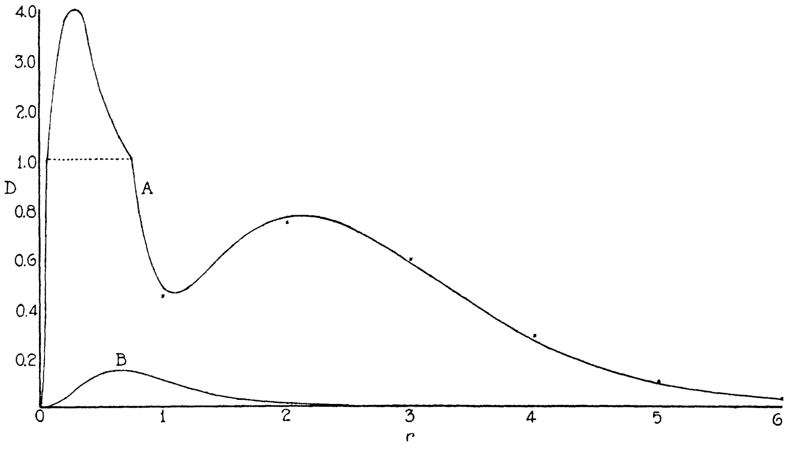

Fig 1.

A is electron density $\times r^2$ with $\alpha=0$, crosses indicate values when $\alpha=0.15$.
B is negative of resonance charge density $\times r.^2$

In the elements Be to Ne δ is $0.05-0.06$ less than the "mean effective charge" defined by

$$\bar{z} = n^*(\Sigma\epsilon_i/n)^{1/2}$$

in which $n^*=2$, n is the number of electrons in the L shell, and the ϵ_i are the successive ionization potentials of the L shell expressed in E_H units. It is of interest to have a table of $\bar{z}$ for all the ions, as this relation will probably hold for the stripped atoms as well as for the neutral atoms. These are given in Table II. The $\bar{z}$'s of F and Ne are extrapolated, as well as of the negative ions.

When more than one electron is in the L shell, $\bar{z}$ is seen to increase in steps of unity as the nuclear charge is increased. The addition of each electron after the first $2p$ electron reduces $\bar{z}$ by 0.35.

TABLE II. $\bar{z}$ *of atoms and ions in first row. Numbers in parenthesis are ionization potentials.***

No. of electrons in L shell	1	2	3	4	5	6	7	8
Li	1.260 (.3970)	1.02						
Be	2.316 (1.341)	2.02 (.702)						
B	3.342 (2.793)	3.02 (1.79)	2.63 (.612)	2.28				
C	4.358 (4.747)	4.02 (3.36)	3.63 (1.795)	3.28 (.829)	2.93			
N	5.366 (7.198)	5.02 (5.40)*	4.63 (3.49)	4.28 (2.18)	3.93 (1.97)	3.58		
O	6.372 (10.15)	6.02 (7.97)*	5.63 (5.69)	5.28 (4.05)	4.93 (2.59)	4.58 (1.001)	4.23	
F	7.376	7.02	6.63	6.28	5.93	5.58	5.23	4.88
Ne	8.376	8.02	7.63	7.28	6.93	6.58	6.23	5.88

* Exrapolated potetntials
** R. A. Millikan and I. S. Bowen, Proc. Nat. Acad. **13,** 531, (1927)

INTEGRATION OF J

Upon the introduction of

$$H = \sum h_i(x_i) + \sum 2/r_{ij}$$
$$h_i = -\Delta_i + 2N/r_i \tag{2}$$

into (1) we see that J can be reduced to a function of the integrals

$$g = \int u(1/x)u(s/x)dx$$
$$h_n{}^m = \int u(m/x)\,hu(n/x)dx \tag{3}$$
$$K_{nq}{}^{mp} = \int u(m/x_1)u(n/x_1)\frac{2}{r_{12}}u(p/x_2)u(q/x_2).$$

To facilitate this reduction we define

$$U(P) = PU(1) = Pu(1/x_1)u(1/x_2)u(s/x_3)\cdots$$
$$\Delta(P) = P\Delta(1) = P\delta(-\tfrac{1}{2}/m_{s_1})\delta(\tfrac{1}{2}/m_{s_2})\delta(-\tfrac{1}{2}/m_{s_3})\cdots$$
$$D(P', P'') = \sum_{m_{s_i}}\Delta(P')\Delta(P'').$$

The numerator of (1) becomes

$$\frac{1}{n!}\sum_{m_{s_i}}\int\left\{\sum_{P'}(-1)^{\sigma_{P'}}P'U(1)\Delta(1)\right\}\cdot H\cdot\left\{\sum_{P''}(-1)^{\sigma_{P''}}P''U(1)\Delta(1)\right\}d\tau$$

$$=\frac{1}{n!}\sum_{P'}P'\sum_{m_{s_i}}\int U(1)\Delta(1)H\sum_{P}(-1)^{\sigma_P}PU(1)\Delta(1)d\tau$$

where $P'\cdot P=P''$, and hence $(-1)^{\sigma_{P'}+\sigma_{P''}}=(-1)^{\sigma_P}$.

Since the integrals and summation are independent of P', and since there are in all $n!$ permutations, the numerator reduces to

$$\int U(1)H\sum_{P}(-1)^{\sigma_P}D(1,\,P)PU(1)d\tau. \tag{4}$$

Similarly the denominator becomes

$$\int U(1)\sum_{P}(-1)^{\sigma_P}D(1,\,P)PU(1)d\tau.$$

Observing that $D(1,\,P)$ vanishes whenever two electrons with opposite spin are permuted, and that $u(1/x)$ is orthogonal to $u(a/x)$, $u(b/x)$ and $u(c/x)$, the denominators for Be and the succeeding atoms reduce to

$$\begin{aligned}&\int U(1)[1-(13)]]1-(24)]U(1)d\tau\\&=\left(\int u(1/x_1)u(s/x_3)[1-(13)]u(1/x_1)u(s/x_3)dx_1dx_3\right)^2\\&=(1-g^2)^2.\end{aligned}\tag{5}$$

Here the operator interchanging electrons i and j has been denoted by (ij).

Putting (2) into (4) and using (5) gives the J's for the various atoms in terms of the integrals (3).

$$\begin{aligned}
J_{Be}&=2(h_1{}^1+h_s{}^s-2gh_s{}^1)/(1-g^2)+[K_{11}^{11}+K_{ss}^{ss}+2(2-g^2)K_{1s}^{1s}\\
&\quad+(-2+6g^2)K_{ss}^{11}-4g(K_{1s}^{11}+K_{ss}^{1s})]/(1-g^2)^2\\
J_B&=J_{Be}+h_a{}^a+[2K_{1a}^{1a}+2K_{sa}^{sa}-K_{aa}^{11}-K_{aa}^{ss}+2gK_{aa}^{1s}-4gK_{sa}^{1a}]/(1-g^2)\\
J_c{}^3P&=2J_B-J_{Be}+K_{ab}^{ab}-K_{bb}^{aa}\\
J_N{}^4S&=3J_B-2J_{Be}+2K_{ab}^{ab}-2K_{bb}^{aa}+K_{aa}^{aa}-K_{cc}^{aa}\\
J_0{}^3P&=4J_B-3J_{Be}+3K_{ab}^{ab}-2K_{bb}^{aa}+3K_{aa}^{aa}-K_{cc}^{aa}\\
J_F{}^2P&=5J_B-4J_{Be}+4K_{ab}^{ab}-2K_{bb}^{aa}+6K_{aa}^{aa}-2K_{cc}^{aa}\\
J_{Ne}{}^1S&=6J_B-5J_{Be}+8K_{ab}^{ab}-4K_{bb}^{aa}+6K_{aa}^{aa}-2K_{cc}^{aa}+K_{bb}^{bb}
\end{aligned}$$

These expressions are the same as those given by Peierls[7] except that he has assumed $g=0$ and the equivalence of such integrals as K_{ab}^{ab} and K_{aa}^{aa}

COMPARISON OF ENERGY VALUES

A comparison of the observed energy required to strip the L shell in Be, B, C with the calculated energy of the L shell gives a measure of the approp-

[7] R. Peierls. Zeits. f. Physik **55**, 738 (1929).

riateness of our functions in representing the actual eigenfunctions. This is given in Table III.

TABLE III. *Energy of L shell in volts.*

	Li*	Be	B	C
obs.	5.37	27.64	70.3	145.2
calc.	5.32	25.86	68.1	142.7
error	.05	1.8	2.2	2.5

* Taken from Guillemin and Zener, reference 4.

The calculated energy of the L shell is to be defined as the minimum of J minus the calculated energy of the unperturbed K shell[8]

$$E_K = -2(N-5/16)^2. \tag{6}$$

The calculated energies of the remaining L shells are 258.3, 417.8, 633.5, 919.0 volts for N, O, F, Ne, respectively. A comparison with extrapolated values of the empirical energies gives decidedly worse agreement.

It was found that in a series of ions, such as Be, B^+, C^{++}, the discrepancy remains nearly constant between the empirical energies and those calculated from simple analytic functions. The helium series is of particular interest, where the energy[6] is given by the function

$$\psi = g_h e^{-(N-5/16)(r_1+r_2)}.$$

TABLE IV. *Energy of helium-like ions (volts.)*

	He	Li	Be
obs	78.59	197.05[9]	369.58[9]
Calc.	77.05	195.44	367.94
Error	1.54	1.61	1.64

The multiplet separations have been calculated by the method given by Slater.[5] They are from 1.5 to 2 times too large.

SUMMARY

Approximate solutions for the normal states of the elements in the first row have been calculated. The parameters in these solutions were either found to have nearly fixed values ($n^*=2$, $\gamma=N-5/16$, $\alpha\simeq 0$), or values nearly equal to empirical quantities ($\delta=\bar{z}$). It is to be expected that these parameters will behave similarly in the ions of these atoms. By means of a table which is given for the $\bar{z}$ of the various ions, one may thus write an approximate solution for all the ions, positive and negative, of the atoms in the first row. α will, however, become of increasing importance as the positive charge of the ions increases.

The writer wishes to express his gratitude to Professors Slater and Hartree for illuminating discussions. He also wishes to thank Harvard University for a Sheldon Fellowship which has enabled him to complete this work.

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[8] J. Frenkel, reference 6.

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