WAVE FUNCTIONS FOR SIMPLE ATOMS

Thesis

by

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ABSTRACT

This thesis is a review of the methods which have been used to apply the Schrödinger equation to the problem of atomic structure, an important problem to chemists because it precedes any similar treatment of molecules and valence. Original work includes computations on helium, lithium, and beryllium, together with isoelectronic ions. The Thomas-Fermi statistical atom, the Hartree method of the self-consistent field, Pauling's and Slater's sets of screening constants, and the variation principle are discussed and estimates of their applicability made. Hydrogen, helium, lithium, and beryllium are individually treated and tables showing the results of many investigators included. In the case of lithium the new results give an ionization potential in very close agreement with experiment while the new work on beryllium is a slight but not satisfactory improvement over previous results. The Appendix lists tables of integrals used in the computations.

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CONTENTS

The problem discussed in this thesis was suggested by Professor Linus Pauling, to whom I am also very greatly indebted for advice and guidance during the course of the work.

I - INTRODUCTION

Schrödinger's equation has established itself as a very close approximation to the truth, at least for a wide range of phenomena, including a very large portion of the field of chemistry. However, the practical problem of using it to compute the properties of matter and to explain observed phenomena is still beset with great mathematical difficulties in most cases.

The solution of this equation for simple, isolated atoms is a problem of considerable importance which has never been solved in a really satisfactory manner. Schrödinger[1] himself published the solution for the hydrogen atom, but to advance further to many-electron atoms involves serious practical mathematical difficulties, which, however, can be partially overcome. The attempts which have been made to do this, including a number of original investigations, form the subject of this thesis.

These investigations were carried out for the purpose of obtaining more accurate wave functions for atoms and ions in their normal states than those previously available. These wave functions have a number of uses. They determine many of the physical properties of the atom in question, being necessary for the calculation of atomic radii, diamagnetic susceptibilities, Van der Waals forces, etc. The most important application from a chemical standpoint is the necessity for reasonably accurate atomic wave functions for use in studying the laws of molecule formation. Even in formal applications of quantum mechanics to molecular problems where numerical computations are not

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[1] E. Schrödinger, Ann. der Phys., 79, 361 (1926).

made, it is frequently necessary to justify such assumptions as the use of single-electron wave functions, and that cannot be done unless the atomic problem is attempted. Questions both of molecular stability and of reaction rates are attracting much attention at present, and of course the whole basis for the ideas of valence is quantum-mechanical.

Electron densities are also obtained from atomic wave functions and these are important in several connections. For one thing they give as nearly physical a picture of the atom as is possible with modern theories. Furthermore, they are necessary in the calculation of F-values for use in the experimental study of crystals and gases with x-rays and electron beams.

The other primary quantity which results from studies such as these is the energy of the atom. This is usually, but not always, known experimentally with considerable accuracy from spectroscopy, and so provides an observational check on the validity of the approximations used. In some cases spectroscopists have not yet been able to obtain complete energy data and for these atoms theoretical calculations provide hitherto unavailable information, which is frequently of great interest. An important case of this kind is the lowest level of carbon, which is as yet uncertain, even as to its term symbol or character. Other examples include highly stripped atoms, which are usually difficult to observe experimentally.

II - UNITS

It is very convenient to introduce a new set of units, called "atomic units", which are tabulated below:

Unit of length, $a_o = h^2/(4\pi^2 m e^2)$, in the Bohr theory the radius of the first orbit in hydrogen, $a_o = .528$ Å units.

Unit of mass, m, the mass of the electron.

Unit of charge, e, the magnitude of the charge on the electron.

Unit of time, $1/(4\pi c R) = h^3/(8\pi^3 m e^4)$

Unit of energy, $e^2/a_0 = 2Rhc$, twice the ionization energy of the hydrogen atom with fixed nucleus.

Unit of action, $h/2\pi$.

Unit of angular momentum, $h/2\pi$.

These units form a consistent set so that ordinary equations of physics are still valid when expressed in terms of them. They will be used throughout unless otherwise noted. Since, however, experimental data are generally published in more usual units, the following conversion table, based on Birge's compilation,[1] is included:

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[1] R.T.Birge, Phys.Rev., Supplement, 1, 1 (1929).

TABLE I - ENERGY UNITS

Multiply	by	to Obtain
atomic units	27.06	electron-volts
"	6.239×10^{5}	15° calories per mole
"	2.194×10^{5}	wave-numbers
"	6.575×10^{15}	frequency units
"	4.3056×10^{-11}	ergs
electron-volts	3.695×10^{-2}	atomic units
"	2.3055×10^{4}	15° calories per mole
"	8.106×10^{3}	wave numbers
"	$2.430_{3} \times 10^{14}$	frequency units
"	1.5911×10^{-12}	ergs
15° calories per mole	1.6028×10^{-6}	atomic units
"	4.3375×10^{-5}	electron-volts
"	3.516×10^{-1}	wave-numbers
"	1.054×10^{10}	frequency units
"	$6.90_{1} \times 10^{-17}$	ergs
wave-numbers	4.558×10^{-6}	atomic units
"	$1.233_{6} \times 10^{-4}$	electron-volts
"	2.84_{4}	15° calories per mole
"	$2.9979_{6} \times 10^{10}$	frequency units
"	1.9628×10^{-16}	ergs
frequency-units	1.5209×10^{-16}	atomic units
"	$4.11_{47} \times 10^{-15}$	electron-volts
"	$9.48_{6} \times 10^{-11}$	15° calories per mole
"	3.33560×10^{-11}	wave-numbers
"	$6.54_{7} \times 10^{-27}$	ergs

TABLE I - continued

Multiply	by	to obtain
ergs	2.322×10^{10}	atomic units
"	$6.28_5 \times 10^{11}$	electron-volts
"	$1.44_9 \times 10^{16}$	15° calories per mole
"	$5.09_5 \times 10^{15}$	wave-numbers
"	$1.52_7 \times 10^{26}$	frequency units

III - THE SCHROEDINGER EQUATION

The Schrödinger wave-equation may be written

$$H \psi_n = W_n \psi_n \qquad (1)$$

where H is an operator formed by replacing each momentum p_i in the classical Hamiltonian $H(p_i, q_i)$ by $\frac{h}{2\pi i} \frac{\partial}{\partial q_i}$. If it is desired to use generalized coordinates, the transformation from Cartesian to the new coordinates is made after the substitution indicated above.

ψ_n has the physical significance of a probability amplitude; that is, the square of its absolute value gives the probability of finding the system within any differential volume element of configuration space. Boundary conditions are imposed upon ψ_n, namely that it must be single-valued, vanish at infinity, and be finite and twice differentiable over the whole of coordinate space, except that it may become infinite at a few points if $\int \cdots \int |\psi_n|^2 d\tau$ converges to a finite value even when these points are included.[1]

For the hydrogen atom, the Hamiltonian is:

$$H(p,q) = \frac{1}{2m}\left(p_{x_1}^2 + p_{y_1}^2 + p_{z_1}^2\right) + \frac{1}{2M}\left(p_{x_2}^2 + p_{y_2}^2 + p_{z_2}^2\right) - \frac{Ze^2}{r} \qquad (2)$$

where m is the mass of the electron

M is the mass of the nucleus

x_1 y_1 z_1 are the coordinates of the electron

x_2 y_2 Z_2 are the coordinates of the nucleus

Z is the atomic number.

If the substitution for p is made as stated above:

$$H = -\frac{h^2}{8\pi^2 m} \nabla_1^2 - \frac{h^2}{8\pi^2 M} \nabla_2^2 - \frac{Ze^2}{r} \qquad (3)$$

is obtained, where:

$$\nabla_1^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \qquad (4)$$

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[1] J.H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities" Oxford 1932. p. 122.

This operator gives an equation (1) which is completely soluble, even when the motion of the nucleus with respect to the center of gravity of the molecule is considered, but since in the work on heavier atoms this nuclear motion causes effects which are smaller than the other errors, it will not be considered further except to note that it is responsible for an isotope effect in certain spectra.

With the approximation of fixed nucleus, the wave-equation for hydrogen becomes

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2}\left(W + \frac{Ze^2}{r} \right) \psi = 0 \tag{5}$$

This is greatly simplified by the introduction of the values of the constants in atomic units:

$$\frac{1}{2} \nabla^2 \psi + \left(W + \frac{Z}{r} \right) \psi = 0 \tag{6}$$

Schrödinger[1] obtained the solutions for (5) and these will be considered in more detail in section IV, since they form the basis of the treatment of heavier atoms.

With the same assumption of fixed nucleus, the wave-equation in atomic units for an atom with n electrons and atomic number Z is seen to be:

$$\frac{1}{2} \sum_{i=1}^{n} \nabla_i^2 \psi + (W - V) \psi = 0 \tag{7}$$

where

$$V = \frac{1}{2} \sum_{i,j=1}^{n}{}' \frac{1}{r_{ij}} - Z \sum_{i=1}^{n} \frac{1}{r_i} . \tag{8}$$

with

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} . \tag{9}$$

r_{ij} = distance between electrons i + j.

r_i = distance between electron i and nucleus.

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[1] E. Schrodinger, Ann. der Phys., 79, 361 (1926).
Condon and Morse, "Quantum Mechanics" New York 1929. p. 58.

In all the considerations of this work electromagnetic interaction energies such as that of the electron spin with the field due to its motion have been neglected. This is usually legitimate in view of the small magnitude of these energies. However, it is essential that the spin be taken into account by way of the symmetry properties of the wave functions, in connection with the Pauli exclusion principle, and this question will be treated in section V.

IV - THE HYDROGEN ATOM SOLUTIONS

Equation III-6 is separable in spherical polar coordinates, for which:[1]

$$\nabla^2 = \frac{1}{r^2 \sin\vartheta}\left\{ \sin\vartheta \cdot \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{\partial}{\partial\vartheta}\left(\sin\vartheta \frac{\partial}{\partial\vartheta}\right) + \frac{1}{\sin\vartheta}\frac{\partial^2}{\partial\varphi^2}\right\} \quad (1)$$

The solutions which satisfy the boundary conditions are

$$\psi_{nlm} = N e^{im\varphi} \cdot \sin^{|m|}\vartheta \cdot P_l^{|m|}(\cos\vartheta) \cdot \left(\frac{2rZ}{n}\right)^{l} \cdot e^{-\frac{Zr}{n}} \cdot L_{n+l}^{2l+1}\left(\frac{2rZ}{n}\right) \quad (2)$$

where

$$N = \sqrt{\frac{(2l+1)(l-|m|)!\,(n-l-1)!\,Z^3}{\pi\, n^4\, (l+|m|)!\,[(n+l)!]^3}} \quad . \quad (3)$$

is the normalizing factor.

$P_l^{|m|}(\cos\vartheta)$ is an associated Legendre polynomial

$L_{n+l}^{2l+1}\left(\frac{2rZ}{n}\right)$ is a polynomial (See Condon and Morse, l.c., p. 63)

For the first few sets of quantum numbers n, l, m, these reduce to:

$$\psi_{100} = \sqrt{\frac{Z^3}{\pi}}\, e^{-Zr} \quad (4)$$

$$\psi_{200} = \frac{1}{2}\sqrt{\frac{Z^3}{2\pi}}\, e^{-\frac{Z}{2}r}\left(\frac{Z}{2}r - 1\right) \quad (5)$$

$$\psi_{210} = \frac{Z}{4}\sqrt{\frac{Z^3}{2\pi}}\, \cos\vartheta \cdot r e^{-\frac{Z}{2}r} \quad . \quad (6)$$

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[1] for ∇^2 in different coordinates, see. E.P.Adams, Smithsonian Mathematical Formulae. Washington 1922. p. 100.

$$\psi_{211} = \frac{Z}{8}\sqrt{\frac{Z^3}{\pi}}\,\sin\vartheta\cdot e^{i\varphi}\cdot r\,e^{-\frac{Z}{2}r} \qquad (7)$$

$$\psi_{21\bar{1}} = \frac{Z}{8}\sqrt{\frac{Z^3}{\pi}}\,\sin\vartheta\cdot e^{-i\varphi}\cdot r\,e^{-\frac{Z}{2}r} \qquad (8)$$

The quantum numbers n, ℓ, m can take on the values

$$\begin{aligned} n &= 1, 2, 3, \ldots \\ \ell &= 0, 1, 2, \ldots\ n-1 \\ m &= -\ell, -\ell+1, \cdots\ 0, 1, 2, \cdots \ell. \end{aligned} \qquad (9)$$

The quantum number m measures the component of angular momentum in the direction of the pole. $\ell(\ell+1)$ is the square of the total orbital angular momentum of the atom in atomic units. In the case of hydrogen and other one-electron atoms, to the approximation we have considered the energy depends upon n only. If the electron moved in a non-coulomb field as in more complicated atoms, n and ℓ both would affect the energy.

The energy levels for hydrogenic atoms, the characteristic values of equation III-6, are:

$$W_n = -\frac{Z^2}{2n^2} \quad \text{atomic units (a.u.)} \qquad (10)$$

which is in agreement with experiment.

The electron density is:

$$\rho = |\psi_n|^2 \qquad (11)$$

Frequently this is integrated over all angles to obtain a new quantity, sometimes called the electron distribution:

$$D = \int_0^{2\pi}\int_0^{\pi} |\psi_n|^2 r^2 \sin\vartheta\, d\vartheta\, d\varphi \qquad (12)$$

If ψ_n is independent of φ, ϑ:

$$D = 4\pi\rho r^2. \qquad (13)$$

V - SYMMETRY CONSIDERATIONS

The Pauli exclusion principle states that no two electrons in the same atom can have the same set of quantum numbers, if the latter includes the spin quantum number. The quantum-mechanical analogue of this is the requirement that every wave function for a group of electrons be completely anti-symmetric in the electrons. This means that interchanging the coordinates of any two electrons merely alters the sign of the wave function.

If the interaction of the electrons is completely disregarded, equation III-7 for a many-electron atom will separate into equations for each electron. Therefore a solution for the atom is:

$$\psi = A_1 B_2 C_3 \ldots G_n \qquad (1)$$

where A, B, C, etc. are the solutions of the separated single-electron equations and the subscripts refer to the number of the electron. But an equally good solution would be:

$$\psi = P A_1 B_2 C_3 \ldots G_n \qquad (2)$$

where P is a permutation operating on the subscripts (or on the letters).

Perturbation theory leads to the result that the best solution will be a linear combination of these $n!$ permuted products. It also gives the possible sets of coefficients, which will be such that:

$$\psi = \frac{1}{\sqrt{n!}} \sum_{P} \pm P A_1 B_2 C_3 \cdots G_n \qquad (3)$$

There will be $n!$ such combinations, depending on the distribution of the plus and minus signs. To introduce the electron spin into the solution, Slater[1] suggested that each single-electron function A, B, C, etc. could contain a spin factor or:

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

$$A = a\ \delta(m_s, s) \tag{4}$$

where a is the orbital function and

$$\delta(m_s, s) = \begin{cases} 0 & \text{if} \quad s \neq m_s \\ 1 & \text{if} \quad s = m_s \end{cases} \tag{5}$$

with m_s the spin quantum number.

Hereafter A, B, etc. will either be as above the complete spin and orbit function with unspecified spin, or in contrast to $\overline{A}$, $\overline{B}$, etc. which will refer to orbit plus negative spin, A, B, C will mean orbit with positive spin.

To obtain a function ψ which is anti-symmetric, it is necessary to use one special linear combination (3), namely the one in which the plus sign is used with permutations made up of an even number of interchanges and the negative sign for odd permutations. Then the interchange of any pair of subscripts will merely change the sign of ψ.

Equation (3), with this rule of signs, may also be written as a determinant:

$$\psi = \frac{1}{\sqrt{n!}} \begin{vmatrix} A_1 & B_1 & C_1 & \cdots & G_1 \\ A_2 & B_2 & C_2 & \cdots & G_2 \\ \vdots & \vdots & \vdots & & \vdots \\ A_n & B_n & C_n & \cdots & G_n \end{vmatrix} \tag{6}$$

If more general types of wave functions are used, which may include those with interaction terms between the electrons, the same device insures that ψ will be completely anti-symmetric. For example

$$\psi = \sum_P \pm P A_1 B_2 C_3 \cdots G_n\, f(1,2,3) \tag{7}$$

or

$$\psi = \sum_P \pm P A_{1,2}\, B_{3,4} \cdots \tag{8}$$

where here P permutes the coordinates of the electrons and in (3) operates on f(1,2,3) as well as on the other factors.

VI - THE THOMAS-FERMI STATISTICAL ATOM

L.H.Thomas[1] was the first to apply statistical methods to the calculation of electron distribution and atomic fields in heavy atoms. He treated the electron cloud as a degenerate gas acted upon by a field due to the nucleus and the electrons themselves, and obtained two relations between the electron density and the potential, the first being Poisson's equation and the second the analogue of Boltzmann's distribution law, modified by the degeneracy.

The fundamental assumption of this treatment is that the electrons are uniformly distributed in the six-dimensional phase space with a density of two to each element of volume h^3. The Fermi-Dirac[2] statistics is based on the principle that no more than two electrons can occupy each volume element of this size in phase space and in this application it is further assumed that the atom is in the lowest possible energy state so that all the lowest lying cells will be completely filled giving the uniform distribution postulated above.

The energy of an electron in the field about the nucleus is:

$$E = \frac{1}{2m} p^2 - e V \tag{1}$$

where e is the magnitude of the electronic charge

m is the electronic mass

p is the moment of the electron

V is the potential at any point.

The zero of energy is such that an electron at rest at infinity has zero energy; therefore E is negative, giving the relation:

$$p < (2meV)^{1/2} \tag{2}$$

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[1] L.H.Thomas, Proc.Camb.Phil.Soc., 23, 542 (1927)

[2] E.Fermi, Zeit.f.Physik, 36, 902 (1926);
P.A.Dirac, Proc.Roy.Soc., A 112, 661 (1926).

To find the density in ordinary (coordinate) space it is necessary to integrate over momentum space, with limits given by (2)

$$\therefore \quad \rho = \frac{2}{h^3} \iiint dP_x \, dP_y \, dP_z \tag{3}$$

Making a change to polar coordinates:

$$\begin{aligned} P_x &= P \sin \vartheta \cos \varphi \\ P_y &= P \sin \vartheta \sin \varphi \\ P_z &= P \cos \vartheta . \end{aligned} \tag{4}$$

where P is therefore the magnitude of the total momentum.

$$\therefore \quad \rho = \frac{2}{h^3} \int_0^{2\pi} \int_0^{\pi} \int_0^{\sqrt{2meV}} P^2 \sin \vartheta \, dP \, d\vartheta \, d\varphi \tag{5}$$

$$= \frac{8\pi}{3h^3} (2meV)^{3/2} . \tag{6}$$

This is one relation between ρ and V ; the other is Poisson's equation:

$$\nabla^2 V = 4\pi e \rho . \tag{7}$$

Combining the two gives: (V is spherically symmetric)

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dV}{dr} \right) = \frac{32\pi^2 e}{3h^3} (2meV)^{3/2} . \tag{8}$$

The boundary conditions are

$$\lim_{r \to 0} rV \to Ze$$

and

$$\int \rho \, d\tau = Z \tag{9}$$

The first condition asserts that the field for small r is due to the nucleus alone; i.e. that the electrons are all outside of this region, while the second condition specifies that the atom is neutral.

Fermi[1] has obtained a numerical solution to this problem, first making the substitutions:

$$\chi = r/\mu \quad ; \quad \Psi = V/\gamma \tag{10}$$

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[1] E. Fermi, Zeit. f. Physik, 49, 550 (1928).

where $$\mu = \frac{3^{2/3}\hbar^2}{2^{13/3}\pi^{4/3} m e^2 Z^{1/3}} = \frac{3^{2/3}\pi^{2/3} a_0}{2^{7/3} Z^{1/3}}$$

$$\cong 0.8853\, a_0/Z^{1/3} \cong 0.467/Z^{1/3}\ A^{\circ}U. \tag{11}$$

and $$y = \frac{2^{13/3}\pi^{4/3} m e^3 Z^{4/3}}{3^{2/3}\hbar^2} = \frac{2^{7/3}}{3^{2/3}\pi^{2/3}}\frac{e}{a_0}Z^{4/3}$$

$$\cong 1.130\,\frac{e}{a_0}Z^{4/3}. \tag{12}$$

which give: $$\frac{d^2\Psi}{dx^2} + \frac{2}{x}\frac{d\Psi}{dx} = \Psi^{3/2} \tag{13}$$

with

$$\lim_{x\to 0} x\Psi = 1 \tag{14}$$

$$\int_0^{\infty}\Psi^{3/2}x^2\,dx = 1. \tag{15}$$

To obtain (15), (6) is first used with the second part of (9) before making the substitutions (10).

A further simplification follows from

$$\varphi = x\Psi \tag{16}$$

which gives: $$\frac{d^2\varphi}{dx^2} = \varphi^{3/2}/\sqrt{x}. \tag{17}$$

and $$\varphi(0) = 1 \ ; \quad \int_0^{\infty}\varphi^{3/2}\sqrt{x}\,dx = 1 \tag{18}$$

Fermi gives the following table, which is the result of a numerical integration of equation (17).

TABLE II

x	(x)	x	(x)	x	(x)
0	1.000	1.5	.315	10	.024
.1	.882	2.0	.244	11	.020
.2	.793	2.5	.194	12	.017
.3	.721	3.0	.157	13	.014
.4	.660	3.5	.130	14	.012
.5	.607	4	.108	15	.011
.6	.562	5	.079	16	.009
.7	.521	6	.059	17	.008
.8	.485	7	.046	18	.007
.9	.453	8	.037	19	.006
1.0	.425	9	.029	20	.005

Then

$$V = \frac{Ze}{r}\,\varphi\left(\frac{r}{\mu}\right) \tag{19}$$

and

$$\rho = \frac{2^{9/2}\pi m^{3/2} Z^{3/2} e^{3}}{3h^{3}}\,\frac{1}{r^{3/2}}\,\varphi^{3/2}\left(\frac{r}{\mu}\right)$$

$$= \frac{2^{3/2}\;Z^{3/2}}{3\pi^{2}\;a_0^{3/2}}\,\frac{1}{r^{3/2}}\,\varphi^{3/2}\left(\frac{r}{\mu}\right) \tag{20}$$

$$\cong 0.1702\;\; Z^{3/2}/a_0^{3/2}\cdot 1/r^{3/2}\cdot\varphi^{3/2}\left(\frac{r}{\mu}\right). \tag{21}$$

The effective nuclear charge, $Z_{eff.}$, defined by:

$$Z_{eff.} = -\frac{r^{2}}{e}\frac{dV}{dr} \tag{22}$$

is given by

$$Z_{eff.} = Z\left[1-\int_0^x x^{\frac{1}{2}}\varphi^{3/2}(x)\cdot dx\right] \tag{23}$$

where x is related to r by (10) and the integral can be obtained by numerical integration using the values of φ in Table II. However, Thomas[1] has given such a table for Cs (Z = 55), together with relations for obtaining the corresponding quantities for any atom.

For any neutral atom:

$$R = R_0\left(\frac{55}{Z}\right)^{1/3};\quad Z_{eff.} = Z^{0}_{eff.}\left(\frac{Z}{55}\right);\quad \psi = \psi_0\left(\frac{Z}{55}\right)^{4/3} \tag{24}$$

where R is r measured in atomic units

ψ is V measured in atomic units.

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[1] Ref. 1 p. 12.

TABLE III

R_0	Z_0	V_0	R_0	Z_0	V_0
.001517	55.0	35960	.04800	52.5	906.8
.001910	55.0	28500	.06040	51.5	683.8
.002404	55.0	22580	.07603	50.3	510.4
.003027	55.0	17870	.09572	48.7	376.4
.003811	55.0	14140	.1205	47.7	273.9
.004800	55.0	11170	.1517	44.2	196.1
.006040	55.0	8809	.1910	41.3	138.0
.007603	54.9	6936	.2404	38.0	95.15
.009572	54.9	5450	.3027	34.2	64.18
.01205	54.8	4273	.3811	30.1	42.26
.01517	54.6	3340	.4800	25.8	27.10
.01910	54.4	2601	.6040	21.6	16.90
.02404	54.0	2018	.7603	17.5	10.23
.03027	53.8	1556	.9572	13.7	6.008
.03811	53.2	1198	1.205	10.4	3.412
			1.517	7.6	1.887

Numerous assumptions are involved in this treatment and it is not to be expected that the results will be very exact. The use of a statistical method necessitates a large number of particles, so that the results should be accurate only for heavy atoms. Furthermore, except for the choice of statistics, the method is essentially classical, so that the presence of nodes is not observed. Dirac[1] has discussed the whole question of the validity of the Thomas-Fermi model, reaching the decision that it is probably a good approximation for the interior of heavy atoms but inaccurate in the outer part. The separate maxima of the different electron shells within the atom do not appear in this treatment, a smooth curve representing an average density resulting instead. The transition from one atom to the next is also perfectly regular without any of the periodic features shown by real atoms.

Milne[2] has used this method to calculate the energy necessary to remove all the electrons from a heavy atom, i.e. the sum of the ionization potentials for the atom. He calculates the electrostatic energy of the charge density ρ in the field V, both obtained from Thomas' procedure and uses the virial theorem to obtain the kinetic energy. His result is:

$$E = 17 N^{7/3} \quad \text{volt-electrons} \qquad (25)$$

Baker[3] has attempted to apply this model to positive ions, using certain approximations. Using the same principles as Milne, he computes the quantity E for positive ions and thus by difference obtains successive ionization potentials.

Sommerfeld[4] has obtained an asymptotic solution of equation (17), good for large x.

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[1] P.M.Dirac, Proc.Camb.Phil.Soc., 26, 376 (1930).

[2] E.A.Milne, Ibid., 23, 794 (1927).

[3] E.B.Baker, Phys.Rev., 36, 630 (1930).

[4] A.Sommerfeld, Rend.R.Accad.Lincei, 15, 788 (1932).

VII - THE VARIATION METHOD

Schrödinger[1] first formulated the new mechanics as a variational principle and for many purposes, particularly where approximate solutions are being sought, this is the most convenient form of the theory to use.

If

$$H = -\frac{1}{2}\nabla^2 + V \tag{1}$$

then the variational problem:

$$\delta \int \psi^* H \psi \, d\tau = 0 \quad , \quad \int \psi^* \psi \, d\tau = 1 \tag{2}$$

leads to the equation:

$$\frac{1}{2}\nabla^2 \psi + (W - V)\psi = 0 \tag{3}$$

by the standard methods of the calculus of variations.[2] Equation (3), the wave equation, is thus the Euler equation for the variation problem (2).

The Ritz[3] method may be used to solve (2), although it is not ordinarily convenient. The function ψ is expanded in a finite number of suitable functions ϕ_n which form part of a complete, orthogonal set:

$$\psi^{(n)} = c_1\phi_1 + c_2\phi_2 + \cdots + c_n\phi_n \tag{4}$$

and the n coefficients $c_1, c_2, \cdots c_n$ are determined by the ordinary methods of maxima and minima problems so that (2) is a minimum. This process is repeated for increasing n so that under the proper conditions

$$\psi^{(1)}, \psi^{(2)}, \psi^{(3)}, \cdots \psi^{(n)} \cdots \tag{5}$$

form a sequence which converges to a limit, the solution of the problem.

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[1] E. Schrödinger, Ann. der Physik, 79, 361 (1926).

[2] Courant-Hilbert, "Methoden der Mathematischen Physik" I. Springer, Berlin, 1924. p. 165
Osgood, "Advanced Calculus" Macmillan, New York. 1928. Chap. XVII.

[3] Courant-Hilbert, loc. cit., p. 157.

Although this method is not very often used, it suggests a modified procedure which is of very great importance. A function ϕ is chosen which depends upon a number of parameters $c_1, c_2, c_3, \cdots c_n$ and this function is substituted for ψ in equation (2). The integral is then minimized with respect to the n parameters, either by the methods of calculus or by actual computation. The resulting values of the parameters, when substituted in ϕ yield a function which is not in general the exact solution of (2), because of the restricted nature of the variation which has been performed, but if a suitable form is chosen for ϕ, a good approximation to ψ may result.

Although it is not easy to estimate the inaccuracy in the function so obtained, something can be said about the energy values.[1] If ϕ were the true solution ψ, then from (3):

$$H \phi = W \phi \qquad (6)$$

and

$$\int \phi^* H \phi \, d\tau = \int \phi^* W \phi \, d\tau = W \qquad (7)$$

If ϕ is not exactly equal to ψ, it may be expanded in a series

$$\phi = \sum_n a_n \psi_n \qquad (8)$$

since it can be shown[2] that the characteristic solutions ψ_n of (3) form a complete orthogonal set. Then

$$E = \int \phi^* H \phi \, d\tau = \sum_{n,m} W_m a_n^* a_m \int \psi_n^* \psi_m \, d\tau = \sum_n W_n |a_n|^2. \qquad (9)$$

In the particular case of the lowest energy state, W_1, the following is true:

$$E - W_1 = \sum_n (W_n - W_1) \, |a_n|^2. \qquad (10)$$

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[1] C. Eckart, Phys. Rev., 36, 878 (1930).

[2] Condon and Morse, loc. cit., p. 40.

Since $W_n \geqslant W_1$, the right-hand side is a positive quantity, therefore $E \geqslant W_1$. This result that the value of the variational integral is an upper bound of the energy of the lowest state, is of great importance. In special cases it may be extended to other than the ground state. If $a_1, a_2, a_3 \cdots a_{n-1}$ are all zero, the theorem applies to W_n. In atomic problems such a case occurs for the lowest state of any specified angular momentum, since

$$a_1 = \int \phi \psi_1^* d\tau = 0 \qquad (11)$$

if ϕ and ψ_1 have different angular momentum quantum numbers. Likewise, the lowest state of any specified multiplicity may be similarly treated.

It is unfortunate that no such definite statement can be made, apparently, concerning the function ϕ itself. The most reasonable criterion for the degree to which ϕ approximates ψ is the smallness of

$$\int [\psi - \phi]^2 A(q)\, d\tau \qquad (12)$$

where $A(q)$ is some weight function of the coordinates and the integration is over the entire coordinate space. What function to choose for A depends upon the purpose for which ϕ is wanted. For some uses it is important that ϕ be a good approximation in certain regions of space and then A should weight those regions. The variational integral (2) corresponds to a special form for A such that the best value for the energy is secured, but it is certain that the function so obtained would not in general be the best, unless the variational problem were completely solved, for the calculation of diamagnetic susceptibilities, say. If (2) be completely solved, then ϕ equals ψ and it is of no consequence which function A is used in (12). The value of the wave-functions obtained by the approximate method described depends upon ϕ being so nearly equal to ψ that (12) is small for any reasonable A.

VIII - METHOD OF THE SELF-CONSISTENT FIELD

Probably the most nearly accurate wave functions and charge distributions for many-electron atoms have been obtained by the method devised by Hartree.[1] He solves numerically the problem of one electron moving in a spherically-symmetric central field created by the nucleus and the other electrons. The solution of such a single-electron wave equation is carried out for each of the electrons in the atom, the central field being assumed in the beginning, and then from these solutions the corresponding charge distribution and field is calculated. The agreement between this field and the one originally assumed forms the criterion for the validity of the wave functions obtained. If the discrepancy is too great, the process is repeated, with the use of a new trial field. In deciding on the field acting on any given electron, it must be remembered that the contribution which that electron makes to the total field of the atom should not be counted in computing the field acting on that electron. Hartree has diagrammed the above steps:

Assumed initial field →
Field corrected for contribution of electron in question →
Solution of wave equation for this electron with above field →
Contribution of electron to charge distribution →
Field for whole atom due to nucleus and total charge density.

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[1] D.R.Hartree, Proc.Camb.Phil.Soc., 24, 89, 111, 426 (1928); 25, 310 (1929).

If either the initial or final fields, or the contribution of any electron to the field, is not spherically symmetric, the approximation is made of averaging it over the surface of a sphere before using it in the above sequence of operations. This is not necessary for s electrons or for closed groups[1] of electrons, because they have spherical symmetry.

In obtaining solutions for each electron, Hartree uses the fact that $r\chi$, where χ is the radial factor of the solution, must vanish at both zero and infinity. Choosing some value of ϵ , the energy parameter, he integrates the wave equation for $r\cdot\chi$ numerically, starting first from zero and then from infinity. For general values of ϵ these two solutions will not meet, but if ϵ is varied, certain values of ϵ - the "characteristic values" - will be found for which the two solutions are identical; i.e. only for discrete values of ϵ will there exist solutions which are zero at both zero and infinity. This laborious process is simplified by numerous practical short-cuts which Hartree describes in detail in his original papers.

The meaning of the characteristic values ϵ was not clear for some time but has been made so by a consideration of the relation between the criterion of the self-consistent field and the variation method.[2] The treatment given here was suggested by Dr. Pauling following the outline given by Slater, and although essentially the same is considerably simpler than that of Fock.

Hartree uses wave functions of the type:

$$\psi = a_1 b_2 c_3 \cdots\cdots g_n \qquad (1),$$

where a_1 , b_2 , etc. are single-electron wave functions for the 1st,

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[1] H. Unsöld, Ann.d.Physik, 85, 355 (1927).

[2] V. Fock, Z.Physik, 61, 126 (1930);
J.C.Slater, Phys.Rev., 35, 210 (1930).

2nd, etc. electrons. His wave function for the whole atom does not therefore have the proper symmetry with regard to interchange of electrons. This neglect of the exchange phenomenon is one of the approximations involved in his treatment. That it is not a necessary approximation will be shown later. However, if the wave function is assumed to be of the form (1), then the variation method (sec. VII) gives a definite criterion for determining a, b, c etc. The condition is:

$$\delta E = \delta \int \psi^* H \psi \, d\tau = \delta \int a_1^* b_2^* c_3^* \cdots g_n^* \, H \, a_1 b_2 c_3 \cdots g_n \, d\tau = 0 \qquad (2)$$

with

$$\int \psi^* \psi \, d\tau = 1 \qquad (3)$$

But

$$H = \sum_i H_i + \frac{1}{2} {\sum_{ij}}' \frac{1}{r_{ij}} \qquad (4)$$

$$H_i = -\frac{1}{2} \nabla_i^2 - Z/r_i \qquad (5)$$

If

$$\int a_1^* a_1 \, d(1) = 1 \quad \text{etc.} \qquad (6)$$

then

$$E = \int a_1^* H_1 a_1 \, d(1) + \int b_2^* H_2 b_2 \, d(2) + \cdots \int g_n^* H_n g_n \, d(n)$$
$$+ \iint a_1^* b_2^* a_1 b_2 \frac{d(1,2)}{r_{12}} + \iint a_1^* c_3^* a_1 c_3 \frac{d(1,3)}{r_{13}} + \cdots (\text{all pairs}). \qquad (7)$$

For minimum E, the variation in E caused by any infinitesimal variation in each of a, b, c etc. must vanish independently, or:

$$\frac{\partial E}{\partial a_1} = \frac{\partial}{\partial a_1} \Big\{ \int a_1^* H_1 a_1 \, d(1) + \iint a_1^* b_2^* a_1 b_2 \frac{d(1,2)}{r_{12}}$$
$$+ \iint a_1^* c_3^* a_1 c_3 \frac{d(1,3)}{r_{13}} + \cdots (\text{all pairs involving } a_1) \Big\} = 0 \qquad (8)$$

If we put
$$\mathcal{H}_1 = H_1 + \int b_2^* b_2 \frac{d(2)}{r_{12}} + \int c_3^* c_3 \frac{d(3)}{r_{13}} + \cdots$$
$$= -\frac{1}{2} \nabla_1^2 - \frac{Z}{r_1} + V_1 \,, \tag{9}$$

where
$$V_1 = \int b_2^* b_2 \frac{d(2)}{r_{12}} + \int c_3^* c_3 \frac{d(3)}{r_{13}} + \cdots \tag{10}$$

is the average potential acting on electron 1 due to the other electrons, then equation (8) is equivalent to:
$$\frac{\partial E}{\partial a_1} = \frac{\partial}{\partial a_1} \int a_1^* \mathcal{H}_1 a_1 \, d(1) = 0 \tag{11}$$
and similar equations hold for b_2, c_3 ... g_n.

Hartree solves, for each electron, an equation
$$\frac{1}{2} \nabla^2 a_1 + \left(\epsilon - V_1 + \frac{Z}{r_1}\right) a_1 = 0 \tag{12}$$
where V_1 is the average potential acting on the electron due to the other electrons and is of course given by (10). To solve (12) the variation principle may be invoked once more, giving
$$\delta \int a_1^* \left(-\frac{1}{2} \nabla^2 + V_1 - \frac{Z}{r_1}\right) a_1 \, d(1) = \delta \int a_1^* \mathcal{H}_1 a_1 \, d(1) = 0 \tag{13}$$

This equation, which results from Hartree's criterion, is the same as (11), which was obtained from an application of the variation principle to the wave equation of the whole atom, so that the two criteria are equivalent.

In this derivation the deviation from spherical symmetry which may occur in V_1 etc. is not averaged out, but is rigorously treated. In the practical application of Hartree's method, averages over a sphere are used, which introduces a further approximation.

As previously mentioned, it is not necessary to neglect interchange. Fock has included this, but the following treatment is simpler. Assume that ψ has the following form:
$$\psi = \frac{1}{\sqrt{n!}} \sum_P \pm P \, A_1 B_2 C_3 \cdots G_n \tag{14}$$

where P represents a permutation on the electrons 1, 2, 3 ... (subscripts). Even permutations have the plus sign. The symbols A_1, B_2 ... represent single-electron wave functions including the spin factor:

$$
\begin{aligned}
E = \int \psi^* H \psi \, d\tau &= \frac{1}{n!} \sum_{P,P'} \pm \int P A_1^* B_2^* \cdots H P' A_1 B_2 \cdots d\tau \\
&= \sum_P \pm \int A_1^* B_2^* \cdots H \; P A_1 B_2 \cdots d\tau \\
&= \sum_P \pm (A_1 | H_1 | P A_1)(B_2 | 1 | P B_2) \cdots + \sum_P \pm (A_1 | 1 | P A_1)(B_2 | H_2 | P B_2) \cdots \\
&\quad + \cdots + \sum_P \pm \left(A_1 B_2 \middle| \frac{1}{r_{12}} \middle| P A_1 \, P B_2\right)(C_3 | 1 | P C_3) \cdots + \text{all pairs.}
\end{aligned}
\tag{15}
$$

where

$$(A_1 | X | P A_1) = \int A_1^* \, X \, P A_1 \, d(1) \quad \text{etc.} \tag{16}$$

$$(A_1 B_2 | X | P A_1 \, P B_2) = \iint A_1^* B_2^* \, X \, P A_1 \, P B_2 \; d(1,2). \tag{17}$$

and PA_1 means the letter which has the subscript 1 after the operation of the permutation P in (14). If A_1, B_2 etc. are kept normal and orthogonal, then:

$$(A_1 | 1 | P A_1) = \begin{cases} 0 & \text{if} \quad P A_1 \neq A_1 \\ 1 & \text{if} \quad P A_1 = A_1 \end{cases} \tag{18}$$

and terms with the factor $\left(A_1 B_2 \middle| \frac{1}{r_{12}} \middle| P A_1 \cdot P B_2\right)$ will vanish unless:

$$P A_1 \, P B_2 = A_1 B_2 \qquad \text{or} \qquad P A_1 \, P B_2 = B_1 A_2 \tag{19}$$

because of the factors like (18) which multiply it.

$$
\begin{aligned}
\therefore \frac{\partial E}{\partial A} = \frac{\partial}{\partial A} \Big\{ & (A_1 | H_1 | A_1) + \left(A_1 B_2 \middle| \frac{1}{r_{12}} \middle| A_1 B_2\right) + \left(A_1 C_3 \middle| \frac{1}{r_{13}} \middle| A_1 C_3\right) + \cdots \\
& - \left(A_1 B_2 \middle| \frac{1}{r_{12}} \middle| A_2 B_1\right) - \left(A_1 C_3 \middle| \frac{1}{r_{13}} \middle| A_3 C_1\right) - \cdots \text{(all pairs involving A)} \Big\} \\
= \frac{\partial}{\partial A} \Big\{ & \int A_1^* \mathcal{H}_1' A_1 \, d(1) \Big\} = 0
\end{aligned}
\tag{20}
$$

The set of such equations, with B, C etc. replacing A, is equivalent to the condition:

$$\delta E = \delta \int \psi^* H \psi \, d\tau = 0 \qquad (21)$$

if

$$\mathcal{H}_1' = H_1 + \int B_2^* B_2 \frac{d(2)}{r_{12}} + \int C_3^* C_3 \frac{d(3)}{r_{13}} + \cdots\cdots$$

$$- \frac{B_1}{A_1} \int A_2 B_2^* \frac{d(2)}{r_{12}} - \frac{C_1}{A_1} \int A_3 C_3^* \frac{d(3)}{r_{13}} - \cdots\cdots \qquad (22)$$

Just as before, the integrals in $\mathcal{H}'$ give the average potential acting on electron 1 due to the other electrons, only now there are additional terms representing interchange effects. If the Hartree method were applied in such a manner that the criterion was the agreement between the assumed initial field and the field obtained from the charge density plus the interchange terms, the former giving rise to the terms $\int B_2^* B_2 \frac{d(2)}{r_{12}}$ etc. in $\mathcal{H}'$ and the latter terms like $-\frac{B_1}{A_1}\int A_2 B_2^* \frac{d(2)}{r_{12}}$, then the result would be the best wave functions obtainable of the form (14) and would include the effect of resonance.

The energy of the atom is:

$$E = (A_1|H_1|A_1) + (B_2|H_2|B_2) + \cdots\cdots + (A_1 B_2|\tfrac{1}{r_{12}}|A_1 B_2) + \cdots\cdots$$

$$- (A_1 B_2|\tfrac{1}{r_{12}}|A_2 B_1) - \cdots\cdots \qquad \text{(all pairs)}. \qquad (23)$$

The characteristic value ϵ_1 for the electron 1 in the central field V, (including resonance) is:

$$\epsilon_1 = (A_1|\mathcal{H}_1'|A_1) = (A_1|H_1|A_1) + (A_1 B_2|\tfrac{1}{r_{12}}|A_1 B_2) + \cdots\cdots$$

$$- (A_1 B_2|\tfrac{1}{r_{12}}|A_2 B_1) - \cdots\cdots \qquad \text{(all pairs involving A)} \qquad (24)$$

$$\epsilon_2 = (B_2|\mathcal{H}_2'|B_2) = (B_2|H_2|B_2) + (B_2 A_1|\tfrac{1}{r_{12}}|B_2 A_1) + \cdots\cdots$$

$$- (B_2 A_1|\tfrac{1}{r_{12}}|B_1 A_2) - \cdots\cdots \qquad \text{(all pairs involving B)} \qquad (25)$$

$$E = \sum_{i=1}^{n} \epsilon_i - \left(A_1 B_2 \left| \frac{1}{r_{12}} \right| A_1 B_2\right) - \cdots\cdots$$

$$+ \left(A_1 B_2 \left| \frac{1}{r_{12}} \right| A_2 B_1\right) + \cdots\cdots \qquad \text{(all pairs)} \qquad (26)$$

The total energy of the atom thus differs from the sum of the characteristic values due to the fact that such a sum counts both the coulomb and exchange integrals twice.

Hartree has not included exchange effects in computing his wave functions, although it seems as if it should be possible to do so. He has, however, in his latest paper[4] calculated the total energy by inserting the single-electron wave functions obtained without resonance into (23) so that the energy is correctly calculated but is not of course the best which could be obtained with the form (14) because of the neglect of exchange in obtaining A, B, ...

Calculations of the wave functions have been made for He, Li^+, Be^{++}, Be, B^{+++}, O^{+++}, O^{++}, O^+, O, F^-, Ne, Na^+, Al^{+++}, Al^+, Si^{++++}, Cl^-, A, K^+, Ca^{++}, Cu^+, Rb^+, Cs^+, but unfortunately the results of most of these have not been published. Slater[5] has published a table for the 2s, 3s and 3d functions of Rb^+ (not orthogonal) which he obtained from Hartree.

In this paper Slater considered analytic expressions which fit closely the numerical results of Hartree. He fitted Si^{4+}, K^+, Cu^+, Rb^+ and Cs^+ in this way and gave curves for interpolating others. The functions he used were:

1s : $e^{-a,r}$; 2s : $e^{-br} - c\,r\,e^{-dr}$ etc.

His results should be rather accurate for the range of ions to which they are applicable.

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[4] D.R.Hartree and M.M.Black, Proc.Roy.Soc., A 139, 311 (1933).

[5] J.C.Slater, Phys.Rev., 42, 33 (1932).

IX - Sets of Screening Constants.

Pauling[1] and Slater[2] have both published rules for constructing approximate wave functions for any atom. Both base their solutions on modified hydrogen-like functions; i.e., they use a wave-function for the whole atom of the determinant type given by equation V-6 in which the single-electron functions a, b, c etc. are related to the solutions of the hydrogen atom discussed in Section IV. Pauling modifies these functions by the use of a screening constant s such that Z in equations IV-4 - IV-8 is replaced by (Z-s), thus idealizing the interaction of the electrons by assuming that they affect each other by shielding the nucleus. The screening constants he used were obtained from theoretical and empirical sources and while they yield wave functions inferior in accuracy to those of Hartree, for many atoms they afford the best available approximate solutions.

Slater bases his functions on the work of Zener[3] on the lighter atoms, in which the variation method was applied in order to determine the best values of the parameters in a modified hydrogen-like wave function. Slater uses single-electron functions of the type:

$$r^{n^*-1} e^{-\frac{(Z-s)}{n^*} r} \qquad (1)$$

and determines the values to be assigned n* and s from empirical considerations. These functions do not have any nodes, as do the hydrogen solutions, but neither are solutions (1) with different values of n* mutually orthogonal and if they are made so by the process of taking the proper linear combinations of functions (1) with different values of n*, the nodes reappear.

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[1] L. Pauling and J. Sherman, Zeit. f. Krist., 81, 1 (1932); L. Pauling, Proc. Roy. Soc., A 114, 181 (1927).

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

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

For the light atoms for which Zener has carried out the variation treatment, these functions are remarkably accurate, considering their simplicity. As the atom becomes more complicated, however, they diverge from the correct expressions. For the heavy atoms for whichSlater's generalization was designed no comparisons with Hartree's or Pauling's wave functions have been published.

X - CHARGE DENSITIES, ATOMIC FIELDS AND F-VALUES

$|\psi|^2 d\tau$ gives the probability of finding the system in any given element of configuration space $d\tau$. In order to calculate the total electron density ρ it is necessary to integrate over the coordinates of all the electrons but one, thus giving the probability of finding that one electron in a specified volume element regardless of the positions of the other electrons, and then to add together similar expressions for all the electrons. However, since the total wave function for the atom should be antisymmetric in the electrons, the contribution of each electron will be identical, so that:

$$\rho = N \int_2 \cdots \int_n |\psi(1,2,3\cdots n)|^2 d(2)\, d(3) \cdots d(n). \quad (1)$$

In the special case in which ψ is of the determinant form (V-6), (1) becomes:

$$\rho = \frac{1}{(N-1)!} \sum_{P,P'} \int_2 \cdots \int_n P A_1^* B_2^* \cdots G_n^* \cdot P' A_1 B_2 \cdots G_n \, d(2) \cdots d(n) \quad (2)$$

and if A_1, B_1 etc. are mutually orthogonal and normalized, this takes on the simple form:

$$\begin{aligned} \rho &= \frac{1}{(n-1)!} \sum_{P,P'} P A_1^* \, P' A_1 \int_2 P B_2^* \cdot P' B_2 \, d(2) \cdots\cdots \int_n P G_n^* \, P' G_n \, d(n) \\ &= \frac{1}{(n-1)!} \sum_{P} P A_1^* \, P A_1 \qquad (P \text{ operates on letters}) \\ &= |A_1|^2 + |B_1|^2 + |C_1|^2 + \cdots\cdots + |G_1|^2. \end{aligned} \quad (3)$$

since from the orthogonality P must equal P' and then there will be (N-1)! P's with the same letter assigned to the subscript 1, cancelling the factor 1/(N-1)! . It is important to notice that if A, B, etc. are not orthogonal, then it is necessary to include cross terms in the expression for ρ.

The potential at any point R, ϑ, φ due to a charge density $-e\rho$ is:

$$\Phi\,(R, \vartheta, \varphi) = -e \int \frac{\rho}{s}\, d\tau \qquad (4)$$

where s is the distance from R, ϑ, φ to the volume element $d\tau$.

In the special case in which ρ is spherically symmetric, Φ becomes (including the effect of the nucleus):

$$\Phi\,(R) = \frac{Ze}{R} - \frac{8\pi e}{R} \int_0^R r^2 \rho\, dr - 8\pi e \int_0^\infty \rho\, r\, dr. \qquad (5)$$

A quantity which is important in crystal structure and electron beam experiments is the atomic scattering factor or F-value, which for an isolated atom is given by:

$$F(D) = \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} \rho\, e^{2\pi i \frac{r}{D} \cos\vartheta}\, r^2\, dr\, \sin\vartheta\, d\vartheta\, d\varphi \qquad (6)$$

where D is the effective interplanar distance in the crystal. If ρ is spherically symmetric this becomes:

$$F(D) = 2D \int_0^\infty \rho \sin\frac{2\pi r}{D}\, r\, dr. \qquad (7)$$

X - HELIUM

Neutral helium has been treated with complete success, at least for the normal state. However, it is interesting to compare the results obtained by the many different methods which have been applied to this atom. Even the Thomas-Fermi model has been tried, although two particles can hardly be sufficient for such a statistical method.

The simplest analytical treatment is that of Unsöld[1] who used hydrogen single-electron functions with nuclear charge two. In all these discussions of helium, the lowest state is understood and the spin factors can be taken out of the determinant (V-6), leaving an orbital part of the form:

$$\psi = q_1 q_2 \qquad (1)$$

This separation of spin and orbit is not possible for more complicated atoms. In Table IV are listed a number of the wave functions which have been used for helium together with the energy of the atom calculated by means of them.

Unsöld's treatment is equivalent to a direct first order perturbation problem, with the interaction of the electrons as the perturbation. Lennard-Jones[2] has shown how part of the second order correction to the energy may be easily obtained and I have applied this to helium. As seen from Table IV, this correction is too large.

Frenkel[3] and others very considerably improved the value of the energy by introducing a parameter, the effective nuclear charge,

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[1] A. Unsöld, Ann. d. Physik, 82, 355 (1927).

[2] J. E. Lennard-Jones, Proc. Roy. Acad. 129, 598 (1930).

[3] J. Frenkel, "Einführung in die Wellenmechanik," Berlin 1929, p. 291.

into the hydrogen-like wave function, this parameter being evaluated by the variation method (Sec. VII). His wave-function and energy value are listed in Table IV under No. 5. I applied the Lennard-Jones term to this also, with even poorer results.

No. 7 and 8 in the table are two functions which were tried without success, since they both reduced to simpler functions. This may be of interest because No. 7 especially is of a form which qualitative notions regarding the effect of the electron interaction would tend to support, yet it seems to be valueless.

The next entry is one of the best functions which is separable into single-electron factors. I calculated this because it is similar to the functions used for the 2s electron in later work.

Hylleraas[4] and Eckart[5] published No. 10. The method of Hartree (Sec. VIII) has been used by Gaunt,[6] who substituted the numerical wave functions obtained by this procedure into the variational integral in order to secure the energy. Since no interchange or deviation from spherical symmetry occurs in helium, this should be the best function possible of the factorable form (1).

The remainder of the functions listed in the table are due to Hylleraas[7] who has practically completed the solution of normal helium through his comprehensive and **successful** investigations. As seen from the selection of his trial functions listed in Table IV, wave functions are now available for helium of almost any desired degree of accuracy. *The only reason for enumerating so many is that for*

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[4] E.A.Hylleraas, Zeit.f.Physik, 54, 347 (1929), Eq. (11).

[5] C.Eckart, Phys.Rev., 36, 878 (1930).

[6] J.A.Gaunt, Proc.Camb.Phil.Soc., 24, 328 (1928).

[7] E.A.Hylleraas, Zeit.f.Physik, 48, 469 (1928); Ref. 4; 65, 209 (1930).

many applications a simple function of intermediate accuracy, such as No. 13, is satisfactory.

Table IV - Approximate Wave-Functions and Energies for Normal Helium.

	Wave-functions	Energy	Diff.	Parameters
1	Experimental	-2.905	-	
2	Perturbation Method, zeroth order	-4.000	-1.095	$Z_{eff.} = 2$
3	" " first order	-2.750	.155	"
4	" " Lennard-Jones	-3.026	-1.121	"
5*	Screening constant $a_1 = e^{-\zeta r_1}$	-2.8476	.057	$\zeta = 2 - \frac{5}{16}$
6	" " Lennard-Jones	-3.1627	- .258	
7	$\psi = e^{-\zeta s}(1 - e^{-cu})$	see no. 5		$c \to \infty$
8	$\psi = e^{-\zeta s} + cu\, e^{-\eta s}$	see no. 13		$\eta \to \zeta$
9*	$a_1 = e^{-\zeta r_1} + \alpha e^{-\eta r_1}$	-2.8603	.045	$\zeta = 2.249$ $\alpha = .75\,;\ \eta = 1.349$
10	$\psi = e^{-\zeta r_1 - \eta r_2} + e^{-\zeta r_2 - \eta r_1}$	-2.8754	.030	$\zeta = 2.14\,;\ \eta = 1.19$
11	Hartree method	-2.875	.030	
12	$\psi = e^{-\zeta s}(1 + ct^2)$	-2.8768	.028	
13	$\psi = e^{-\zeta s}(1 + cu)$	-2.8912	.014	$\zeta = 1.849\,;\ C = 0.364$
14	$\psi = e^{-\zeta s} e^{cu}$	-2.8896	.015	$\zeta = 1.86\,;\ c = 0.26$
15	$\psi = e^{-\zeta s}(1 + c_1 u + c_2 t^2)$	-2.9024	.003	$\zeta = 1.816\,;\ c_1 = 0.30$ $c_2 = 0.04$
16	$\psi = e^{-\zeta s}(1 + c_1 u + c_2 t^2 + c_3 s + c_4 s^2 + c_5 u^2)$	-2.9032	.002	$\zeta = 1.818$ $c_1 = 0.3530$ $c_2 = 0.128$ $c_3 = -0.1006$ $c_4 = 0.033$ $c_5 = 0.032$
17	Hylleraas' best function $\psi = \sum_{n,l,m} c_{nlm} e^{-s/2} s^n t^l u^m$	-2.905	.000	12 terms.

* ψ' for this function is of the form (1)
$s = r_1 + r_2$; $u = r_{12}$; $t = r_1 - r_2$

37.

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Wave Functions for the Ground State of Lithium and Three-Electron Ions

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Improved wave functions and ionization potentials have been obtained for the configuration $1s^2\ 2s$, by using the variation method with a variation function containing four parameters. The wave function for the whole atom is of the determinant form, built up of K and L single-electron functions. The K function used is hydrogen-like with one parameter, the effective nuclear charge, and the L function is of the form $\alpha r e^{-\eta r}-e^{-\zeta r}$. A simple rule is obtained by means of which it is possible to write down the wave function for any three-electron ion without further calculation. The deviation of the calculated ionization potentials from the observed values is 0.9 percent for Li I and decreases to 0.3 percent for C IV. Comparison is made with the results of other investigators and curves showing the wave functions and electron density functions are given.

Introduction

The solution of the Schrödinger equation for the hydrogen atom and for the ground state of the helium atom[1] has been carried out to a high degree of exactness, but the best approximation which has been obtained for the lowest state of lithium is not nearly so accurate. While it is probably not feasible at present to obtain a result for the energy which is superior to the experimental value in accuracy, it was thought worth while to test out on lithium various possible approximate solutions, partly because the better agreement with the experimental energy and the correspondingly improved wave function and electron-density function were considered important in themselves and partly because this study would provide a basis for similar investigations of heavier atoms.

General Method

Slater[2] has shown how to build up a properly antisymmetric wave function for a many-electron atom by using a determinant whose elements are functions of the coordinates of a single electron only. In particular, if the interaction of the electrons with each other is regarded as a perturbation and neglected in obtaining the zero$^{\text{th}}$ order approximation to the solution of the wave equation, there results for lithium:

$$\psi^\circ=\frac{1}{6^{\frac{1}{2}}}\begin{vmatrix}A_1 & A_2 & A_3\\ \bar{A}_1 & \bar{A}_2 & \bar{A}_3\\ B_1 & B_2 & B_3\end{vmatrix}\tag{1}$$

where A_1 is the $1s$ hydrogen-like wave function with positive spin for the first electron; $\bar{A}_2$ is the same function with negative spin for the second electron, and B_3 is the $2s$ hydrogen-like function with plus spin for the third electron.

The method adopted in this work was to seek a better approximation by the use of new functions for B based on the hydrogen-like functions but generalized by the introduction of parameters whose values were then determined by the application of the variation method.

The solution of the variation problem:

$$\delta E=\delta\left[\int\psi^*H\psi d\tau/\int\psi^*\psi d\tau\right]=0,\tag{2}$$

where ψ is the function varied and H is the Hamiltonian operator for the system, is equivalent to solving the wave equation

$$H\psi=W\psi\tag{3}$$

with the usual boundary conditions. In particular if this variation problem is not completely solved but instead a trial function ψ used which contains a number of parameters which are varied until E is a minimum, then it can be shown[3] that E is an upper limit to the energy, and ψ is assumed to be an approximate solution. The method which was used in this problem is

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[1] E. A. Hylleraas, Zeits. f. Physik 65, 209 (1930).

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

[3] C. Eckart, Phys. Rev. 36, 878 (1930).

applicable to the lowest state of any multiplicity or total angular momentum.

PREVIOUS WORK ON LITHIUM

Hargreaves[4] has applied the method of Hartree to lithium, but his results have not appeared in a very usable form. Hartree's method of the "self-consistent field" is not based on the variation principle, but Slater[5] has shown the relation between these two procedures and in addition has pointed out that several important corrections are needed before the energy values obtained can be compared with the experimental ionization potentials. The curve Hargreaves publishes for the wave function cannot be used for comparison since he gives no scales and has not made the L function orthogonal to the K function, so that its shape is of little significance. However, he does give a table of the self-consistent field, and these values will be compared with other results in Table III.

Eckart,[3] using essentially the same method as is described in this paper, employed hydrogen-like functions with two parameters, the effective nuclear charges for the K- and L-shells. Thus if we use a, b, c, $\cdots$, to represent single electron-orbit functions without the spin factor and $A, B, C, \cdots; \bar{A}, \bar{B}, \bar{C}, \cdots$, for the same functions with plus and minus spin, respectively, Eckart's solutions are

$$\begin{aligned} &(K\text{-shell functions})\ a = e^{-\xi r} \\ &(L\text{-shell functions})\ b = e^{-\eta r}(\eta r - 1). \end{aligned} \tag{4}$$

There appears to be an error in his energy value for lithium so this has been recalculated and will be found in Table I.

Guillemin and Zener[6] introduced an additional parameter (α) into b, obtaining thereby a considerable improvement in the energy. Their function is:

$$b = e^{-\eta r}(\alpha r - 1) \tag{5}$$

and values for the energy will also be found in Table I and of the parameters in Table II. In addition these authors varied the exponent of r in the coefficient, but found in this case that its best value was one, the hydrogen-like value.

TABLE I. *Energies and ionization potentials (atomic units: e^2/a_0).*

	Total energy	Diff.	%	Ionization potential	Diff.	%
			Li I			
Experimental	−7.4837	—	—	0.1983	—	—
4-Parameter	−7.4192	0.0645	0.86	.1965	0.0018	0.91
Guillemin-Zener	−7.4183	.0654	.87	.1956	.0027	1.36
Slater	−7.4179	.0658	.88	.1953	.0030	1.51
Hydrogen-like	−7.3922	.0915	1.22	.1696	.0287	14.5
			Be II			
Experimental	−14.3422	—	—	.6704	—	—
4-Parameter	−14.2639	.0783	.55	.6663	.0041	.61
Slater	−14.2584	.0838	.58	.6607	.0097	1.45
			B III			
Experimental	−23.476	—	—	1.395	—	—
4-Parameter	−23.363	.113	.48	1.390	.005	.36
Slater	−23.350	.126	.54	1.378	.017	1.22
			C IV			
Experimental	−34.778	—	—	2.3722	—	—
4-Parameter	−34.713	.065	.19	2.3650	.0072	.30
Guillemin-Zener	−34.698*	.080	.23	2.3496*	.0226	.95
Slater	−34.690	.088	.25	2.3422	.0300	1.26

* This is probably not quite the best value obtainable with this function.

TABLE II. *Parameter values, except for four-parameter function.*

	ξ	η	α	ξ	η	α
		Li I			Be II	
Guillemin-Zener[6]	2.688	0.630	5.56	3.688	1.158	5.88
Slater	*2.688*	*.630*	—	*3.682*	*1.09*	—
Hydrogen-like[3]	2.686	.888	—	3.70	1.42	—
		B III			C IV	
Guillemin-Zener[6]	4.688	1.671	5.56	5.688	2.179	5.88
Slater	4.676	1.52	—	5.672	1.95	—
Hydrogen-like[3]	4.72	1.96	—	5.71	2.48	—

Zener[7] and Slater[8] noted that α is fairly large and concluded that a good result would be obtained with the very simple function

$$b = re^{-\eta r}. \tag{6}$$

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[4] J. Hargreaves, Proc. Camb. Phil. Soc. **25**, 75 (1929).

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

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

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

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

This function was tried and, as is seen in Table I, found to be remarkably good considering its simplicity. It is better than the hydrogen-like function with screening constant used by Eckart, although, of course, not as good as Guillemin and Zener's function, of which it is a special case.

FUNCTIONS INVESTIGATED

The type of function which has been used in this paper, a natural generalization of Guillemin and Zener's function, is

$$b=\alpha re^{-\eta r}-e^{-\zeta r}. \tag{7}$$

The same type has been used by Slater[9] in seeking analytical expressions for Hartree's graphical wave functions. Results which are obtained by using (7) are listed in Table I under the heading "4-parameter" function.

The following form was also tried but found not to give as good results as (7):

$$b=\alpha re^{-\eta r}+re^{-\zeta r}. \tag{8}$$

Since the variation principle is applicable to the lowest P state of the atom, the following function was tried for the configuration $1s^2\ 2p$ of lithium:

$$c=(\gamma e^{-\kappa r}+e^{-\lambda r})r\cos\vartheta. \tag{9}$$

However, the surprising result was obtained, on varying the parameters, that this function reduced to the simple screening constant type used by Eckart. In other words, the best values of the parameters γ, κ and λ were such that $\gamma=0$; $\kappa=\lambda$. Therefore, the calculated total energy for this configuration, $-7.35039\ e^2/a_0$, is not different from Eckart's value, but by combining this with the best calculated value for the ground state, $-7.41915\ e^2/a_0$, a new result for the resonance potential of lithium is obtained, $0.06876\ e^2/a_0$, which is to be compared with the experimental value, $0.06794\ e^2/a_0$. The difference is $0.0082\ e^2/a_0$ or 1.2 percent.

The calculated energy of removal of the $2p$ electron from $1s^2\ 2p$ of lithium is 2.2 percent greater than that for a $2p$ hydrogen atom, $e^2/8a_0$, whereas the experimental value is 4.2 percent greater than $e^2/8a_0$. The discrepancy of 2 percent is probably to be attributed to the effect of polarization of the K-shell by the valence electron, the effect of which is not taken into consideration by any of the variation functions used in this paper, approximate calculations of the polarization energy[10] leading to somewhat larger values than the 2 percent needed. It is of interest that these calculations show, as suggested by Pauling and Goudsmit,[11] that there is appreciable interaction of the valence electron with the core of the atom other than polarization even for "nonpenetrating" orbits.

DETAILS OF METHOD

When the units $a_0=h^2/(4\pi^2\mu e^2)$, $2Rhc=e^2/a_0$ and e are used for length, energy and charge, respectively, Schrödinger's equation for the three-electron problem becomes

$$H\psi=(-\tfrac{1}{2}\nabla^2+V)\psi=W\psi \tag{10}$$

where

$$V=1/r_{12}+1/r_{23}+1/r_{13}-Z/r_1-Z/r_2-Z/r_3. \tag{11}$$

∇^2 is the Laplacian for the coordinates of the three electrons, and Z is the atomic number of the atom or ion. As pointed out by Hylleraas,[12] application of Green's theorem to the term in (2) involving the Laplacian yields for E:

$$E=(M'-2L')/2N' \tag{12}$$

where

$$\left.\begin{aligned} M'&=\int|\mathrm{grad}\ \psi|^2d\tau\\ L'&=-\int\psi^*V\psi d\tau\\ N'&=\int\psi^*\psi d\tau\end{aligned}\right\}. \tag{13}$$

Further, if the change in scale:

$$r'=\xi r;\quad \eta'=\eta/\xi;\quad \zeta'=\zeta/\xi \tag{14}$$

is made, it is possible to differentiate E with respect to ξ, solve for the minimizing value of ξ and insert this value in E. The result is

$$E=-L^2/2MN \tag{15}$$

where L, M, N differ from L', M', N' only in that the substitutions (14) have been made.

The other parameters enter in such a complicated fashion that it is not feasible to obtain the

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[9] J. C. Slater, Phys. Rev. **42**, 33 (1932).

[10] L. Pauling and S. Goudsmit, *The Structure of Line Spectra*, McGraw-Hill, New York, 1930, p. 47.

[11] Reference 10, p. 48.

[12] E. A. Hylleraas, Zeits. f. Physik **54**, 347 (1929).

minimum by differentiation so resort was had to actually computing E for various values of the parameters and graphically determining the minimum. This is a tedious process at best; the quickest and most certain method was found to involve constructing rough contour maps of the energy surface. An estimate was first made of the probable values of parameters. One of these (usually η') was inserted in the formula for E and a survey of the ζ', α' plane made by giving ζ' a number of fixed values and plotting E as a function of α'. Each of these curves then gives a section of the energy surface, with E thought of as a function of α' and ζ' only. From these a contour map can be constructed and an estimate made of the best values of α' and ζ' for the value of η' originally chosen. With these values of α' and ζ', η' is then varied until a minimum is found. A contour map may be constructed for the α', ζ' plane with this new value of η' and the best values redetermined.

K-Shell Functions

In all the cases discussed here, with the exception of Hargreave's paper, the function used for the K electrons was the same as in Eckart's work, i.e., a hydrogen-like function with one parameter, the effective nuclear charge, as in Eq. (4). It is well known that this is not the best function to represent the K electrons, some term such as one of those used by Hylleraas,[12] for example, to correct more exactly for the repulsion of the electrons giving a better result. However, the introduction of even the simplest of these interaction factors, such as $(1+\gamma r_{12})$, enormously complicates the problem in the case of lithium and so was not regarded as practicable. Instead, the ionization potential was calculated by subtracting the energy of the Li^+ ion computed by using the same type of $1s$ wave function, the value of the energy so calculated being: 7.22266 e^2/a_0 for Li^+; 13.59766 e^2/a_0 for Be^{++}; 21.97266 e^2/a_0 for B^{+++}; and 32.34766 e^2/a_0 for C^{++++}. Although the total energy of the lithium atom is, therefore, in error by about 0.065 e^2/a_0 or 0.86 percent in all these examples due to the inaccuracy of the K functions, the assumption made that this error is nearly equal in the ion and in the atom is well justified by the close agreement between the experimental and theoretical ionization potentials as given in Table I.

Comparison of *L* Functions

The $2s$ functions which have been enumerated do not, at first glance, appear to be very similar, and it may seem strange that such different functions can all be even moderately good approximations to the true solution. The reason for the discrepancy is the use of single-electron wave functions for comparison instead of the wave function for the atom as a whole. Slater[9] has pointed out that it is possible to make the $2s$ function orthogonal to the $1s$ function by adding to the $2s$ a certain fraction of the $1s$ function. Since the wave function for the whole atom is a determinant, it possesses the property that the addition of the members of any row multiplied by any factor to the members of any other row does not change the value of the determinant. Thus:

$$\psi=\frac{1}{6^{\frac{1}{2}}}\begin{vmatrix} A_1 & A_2 & A_3 \\ \bar{A}_1 & \bar{A}_2 & \bar{A}_3 \\ B_1 & B_2 & B_3 \end{vmatrix}=\frac{1}{6^{\frac{1}{2}}}\begin{vmatrix} A_1 & A_2 & A_3 \\ \bar{A}_1 & \bar{A}_2 & \bar{A}_3 \\ B_1+\beta A_1 & B_2+\beta A_2 & B_3+\beta A_3 \end{vmatrix} \tag{16}$$

and in particular β may be so chosen that

$$\int A_1(B_1+\beta A_1)d\tau=0. \tag{17}$$

With this value of β, the single-electron functions are mutually orthogonal, since A_1 and $\bar{A}_1$ have opposite spins. In addition, the functions a and b later tabulated have been normalized to 4π, i.e.,

$$\int A_1^2 d\tau=\int B_1^2 d\tau=4\pi. \tag{18}$$

The orthogonalization and normalization make a and b unique (as long as functions of different spins are not combined), and it is thus possible to compare the different approximations which have been obtained.

As shown by Fig. 3, the four approximations already enumerated are remarkably near to each other. The only one showing any great deviation is the hydrogen-like function, which is also the one giving the poorest energy value. The simple, so-called "nodeless" function of Slater[8] is seen to be miscalled, since, when it is orthogonalized, it has a node in practically the same place as the more precise functions.

RESULTS

The parameter values obtained for the functions of Guillemin and Zener, Slater, and Eckart are found in Table II. In the case of the four-parameter function, the best parameter values fit into a very convenient rule if we introduce the idea of screening constants. The function for the L electron which has been used, Eq. (7), consists of two terms (before orthogonalization), and it is seen that the first term is the more important at large distances, because of the factor r and the smaller coefficient in the exponent, while the second term is the more important for small values of r. In the simple hydrogen-like function analogous to this, there is only one exponential, whose exponent is $Z_{\mathrm{eff.}}/2$, or $(Z-\sigma)/2$ if we define the quantity σ, the screening constant. σ thus represents the shielding effect of the inner electrons which reduces the attraction of the nucleus for the L electron. Likewise in our more complicated function the idea of the screening constant can be introduced, only here two different screening constants for the L electron are needed, since there are two exponentials. The results which are obtained are that these screening constants are essentially independent of the nuclear charge and, therefore, provide a convenient method of summarizing the results of the variation problem. Furthermore, to a sufficiently close approximation, the screening constant for the inner part of the $2s$ function is zero, so that in a sense the four parameters originally used have been reduced to three.

The parameter α can also be related for the ions of different atomic number. It is found that in all four cases investigated α' comes so close to 0.5 that it is very convenient to assume that

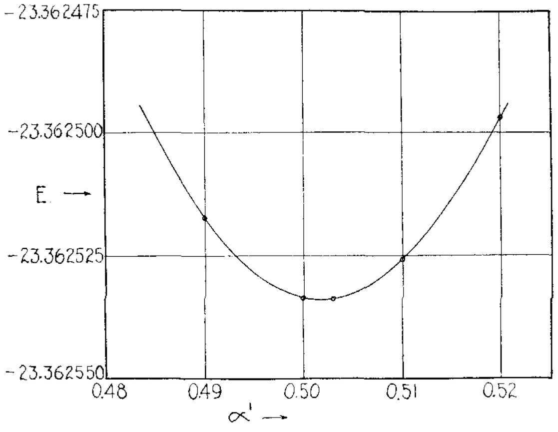

FIG. 1. Curve showing the variation of E with the parameter α' for B III, with the four-parameter function with $\sigma_1=0.31$, $\sigma_2=1.67$, $\zeta=Z/2$.

value for all three-electron ions. Fig. 1 shows the way E varies with α' in the case of B III. Since $\alpha=\alpha'\xi$ and $\xi=Z-\sigma_1$, if σ_1 is the K-shell screening constant, therefore,

$$\alpha=0.5(Z-\sigma_1)=0.5(Z-0.31). \tag{19}$$

Introducing the values indicated above for the parameters η, ζ, α and ξ, we obtain for the best wave function for the state $1s^2\ 2s\ {}^2S$ of any three-electron atom or ion the expression

$$\psi=(1/6^{\frac{1}{2}})\textstyle\sum_P \pm PA_1\bar{A}_2B_3. \tag{20}$$

$$a=(\xi^3/\pi)^{\frac{1}{2}}e^{-\xi r} \tag{21}$$

$$b=k\{\alpha re^{-\eta r}-e^{-\zeta r}+\beta e^{-\xi r}\} \tag{22}$$

where

$$\left.\begin{matrix}\xi=Z-\sigma_1 & \zeta=Z/2\\ \eta=(Z-\sigma_2)/2 & \alpha=0.5(Z-\sigma_1)\end{matrix}\right\} \tag{23}$$

$$\beta=8\xi^3\left\{\frac{1}{(\zeta+\xi)^3}-\frac{3\alpha}{(\eta+\xi)^4}\right\}\quad \text{orthogonality constant}$$

$$K=\left\{\pi\left[3\frac{\alpha^2}{\eta^5}+\frac{1}{\zeta^3}+\frac{\beta^2}{\xi^3}-\frac{48\alpha}{(\eta+\zeta)^4}+\frac{48\alpha\beta}{(\eta+\xi)^4}-\frac{16\beta}{(\zeta+\xi)^3}\right]\right\}^{-\frac{1}{2}}$$

and $Z=$ atomic number of ion; and $\sigma_1=0.31$, K-shell screening constant. $\sigma_2=1.67$, L-shell screening constant. The sum in Eq. (20) is over all permutations P of the numbers 1, 2, 3, odd permutations having the negative sign. (This is another way of writing the determinant of Eq. (1).) The single-electron functions a and b as given above are individually normalized to unity and are mutually orthogonal.

The energies obtained with the various functions are tabulated in Table I, which also contains the calculated ionization potentials. The experimental energy values are listed in the same table, together with deviations and percent deviations of the calculated and observed quantities. It is seen that the poorest values are those obtained with the hydrogen-like function of Eq. (4), even the simpler function put forward by Slater and given in Eq. (6) being considerably better. The error in the ionization potential computed by the use of the four-parameter function is only from thirty to seventy percent of the corresponding error found when Guillemin and Zener's function is used.

Fig. 2 is a plot of the four-parameter single-electron function for the $2s$ electron normalized to 4π and with β adjusted so that the L and K functions are orthogonal. Fig. 3 gives $4\pi r^2 b^2$, the distribution function integrated over all angles. On comparing the size of the two maxima in Li I and in hydrogen ($2s$ state), the effect of the core electrons of lithium in reducing the probability of close approach to the nucleus by the valence electron is clearly seen, in agreement with the old concept of the penetrating orbit, in the inner segment of which the electron was speeded up by the increased effective nuclear charge, diminishing the time spent in traversing this segment. Fig. 4 gives the total electron density function for Li I, integrated over all angles. The very steep rise at the K-shell and the more spread-out maximum of the single L electron are shown.

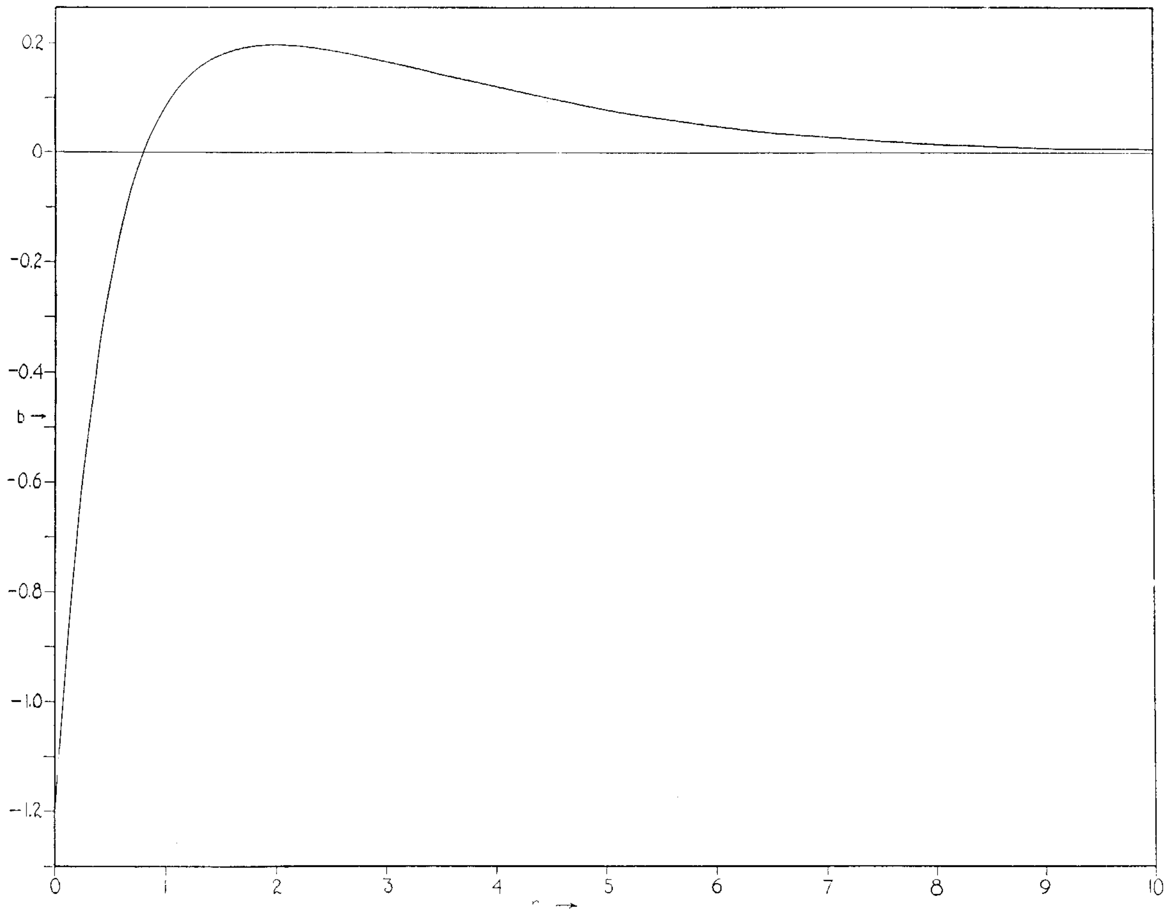

FIG. 2. Plot of four-parameter orthogonalized single-electron wave function b for $2s$ electron, normalized to 4π. r in atomic units. Li I.

THE INTERNAL FIELD

Hargreaves[4] has given a table of values for the self-consistent field for lithium, obtained graphically. This is expressed in terms of the "effective nuclear charge for field," which is the number Z_f such that the charge $Z_f e$ placed at the position of the nucleus would give the same field (not potential) at the point in question as is actually found. In other words:

$$Z_f = r^2(\partial V/\partial r) \qquad (24)$$

in atomic units.

In Table III the values of Z_f found by Hargreaves are listed. In addition there is also given the field due to the nucleus and the two K

TABLE III. *Field due to K electrons. r in atomic units.*

r	Z_f – Hargreaves	Z_f – Eq. (24)	Difference
0	3	3	0
0.1	2.963	2.965	−0.002
.2	2.807	2.811	− .004
.3	2.559	2.559	.000
.4	2.280	2.272	+ .008
.6	1.773	1.748	+ .025
.8	1.425	1.394	.031
1.0	1.219	1.192	.027
1.2	1.108	1.089	.019
1.4	1.050	1.039	.011
1.6	1.022	1.017	.005
1.8	1.009	1.007	.002
2.0	1.003	1.003	.000

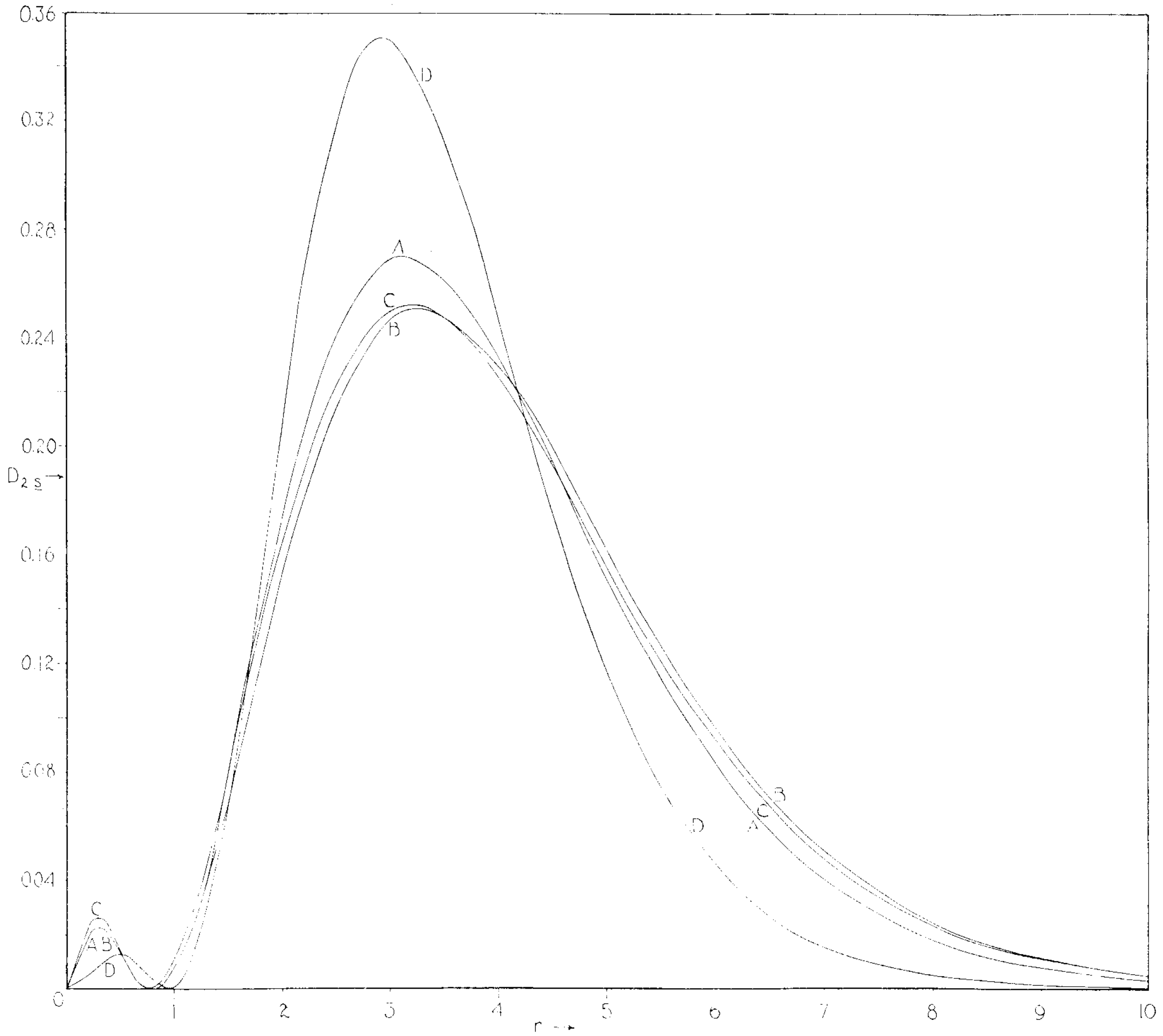

FIG. 3. Plot of electron distribution function for 2s electron, $D_{2s} = 4\pi r^2 b^2$, with different types of functions. Li I. *A*, 4-parameter; *B*, Guillemin-Zener; *C*, Slater; *D*, hydrogen-like.

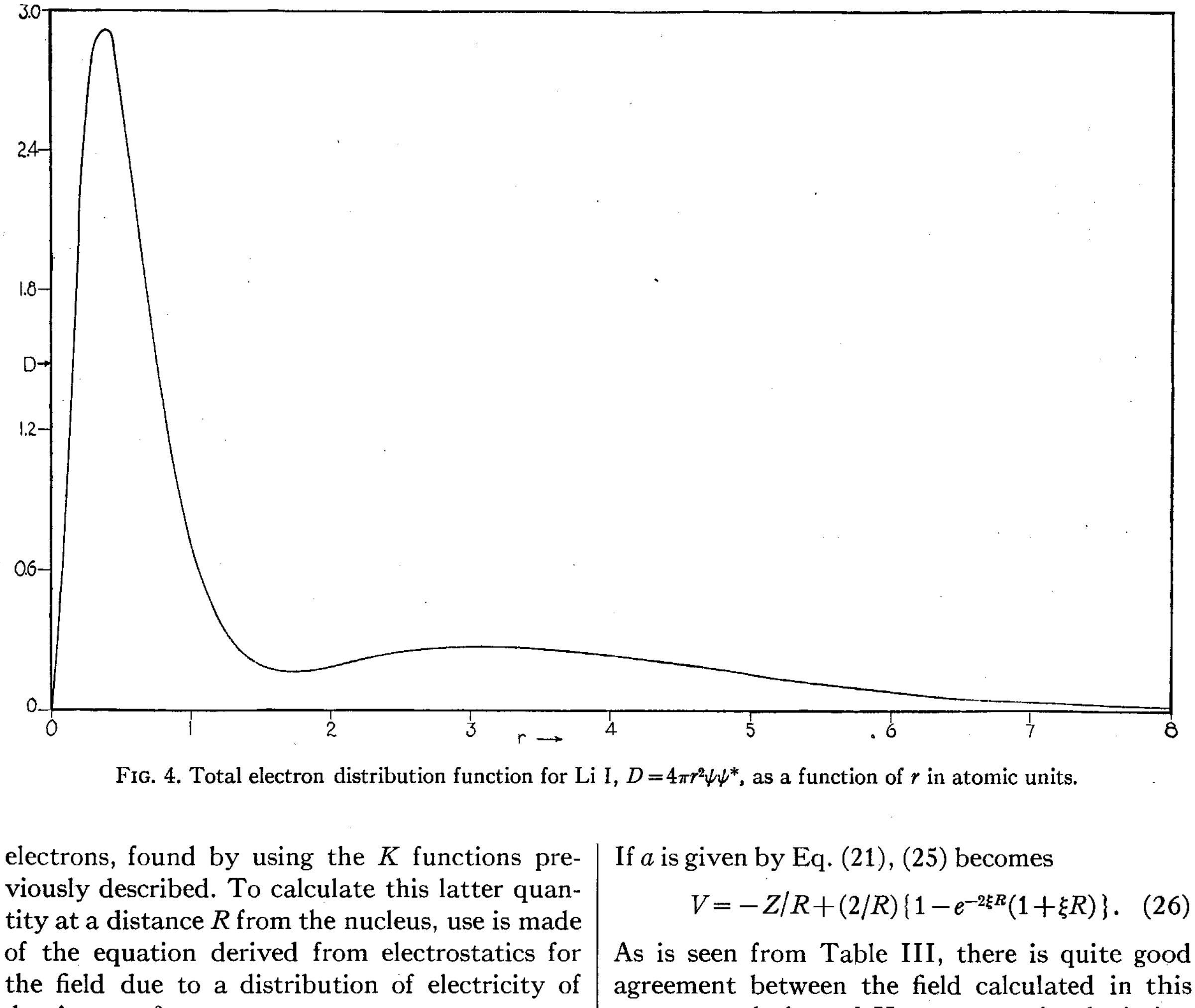

FIG. 4. Total electron distribution function for Li I, $D=4\pi r^2\psi\psi^*$, as a function of r in atomic units.

electrons, found by using the K functions previously described. To calculate this latter quantity at a distance R from the nucleus, use is made of the equation derived from electrostatics for the field due to a distribution of electricity of density $\rho=a^2$

$$V=-\frac{Z}{R}+\frac{8\pi}{R}\int_0^R r^2a^2dr+8\pi\int_R^\infty ra^2dr. \quad (25)$$

If a is given by Eq. (21), (25) becomes

$$V=-Z/R+(2/R)\{1-e^{-2\xi R}(1+\xi R)\}. \quad (26)$$

As is seen from Table III, there is quite good agreement between the field calculated in this manner and that of Hargreaves, the deviation being about 2 percent at most. This comparison refers only to the 1s functions used, and not to the 2s function, however.

EXPRESSIONS FOR N, L, M

Eq. (15) gives the energy in terms of N, L, M, defined by (13). Algebraic expressions for N, L, M for the configuration $(1s)^2\,2s$ and for the 2s functions of (7) are given below:

$$\alpha'=\alpha/\xi;\quad \zeta'=\zeta/\xi;\quad \eta'=\eta/\xi. \quad (27)$$

$$2K=\zeta'+\eta';\quad b=1+\eta';\quad f=1+\zeta';\quad g=1+K. \quad (28)$$

$$N=\pi^3\left\{\frac{3\alpha'^2}{\eta'^5}-576\frac{\alpha'^2}{b^8}+384\frac{\alpha'}{b^4f^3}-3\frac{\alpha'}{K^4}+\frac{1}{\zeta'^3}-\frac{64}{f^6}\right\}. \quad (29)$$

$$L=\pi^3\left\{3(2Z-\tfrac{5}{8})\frac{\alpha'^2}{\eta'^5}+(1.5Z-3)\frac{\alpha'^2}{\eta'^4}+3\frac{\alpha'^2}{b^4}+6\frac{\alpha'^2}{b^5}+(516-384\cdot Z)\frac{\alpha'^2}{b^7}-576\cdot Z\frac{\alpha'^2}{b^8}-\frac{384\alpha'^2}{b^4(2+b)^3}\right.$$

$$-\frac{1152\alpha'^2}{b^4(2+b)^4}+(4-2Z)\frac{\alpha'}{K^3}-4\frac{\alpha'}{g^3}-6\frac{\alpha'}{g^4}+(128\cdot Z-256)\frac{\alpha'}{f^3b^3}+192Z\frac{\alpha'}{b^4f^2}+(384Z-384)\frac{\alpha'}{b^4f^3}$$

$$+\frac{128\alpha'}{f^3(2+b)^3}+\frac{384\alpha'}{f^3(2+b)^4}+\frac{1536\alpha'}{b^4f^3(2+f)^2}+\frac{1536\alpha'}{b^4f^2(2+f)^3}+\frac{128\alpha'}{f^3(f+b)^3}+\frac{192\alpha'}{f^2(f+b)^4}-3(2Z-\tfrac{5}{8})\frac{\alpha'}{K^4}$$

$$\left.+(2Z-\tfrac{5}{8})\frac{1}{\zeta'^3}+(Z-2)\frac{1}{\zeta'^2}+\frac{2}{f^2}+\frac{2}{f^3}+(20-64Z)\frac{1}{f^5}+(128-64Z)\frac{1}{f^6}-\frac{512}{f^6(2+f)^2}-\frac{512}{f^5(2+f)^3}\right\}. \quad (30)$$

$$M=\pi^3\left\{\frac{6\alpha'^2}{\eta'^5}+\frac{\alpha'^2}{\eta'^3}+384\frac{\alpha'^2}{b^7}-576\frac{\alpha'^2}{b^8}-1152\frac{\eta'\alpha^2}{b^8}-6\frac{\alpha'}{K^4}-3\frac{\zeta'\eta'\alpha'}{K^4}-128\frac{\alpha'}{b^3f^3}+384\frac{\alpha'}{b^4f^3}+2\frac{\alpha'\zeta'}{K^3}\right.$$

$$\left.+384\frac{\alpha'\zeta'}{b^4f^3}+384\frac{\alpha'\eta'}{b^4f^3}+\frac{2}{\zeta'^3}+\frac{1}{\zeta'}-128\frac{\zeta'}{f^6}-64\frac{1}{f^6}\right\}. \quad (31)$$

I wish to express my appreciation of the assistance of Professor Linus Pauling, who proposed this problem and made many useful suggestions during the progress of the work. I am also indebted to Mr. L. G. Bonner for much of the numerical computation.

In addition to the functions just described, I attempted to calculate the energy of lithium, using wave functions with interaction terms. The complications involved made the problem seem impractical at the time and this line of attack was abandoned.

The first function of this type tried was:

$$\psi = \psi^{\circ}\left[1 + c\,(r_{12} + r_{23} + r_{13})\right] \tag{32}$$

where ψ° is a determinant type function using hydrogen-like functions, similar to those in equation (4).

The difficulties encountered were so great with this function, which includes the interactions between each pair of electrons, that a simpler one was attempted, namely:

$$\psi = \frac{1}{\sqrt{6}} \sum_{P} (-)^{p}\, P A_1 \bar{A}_2 B_3 f_{12} \tag{33}$$

$$f_{12} = 1 + c\, r_{12} \tag{34}$$

A and B are given, as before, by equation (4). This function has interaction terms only for the repulsion of the electrons in the K shell. The permutation operator P acts on f_{12} as well as the orbit functions A and B so that ψ is anti-symmetric. Even this wave function, however, proved impractical, but it is quite reasonable to expect that one modeled closely upon this may prove to be feasible in the future.

XIII - BERYLLIUM

The normal state of beryllium has the configuration $1s^2 2s^2\ ^1S$. The presence of two electrons in the L shell instead of one as in lithium introduces an additional strong interaction which makes the computation of the energy a much harder problem than lithium. A satisfactory analytic solution has not yet been obtained, although practically all the functions which are fairly successful for lithium have been tried. Slater[1] includes Be in the list of atoms for which Hartree has computed the wave function but not the energy, using the self-consistent field criterion. Zener's function:

$$\psi_1 = e^{-\eta r_1}(\alpha r_1 - 1) \tag{1}$$

has been worked out.[2] The results, listed in Table V, show an error much greater than the corresponding treatment of lithium. The simple function:

$$\psi_1 = r_1 e^{-\eta r_1} \tag{2}$$

gives very nearly the same results.

I have tried the L function which was used with success for lithium, namely:

$$\psi_1 = \alpha r_1 e^{-\eta r_1} - e^{-\xi r} \tag{3}$$

The computation is excessively complicated and the numerical variation of parameters was not very thoroughly carried out, instead only a few parameter values were tried which seemed to be the most reasonable. The best energy obtained is so little better than that given by the very much simpler expression (2) that the work was abandoned. It is of course possible that a further exploration of the minimum of the

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[1] J.C.Slater, Phys.Rev., 42, 33 (1932).

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

energy integral would yield better results, but this seems doubtful. Another possibility is that an error exists in the rather elaborate computations.

Another function which I have applied to beryllium without great success as yet is:

$$b = r\left(\alpha e^{-\eta r} + e^{-\zeta r}\right) \qquad (4)$$

This was also applied to lithium but found to be inferior to the type of equation (3). Only two sets η, ζ havebeen calculated for beryllium and here again the value is not quite as good as that given by (3) although very nearly the same.

The conclusion is, therefore, that if only fair accuracy is needed, a determinant type wave function with K functions:

$$a = e^{-\xi r} \qquad (5)$$

and L functions given by (2) is satisfactory and reasonably easy to use. If better results are desired, it is necessary to use the numerical wave functions of Hartree which are probably not as accurate as the best treatments of lithium. The results of these investigations seem to indicate that no wave function which does not include interaction terms can be an especially good approximation in the case of beryllium.

In the calculations for beryllium, I am indebted to Mr. L.G.Bonner, who performed all the numerical work.

Table V. Wave Functions Energies for Beryllium.

	Wave function	Energy	Diff.	Parameters
1	Experimental	-14.685	——	——
2	Zener Eq.(1)	-14.553	.132	$\alpha = .067$ $\eta = 0.96$ $\xi = 3.6875$
3	$b_1 = r_1 e^{-\eta r_1}$ (2)	-14.557	.128	
4	$b_1 = \alpha r_1 e^{-\eta r_1} - e^{-\xi r_1}$ (3)	-14.559	.126	
5	$b_1 = r_1 (\alpha e^{-\eta r_1} + e^{-\xi r_1})$	-14.557	.128	
6	Hartree	Energy not calculated		

XIV - GENERAL METHODS USED IN COMPUTATIONS

There are certain general methods which apply to any atom and which simplify the computation of parameter values for wave functions such as those which have been discussed under helium, lithium and beryllium.

Define N, L, M by:

$$N = \int \psi^* \psi \, d\tau \qquad (1)$$

$$M = \int |\operatorname{grad} \psi|^2 \, d\tau \qquad (2)$$

$$L = -\int \psi^* \psi \, V \, d\tau \qquad (3)$$

where V is the potential energy. Then it will be shown that:

$$E = \int \psi^* H \psi \, d\tau = \frac{M - 2L}{2N} \qquad (4)$$

To prove this, use the fact that (VII-1):

$$H = -\tfrac{1}{2} \nabla^2 + V \qquad (5)$$

so

$$E = \int \psi^* H \psi \, d\tau = -\tfrac{1}{2} \int \psi^* \nabla^2 \psi \, d\tau + \int \psi^* \psi V \, d\tau \qquad (6)$$

In rectangular coordinates:

$$\nabla^2 = \sum_{i=1}^{3n} \frac{\partial^2}{\partial q_i^2} \qquad (7)$$

so

$$\int \psi^* \nabla \psi \, d\tau = \sum_{i=1}^{3n} \int_{-\infty}^{\infty} \cdots\cdots \int_{-\infty}^{\infty} \psi^* \frac{\partial^2 \psi}{\partial q_i^2} \, dq_1 \cdots dq_i \cdots dq_{3n} \qquad (8)$$

But

$$\int_{-\infty}^{\infty} \psi^* \frac{\partial^2 \psi}{\partial q_i^2} \, dq_i = \left[\psi^* \frac{\partial \psi}{\partial q_i} \right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \frac{\partial \psi^*}{\partial q_i} \frac{\partial \psi}{\partial q_i} \, d\tau \qquad (9)$$

Since both ψ^* and $\frac{\partial \psi}{\partial q_i} \to 0$ as $q_i \to \pm\infty$, the first term vanishes so that:

$$\int \psi^* \nabla \psi \, d\tau = -\sum_{i=1}^{3n} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \frac{\partial \psi^*}{\partial q_i} \frac{\partial \psi}{\partial q_i} \, dq_1 \cdots dq_{3n}. \qquad (10)$$

But

$$|\operatorname{grad} \psi|^2 = \sum_{i=1}^{3n} \frac{\partial \psi^*}{\partial q_i} \frac{\partial \psi}{\partial q_i} \qquad (11)$$

From these, (4) follows immediately.

It usually is convenient to make a change of scale which will eliminate the effective nuclear charge for the K electrons. To do this put

$$\xi q_i = q_i'$$

$$\therefore \frac{\partial^2}{\partial q_i^2} = \xi^2 \frac{\partial^2}{\partial q_i'^2} \; ; \quad dq_1 \cdots dq_{3n} = \frac{1}{\xi^{3n}} dq_1' \cdots dq_{3n}' \qquad (12)$$

$$V(q) = -\frac{Z}{r_1} \cdots\cdots = -\frac{\xi Z}{r_1'} \cdots\cdots = \xi V(q')$$

$$\therefore \quad N(q) = \frac{1}{\xi^{3n}} N(q') = N'/\xi^{3n}$$

$$M(q) = \frac{1}{\xi^{3n-2}} M(q') = M'/\xi^{3n-2}$$

$$L(q) = \frac{1}{\xi^{3n-1}} L(q') = L'/\xi^{3n-1} \qquad (13)$$

$$\therefore \quad E = \frac{\xi^2 M' - 2\xi L'}{2N'} \qquad (14)$$

For minimum E:

$$\frac{\partial E}{\partial \xi} = \frac{\xi M' - L'}{N'} = 0 \qquad (15)$$

or

$$\xi = \frac{L'}{M'} \qquad (16)$$

Substituting this (14):

$$E = \left\{ \tfrac{1}{2} L'^2/M' , - L'^2/M' \right\} / N' = -\frac{L'^2}{2M'N'} \tag{17}$$

which is the expression for the energy from which ξ has been entirely eliminated.

If ψ is of the form:

$$\psi = \frac{1}{\sqrt{n!}} \sum_{P} \pm P A_1 B_2 C_3 \cdots G_n \tag{18}$$

and

$$\int a_1 b_1 \, d\tau_1 = 0 \quad etc. \tag{19}$$

then

$$N = \frac{1}{n} \sum_{P,P'} \pm \int P A_1^* P' A_1 \, d\tau_1 \int P B_2^* P' B_2 \, d\tau_2 \cdots\cdots$$

$$= \frac{1}{n} \sum_{P} \int P A_1^* P A_1 \, d\tau_1 \cdot \int P B_2^* P B_2 \, d\tau_2 \cdots\cdots \tag{20}$$

since from orthogonality P must equal P' . There are $n!$ P's and each will give the same value since they differ only in the order of the integrals.

$$\therefore \quad N = \int a_1^* a_1 \, d\tau_1 \cdot \int b_2^* b_2 \, d\tau_2 \cdots\cdots \tag{21}$$

It should be noted that if an orbit function, say a, is occupied by two electrons, with plus and minus spins, then there will be two factors with a in (21).

In polar coordinates:

$$|\operatorname{grad} \psi|^2 = \sum_{i=1}^{N} \left\{ \left| \frac{\partial \psi}{\partial r_i} \right|^2 + \frac{1}{r_i^2} \left| \frac{\partial \psi}{\partial \vartheta_i} \right|^2 + \frac{1}{r_i^2 \sin^2 \vartheta_i} \left| \frac{\partial \psi}{\partial \varphi_i} \right|^2 \right\} \tag{22}$$

Since ψ is antisymmetric,

$$M = n \int \left\{ \left| \frac{\partial \psi}{\partial r_1} \right|^2 + \frac{1}{r_1^2} \left| \frac{\partial \psi}{\partial \vartheta_1} \right|^2 + \frac{1}{r_1^2 \sin^2 \vartheta_1} \left| \frac{\partial \psi}{\partial \varphi_1} \right|^2 \right\} dr \tag{23}$$

But

$$\frac{\partial \psi}{\partial r_1} = \frac{1}{\sqrt{n!}} \sum_{P} \pm P A_{1*} B_2 C_3 \cdots\cdots \tag{24}$$

where

$$X_{1*} = \frac{\partial X}{\partial r_1} \tag{25}$$

$$\therefore \int \left| \frac{\partial \psi}{\partial r_1} \right|^2 d\tau = \frac{1}{n!} \sum_{P,P'} \pm \int P A_{1*}^* B_2^* C_3^* \cdots \quad P' A_{1*} B_2 C_3 \cdots d\tau \tag{26}$$

For non-zero terms, $P = P'$ since all but 1* factors are orthogonal otherwise.

For $P = P'$, there are (n-1)! permutations which leave the same letter with the subscript 1*, all of which give the same value.

$$\therefore M = \sum_R R \int \left\{ A_{1*}^* A_{1*} + \frac{1}{r_1^2} A_{1\circ}^* A_{1\circ} + \frac{1}{r_1^2 \sin^2 \vartheta_1} A_T^* A_T \right\} d\tau_1 \cdot \tag{27}$$

$$\cdot \int B_2^* B_2 \, d\tau_2 \cdot \int C_3^* C_3 \, d\tau_3 \cdots$$

where

$$A_{1\circ} = \frac{\partial A_1}{\partial \vartheta_1} \ ; \quad A_T = \frac{\partial A_1}{\partial \varphi_1} \ \text{etc. for } B_1, C_1 \cdots \tag{28}$$

and R is an operator which interchanges, in turn, each of the functions B, C, etc. with A in the first bracket.

Since

$$V = \sum_{\substack{i,j=1 \\ i<j}}^{n} 1/r_{ij} - Z \sum_{i=1}^{n} 1/r_i \tag{29}$$

$$L = -\sum_{ij} \int \psi^* \psi \frac{1}{r_{ij}} d\tau + Z \sum_{i=1}^{n} \int \psi^* \psi \frac{1}{r_i} d\tau = -C + D \tag{30}$$

Using (18)

$$D = + \frac{Z}{n!} \sum_{i=1}^{n} \sum_{P,P'} \pm \left(P A_1^* B_2^* C_3^* \cdots \left| \frac{1}{r_i} \right| P' A_1 B_2 C_3 \cdots \right) \tag{31}$$

From the same considerations as under N:

$$D = + Z \sum_R R \int A_1^* A_1 \frac{1}{r_1} d\tau_1 \cdot \int B_2^* B_2 \, d\tau_2 \cdot \int C_3 C_3 \, d\tau_3 \cdots \tag{32}$$

where R is an operator shifting 1/r to each factor in turn. There are n terms in this sum.

$$C = \frac{1}{n!} \sum_{ij} \sum_{P,P'} \pm \left(P A_1^* B_2^* C_3^* \cdots \left| \frac{1}{r_{ij}} \right| P' A_1 B_2 C_3 \cdots \right) \tag{33}$$

For every P there will be two P's for which non-zero terms result; one equal to P, and the other differing from P by the single interchange (ij).

$$\therefore \quad \mathcal{C} = \mathcal{C}_1 - \mathcal{C}_2 \tag{34}$$

$$\mathcal{C}_1 = \sum_R R \int A_1^* B_2^* \frac{1}{r_{12}} A_1 B_2 \, d\tau_{1,2} \cdot \int C_3^* C_3 \, d\tau \cdot \int \cdots \tag{35}$$

where R shifts $1/r_{ij}$ to a different <u>pair</u> A_1B_2, A_1C_3, B_2C_3, etc. There are $n(n-1)/2$ terms in the sum.

$$\mathcal{C}_2 = \sum_R R \int A_1^* B_2^* \frac{1}{r_{12}} B_1 A_2 \, d\tau_{1,2} \cdot \int C_3^* C_3 \, d\tau_3 \cdots \tag{36}$$

This is similar to (35) except that the interchange (ij) has been made. Many of these terms are zero because the spins may not match in the interchange integral.

Certain integrals will occur frequently and may be symbolized:

$$\begin{aligned}
&\int a_1^2 \, d\tau_1 = A &\qquad& \int b_1^2 \frac{1}{r_1} \, d\tau_1 = F \\
&\int b_1^2 \, d\tau_1 = B && \int a_1^2 a_2^2 \frac{1}{r_{12}} \, d\tau_{1,2} = G \\
&\int \left(\frac{\partial a_1}{\partial r_1}\right)^2 d\tau_1 = \mathcal{C}' && \int a_1^2 b_2^2 \frac{1}{r_{1,2}} \, d\tau_{1,2} = H' \\
&\int \left(\frac{\partial b_1}{\partial r_1}\right)^2 d\tau_1 = D' && \int a_1 b_1 a_2 b_2 \frac{1}{r_{12}} \, d\tau_{1,2} = J \\
&\int a_1^2 \frac{1}{r_1} \, d\tau_1 = E' && \int b_1^2 b_2^2 \frac{1}{r_{12}} \, d\tau_{1,2} = K
\end{aligned} \tag{37}$$

By using these and applying the general rules just developed, the following expressions for the three-electron problem, configuration $1s^2 2s$, are obtained:

$$\begin{gathered}
N = A^2 B \qquad M = 2\mathcal{C}' A B + D' A^2 \\
L = 2Z \cdot E' A B + Z F' A^2 - B G - 2 A H' + A J.
\end{gathered} \tag{38}$$

For the four-electron problem, configuration $1s^2 2s^2$, these become:

$$N = A^2 B^2 \qquad M = 2A^2 B D' + 2AB^2 C'$$

$$L = 2ZAB^2E' + 2ZA^2BF' - B^2G - A^2K - 4ABH' + 2ABJ. \tag{39}$$

Tables of integrals such as these, with special wave functions, are given in the appendix.

In carrying out a variation treatment, especially for the same atom in successive states of ionization, it is convenient to calculate the numerical values of the integrals A, B, C' etc. separately and combine these numerical values by means of (39) to get the energy, rather than combining the integrals algebraically by (39) and then performing the numerical computation, because most of the same quantities will occur in all of the different ions and do not need to be recalculated, but merely combined in different ways, such as (38) and (39).

XV - APPENDIX. INTEGRAL TABLES.

A - Basic Triple Integrals.

$$I_{\alpha\beta} = \int_0^\infty \int_0^\infty \int_{|r_1-r_2|}^{r_1+r_2} r_1^{\alpha} r_2^{\beta} e^{-b(r_1+r_2)} \, dr_{12} \, dr_1 \, dr_2 \qquad (1)$$

$$I_{\alpha\beta} = \frac{2\alpha!}{b^{\alpha+\beta+3}} \left\{ (\alpha+1)\beta! - \sum_{t=0}^{\alpha} \frac{(\alpha+1-t)(\beta+t)!}{t! \; 2^{\beta+t+1}} \right\}$$

$$I_{\alpha\beta} = I_{\beta\alpha} \qquad \frac{\partial I_{\alpha\beta}}{\partial b} = -\left(I_{\alpha+1,\beta} + I_{\alpha,\beta+1} \right).$$

Special Values of One Parameter

$$I_{\alpha 0} = I_{0\alpha} = \frac{\alpha!}{2^{\alpha} b^{\alpha+3}} \left\{ 2^{\alpha+1} - 1 \right\}$$

$$I_{\alpha 1} = I_{1\alpha} = \frac{\alpha!}{2^{\alpha+1} b^{\alpha+4}} \left\{ 2^{\alpha+3} - \alpha - 5 \right\}$$

$$I_{\alpha 2} = I_{2\alpha} = \frac{\alpha!}{2^{\alpha+2} b^{\alpha+5}} \left\{ 3 \cdot 2^{\alpha+4} - 34 - 11\alpha - \alpha^2 \right\}$$

$$I_{\alpha 3} = I_{3\alpha} = \frac{\alpha!}{2^{\alpha+3} b^{\alpha+6}} \left\{ 24 \cdot 2^{\alpha+4} - 294 - 119\alpha - 18\alpha^2 - \alpha^3 \right\}$$

$$I_{\alpha 4} = I_{4\alpha} = \frac{\alpha!}{2^{\alpha+4} b^{\alpha+7}} \left\{ 15 \cdot 2^{\alpha+8} - 3096 - 1426\alpha - 275\alpha^2 - 26\alpha^3 - \alpha^4 \right\}$$

Special Cases $I_{\alpha\beta} = I_{\beta\alpha}$

$I_{00} = \frac{1}{b^3}$

$I_{10} = 3/2b^4$

$I_{11} = 5/2b^5$

$I_{20} = 7/2b^5$

$I_{21} = 25/4b^6$

$I_{22} = 33/2b^7$

$I_{30} = 45/4b^6$

$I_{31} = 21/b^7$

$I_{32} = 231/4b^8$

$I_{33} = 837/4b^9$

$I_{40} = 93/2b^7$

$I_{41} = 357/4b^8$

$I_{42} = 1011/4b^9$

$I_{43} = 7533/8b^{10}$

$I_{44} = 8685/2b^{11}$

$I_{50} = 945/4b^8$

$I_{51} = 1845/4b^9$

$I_{52} = 10665/8b^{10}$

$I_{53} = 20295/4b^{11}$

$I_{61} = 22545/8b^{10}$

$I_{62} = 16515/2b^{11}$.

$$I_{\alpha\beta} = \int_0^\infty \int_0^\infty \int_{|r_1-r_2|}^{r_1+r_2} e^{-2r_1-2gr_2}\, r_1^{\alpha} r_2^{\beta}\, dr_{12}\, dr_1\, dr_2 \qquad (2)$$

$$I_{\alpha\beta} = \frac{\alpha!}{2^{\alpha+\beta+2}} \left\{ \frac{(\alpha+1)\beta!}{g^{\beta+1}} - \sum_{s=0}^{\alpha} \frac{(\alpha+1-s)(\beta+s)!}{s!\, b^{\beta+s+1}} \right\}$$

$$\text{or} = \frac{\beta!}{2^{\alpha+\beta+2}\, g^{\beta+2}} \left\{ \alpha!\,(\beta+1)! - \sum_{s=0}^{\beta} \frac{g^{s}(\alpha+s)!\,(\beta+1-s)}{s!\, b^{\alpha+1+s}} \right\}$$

where $b = 1+g$; $I_{\alpha,\beta+1} = -\frac{1}{2}\frac{\partial I_{\alpha,\beta}}{\partial g}$

Special Values of One Parameter

$$I_{0\beta} = \frac{\beta!}{2^{\beta+2}} \left\{ \frac{1}{g^{\beta+1}} - \frac{1}{b^{\beta+1}} \right\} ; \quad I_{1\beta} = \frac{\beta!}{2^{\beta+3}} \left\{ \frac{2}{g^{\beta+1}} - \frac{2}{b^{\beta+1}} - \frac{\beta+1}{b^{\beta+2}} \right\}$$

$$I_{2\beta} = \frac{\beta!}{2^{\beta+3}} \left\{ \frac{3}{g^{\beta+1}} - \frac{3}{b^{\beta+1}} - \frac{2(\beta+1)}{b^{\beta+2}} - \frac{(\beta+2)(\beta+1)}{2\, b^{\beta+3}} \right\}$$

$$I_{3\beta} = \frac{3\beta!}{2^{\beta+4}} \left\{ \frac{4}{g^{\beta+1}} - \frac{4}{b^{\beta+1}} - \frac{3(\beta+1)}{b^{\beta+2}} - \frac{(\beta+2)(\beta+1)}{b^{\beta+3}} - \frac{(\beta+3)(\beta+2)(\beta+1)}{6\, b^{\beta+4}} \right\}$$

$$I_{4\beta} = \frac{3\beta!}{2^{\beta+3}} \left\{ \frac{5}{g^{\beta+1}} - \frac{5}{b^{\beta+1}} - \frac{4(\beta+1)}{b^{\beta+2}} - \frac{3(\beta+2)(\beta+1)}{2\, b^{\beta+3}} - \frac{(\beta+3)(\beta+2)(\beta+1)}{3\, b^{\beta+4}} - \frac{(\beta+4)(\beta+3)(\beta+2)(\beta+1)}{24\, b^{\beta+5}} \right\}$$

Special Cases

$$I_{00} = \frac{1}{4}\left\{ \frac{1}{g} - \frac{1}{b} \right\}$$

$$I_{11} = \frac{1}{8}\left\{ \frac{1}{g^2} - \frac{1}{b^2} - \frac{1}{b^3} \right\}$$

$$I_{12} = \frac{1}{16}\left\{ \frac{2}{g^3} - \frac{2}{b^3} - \frac{3}{b^4} \right\}$$

$$I_{13} = \frac{3}{16}\left\{ \frac{1}{g^4} - \frac{1}{b^4} - \frac{2}{b^5} \right\}$$

$$I_{14} = \frac{3}{16}\left\{ \frac{2}{g^5} - \frac{2}{b^5} - \frac{5}{b^6} \right\}$$

$$I_{15} = \frac{15}{16}\left\{ \frac{1}{g^6} - \frac{1}{b^6} - \frac{3}{b^7} \right\}$$

$$I_{16} = \frac{45}{32}\left\{ \frac{2}{g^7} - \frac{2}{b^7} - \frac{7}{b^8} \right\}$$

$$I_{17} = \frac{315}{32}\left\{ \frac{1}{g^8} - \frac{1}{b^8} - \frac{4}{b^9} \right\}$$

$$I_{21} = \frac{1}{16}\left\{ \frac{3}{g^2} - \frac{3}{b^2} - \frac{4}{b^3} - \frac{3}{b^4} \right\}$$

$$I_{22} = \frac{3}{16}\left\{ \frac{1}{g^3} - \frac{1}{b^3} - \frac{2}{b^4} - \frac{2}{b^5} \right\}$$

$$I_{23} = \frac{3}{32}\left\{ \frac{3}{g^4} - \frac{3}{b^4} - \frac{8}{b^5} - \frac{10}{b^6} \right\}$$

$$I_{24} = \frac{3}{16}\left\{ \frac{3}{g^5} - \frac{3}{b^5} - \frac{10}{b^6} - \frac{15}{b^7} \right\}$$

$$I_{25} = \frac{45}{32}\left\{ \frac{1}{g^6} - \frac{1}{b^6} - \frac{4}{b^7} - \frac{7}{b^8} \right\}$$

$$I_{26} = \frac{45}{32}\left\{ \frac{3}{g^7} - \frac{3}{b^7} - \frac{14}{b^8} - \frac{28}{b^9} \right\}$$

$$I_{31} = \frac{3}{16}\left\{ \frac{2}{g^2} - \frac{2}{b^2} - \frac{3}{b^3} - \frac{3}{b^4} - \frac{2}{b^5} \right\}$$

$$I_{32} = \frac{3}{32}\left\{ \frac{4}{g^3} - \frac{4}{b^3} - \frac{9}{b^4} - \frac{12}{b^5} - \frac{10}{b^6} \right\}$$

$$I_{33} = \frac{9}{16}\left\{ \frac{1}{g^4} - \frac{1}{b^4} - \frac{3}{b^5} - \frac{5}{b^6} - \frac{5}{b^7} \right\}$$

$$I_{34} = \frac{9}{32}\left\{ \frac{4}{g^5} - \frac{4}{b^5} - \frac{15}{b^6} - \frac{30}{b^7} - \frac{35}{b^8} \right\}$$

$$I_{35} = \frac{45}{32}\left\{ \frac{2}{g^6} - \frac{2}{b^6} - \frac{9}{b^7} - \frac{21}{b^8} - \frac{28}{b^9} \right\}$$

$$I_{42} = \frac{3}{16}\left\{ \frac{5}{g^3} - \frac{5}{b^3} - \frac{12}{b^4} - \frac{18}{b^5} - \frac{20}{b^6} - \frac{15}{b^7} \right\}$$

$$I_{43} = \frac{9}{32}\left\{ \frac{5}{g^4} - \frac{5}{b^4} - \frac{16}{b^5} - \frac{30}{b^6} - \frac{40}{b^7} - \frac{35}{b^8} \right\}$$

$$I_{44} = \frac{45}{16}\left\{ \frac{1}{g^5} - \frac{1}{b^5} - \frac{4}{b^6} - \frac{9}{b^7} - \frac{14}{b^8} - \frac{14}{b^9} \right\}$$

$$I_{51} = \frac{15}{16}\left\{ \frac{3}{g^2} - \frac{3}{b^2} - \frac{5}{b^3} - \frac{6}{b^4} - \frac{6}{b^5} - \frac{5}{b^6} - \frac{3}{b^7} \right\}$$

$$I_{52} = \frac{45}{32}\left\{ \frac{2}{g^3} - \frac{2}{b^3} - \frac{5}{b^4} - \frac{8}{b^5} - \frac{10}{b^6} - \frac{10}{b^7} - \frac{7}{b^8} \right\}$$

$$I_{53} = \frac{45}{32}\left\{ \frac{3}{g^4} - \frac{3}{b^4} - \frac{10}{b^5} - \frac{20}{b^6} - \frac{30}{b^7} - \frac{35}{b^8} - \frac{28}{b^9} \right\}$$

$$I_{\alpha\beta} = \int_0^\infty \int_0^\infty \int_{|r_1-r_2|}^{r_1+r_2} r_1^{\alpha} r_2^{\beta} e^{-pr_1-qr_2}\, dr_{12}\, dr_1\, dr_2 \qquad (3)$$

$$I_{\alpha\beta} = \frac{2(\alpha+1)!\,\beta!}{p^{\alpha+2}\,q^{\beta+1}} - \frac{2(\alpha+1)!}{p^{\alpha+2}} \sum_{s=0}^{\alpha+1} \frac{p^s(\beta+s)!}{s!\,(p+q)^{\beta+s+1}} + \frac{2\alpha!}{p^{\alpha+1}} \sum_{s=0}^{\alpha} \frac{p^s((\beta+1+s)!}{s!\,(p+q)^{\beta+2+s}}$$

$$I_{\alpha\beta}(p,q) = I_{\beta\alpha}(q,p); \quad I_{\alpha+1,\beta} = -\frac{\partial I_{\alpha\beta}}{\partial p}; \quad I_{\alpha,\beta+1} = -\frac{\partial I_{\alpha\beta}}{\partial q}$$

Special Values of One Parameter

$$I_{1\beta} = \frac{4\beta!}{p^3 q^{\beta+1}} - \frac{4\beta!}{p^3(p+q)^{\beta+1}} - \frac{2(\beta+1)!}{p^2(p+q)^{\beta+2}}$$

$$I_{2\beta} = \frac{12\beta!}{p^4 q^{\beta+1}} - \frac{12\beta!}{p^4(p+q)^{\beta+1}} - \frac{8(\beta+1)!}{p^3(p+q)^{\beta+2}} - \frac{2(\beta+2)!}{p^2(p+q)^{\beta+3}}$$

$$I_{3\beta} = \frac{48\beta!}{p^5 q^{\beta+1}} - \frac{48\beta!}{p^5(p+q)^{\beta+1}} - \frac{36(\beta+1)!}{p^4(p+q)^{\beta+2}} - \frac{12(\beta+2)!}{p^3(p+q)^{\beta+3}} - \frac{2(\beta+3)!}{p^2(p+q)^{\beta+4}}$$

Special Cases

$$I_{11} = \frac{4}{p^3q^2} - \frac{4}{p^3(p+q)^2} - \frac{4}{p^2(p+q)^3} = 4\,\frac{(p+q)^2+pq}{p^2q^2(p+q)^3}$$

$$I_{12} = \frac{8}{p^3q^3} - \frac{8}{p^3(p+q)^3} - \frac{12}{p^2(p+q)^4}$$

$$I_{22} = \frac{24}{p^4q^3} - \frac{24}{p^4(p+q)^3} - \frac{48}{p^3(p+q)^4} - \frac{48}{p^2(p+q)^5}$$

$$I_{13} = \frac{24}{p^3q^4} - \frac{24}{p^3(p+q)^4} - \frac{48}{p^2(p+q)^5}$$

$$I_{23} = \frac{72}{p^4q^4} - \frac{72}{p^4(p+q)^4} - \frac{192}{p^3(p+q)^5} - \frac{240}{p^2(p+q)^6}$$

$$I_{33} = \frac{288}{p^5q^4} - \frac{288}{p^5(p+q)^4} - \frac{864}{p^4(p+q)^5} - \frac{1440}{p^3(p+q)^6} - \frac{1440}{p^2(p+q)^7}$$

B-Integrals Involving Special Wave Functions.

First Type:

$$a = e^{-r}$$
$$b = \alpha r e^{-\eta r} - e^{-\zeta r} + \beta e^{-r}$$
$$c = (\gamma e^{-\chi r} + e^{-\lambda r}) r \cos\vartheta$$

$$h = 1 + \eta \qquad 2k = \eta + \zeta \qquad t = 1 + k \qquad \beta = \frac{8}{g^3} - \frac{24\alpha}{h^4}$$
$$g = 1 + \zeta \qquad 2m = \lambda + \chi$$

1- $A = \int a_1^2\, d\tau_1 = \pi$

2- $E' = \int a_1^2 \frac{1}{r_1}\, d\tau_1 = \pi$

3- $G = \int a_1^2 a_2^2 \frac{1}{r_{12}}\, d\tau_{1,2} = \frac{5}{8}\pi^2$

4- $C' = \int \left(\frac{\partial a_1}{\partial r_1}\right)^2 d\tau_1 = \pi$

5- $B = \int b_1^2\, d\tau_1 = \pi\left\{\alpha^2\left[\frac{3}{\eta^5} - \frac{576}{h^8}\right] + \alpha\left[\frac{384}{g^3h^4} - \frac{3}{k^4}\right] + \left[\frac{1}{\zeta^3} - \frac{64}{g^6}\right]\right\}$

6- $F' = \int b_1^2 \frac{1}{r_1}\, d\tau_1 = \pi\left\{\alpha^2\left[\frac{1}{\eta^4} - \frac{384}{h^7} + \frac{576}{h^8}\right] + \alpha\left[\frac{192}{g^2h^4} - \frac{2}{k^3} + \frac{128}{g^3h^3} - \frac{384}{g^3h^4}\right] + \right.$
$\left. + \left[\frac{1}{\zeta^2} - \frac{64}{g^5} + \frac{64}{g^6}\right]\right\}$

7- $K = \int b_1^2 b_2^2 \frac{1}{r_{12}}\, d\tau_{12}$ See below.

8- $D' = \int \left(\frac{\partial b_1}{\partial r_1}\right)^2 d\tau_1 = \pi\left\{\alpha^2\left[\frac{1}{\eta^3} + \frac{576}{h^8} - \frac{1152\cdot\eta}{h^8} + \frac{384}{h^7}\right] + \right.$
$\left. + \alpha\left[\frac{2\zeta}{k^3} - \frac{3\eta\zeta}{k^4} - \frac{384}{g^3h^4} - \frac{128}{g^3h^3} + \frac{768\cdot k}{g^3h^4}\right] + \left[\frac{1}{\zeta} + \frac{64}{g^6} - \frac{128\zeta}{g^6}\right]\right.$

9- $\int c_1^2\, d\tau_1 = \pi\left\{\frac{1}{\lambda^5} + \frac{2\gamma}{m^5} + \frac{\gamma^2}{\chi^5}\right\}$

10- $\int c_1^2 \frac{1}{r_1}\, d\tau_1 = \pi\left\{\frac{1}{2\lambda^4} + \frac{\gamma}{m^4} + \frac{\gamma^2}{2\chi^4}\right\}$

11- $\int a_1 b_1\, d\tau_1 = 0$ (β as above)

12- $H' = \int a_1^2 b_2^2 \frac{1}{r_{12}}\, d\tau_{1,2} = \pi^2\left\{\alpha^2\left[\frac{1.5}{\eta^4} + \frac{360}{h^8} - \frac{384}{h^7} - \frac{3}{h^5} - \frac{1.5}{h^4} + \frac{384}{h^4(3+\eta)^3}\right.\right.$
$\left. + \frac{1152}{h^4(3+\eta)^4}\right] + \alpha\left[\frac{2}{t^2} - \frac{2}{k^3} + \frac{2}{t^4} - \frac{240}{h^4g^3} + \frac{192}{h^4g^2} - \frac{192}{h^4(3+\zeta)^2} - \frac{384}{h^4(3+\zeta)^3} + \frac{128}{g^3h^3}\right.$
$\left.\left. - \frac{128}{g^3(3+\eta)^3} - \frac{384}{g^3(3+\eta)^4}\right] + \left[\frac{1}{\zeta^2} - \frac{1}{g^2} - \frac{1}{g^3} - \frac{64}{g^5} + \frac{40}{g^6} + \frac{64}{g^3(3+\zeta)^2} + \frac{128}{g^3(3+\zeta)^3}\right]\right\}$

13- $J = \int a_1 b_1 a_2 b_2 \frac{1}{r_{12}}\, d\tau_{1,2} = \pi^2\left\{\alpha^2\left[\frac{360}{h^8} - \frac{252}{h^7} + \frac{384}{h^4(3+\eta)^3} + \frac{1152}{h^4(3+\eta)^4}\right] + \right.$
$+ \alpha\left[\frac{16}{g^3t^3} + \frac{12}{g^2t^4} - \frac{240}{g^3h^4} - \frac{128}{g^3(3+\eta)^3} - \frac{384}{g^3(3+\eta)^4} + \frac{192}{g^2h^4} - \frac{192}{h^4(3+\zeta)^2}\right.$
$\left.\left. - \frac{384}{h^4(3+\zeta)^2}\right] + \left[\frac{20}{g^5} + \frac{40}{g^6} - \frac{64}{g^5} + \frac{64}{g^3(3+\zeta)^2} + \frac{128}{g^3(3+\zeta)^3}\right]\right\}$

$$7-\ K=\int b_1^2 b_2^2 \frac{1}{r_{12}}\, d\tau_{1,2}=\pi^2\Big\{\alpha^4\Big[\frac{837}{256\cdot\eta^9}+\frac{207360}{h^{16}}-\frac{138240}{h^{15}}-\frac{3456}{h^{13}}$$

$$-\frac{1728}{h^{12}}+\frac{1327104}{h^{12}(2+h)^4}+\frac{442368}{h^{12}(2+h)^3}-\frac{1728}{h^8\eta^4}+\frac{55296}{h^8(1+3\eta)^4}+\frac{147456}{h^7(1+3\eta)^5}$$

$$+\frac{184320}{h^6(1+3\eta)^6}\Big]+\alpha^3\Big[-\frac{276480}{g^3h^{12}}-\frac{55296}{g^3h^{11}}+\frac{2304}{g^3h^9}+\frac{1152}{g^3h^8}+\frac{221184}{g^2h^{12}}$$

$$+\frac{1152}{g^3h^4\eta^4}+\frac{2304}{h^8\kappa^3}+\frac{2304}{h^8t^3}+\frac{3456}{h^8t^4}-\frac{9}{\kappa^4\eta^4}+\frac{36864}{g^3h^8t^3}+\frac{27648}{g^2h^8t^4}$$

$$-\frac{442368}{g^3h^8(2+h)^3}-\frac{1327104}{g^3h^8(2+h)^4}-\frac{221184}{h^{12}(2+g)^2}-\frac{442368}{h^{12}(2+g)^3}+\frac{9}{\kappa^4(\kappa+\eta)^4}$$

$$+\frac{24}{\kappa^3(\kappa+\eta)^5}+\frac{30}{\kappa^2(\kappa+\eta)^6}-\frac{18432}{g^3h^4(1+3\eta)^4}-\frac{49152}{g^3h^3(1+3\eta)^5}-\frac{61440}{g^3h^2(1+3\eta)^6}$$

$$-\frac{18432}{g^3h^4(g+2\eta)^4}-\frac{36864}{g^2h^4(g+2\eta)^5}-\frac{36864}{h^8(g+2\eta)^3}-\frac{73728}{h^7(g+2\eta)^4}$$

$$-\frac{73728}{h^6(g+2\eta)^5}\Big]+\alpha^2\Big[\frac{138240}{g^6h^8}+\frac{82944}{g^6h^7}-\frac{384}{g^6h^5}-\frac{192}{g^6h^4}-\frac{192}{g^6\eta^4}$$

$$+\frac{6144}{g^6(g+2\eta)^4}+\frac{33}{8\kappa^7}-\frac{175104}{g^5h^8}+\frac{12288}{g^5(g+2\eta)^5}-\frac{18432}{g^5h^4t^4}-\frac{24576}{g^6h^4t^3}$$

$$-\frac{1152}{g^2h^8}+\frac{1152}{\zeta^2h^8}-\frac{1152}{g^3h^8}-\frac{1536}{g^3h^4\kappa^3}-\frac{1536}{g^3h^4t^3}-\frac{2304}{g^3h^4t^4}+\frac{12288}{g^3h^4(h+2\kappa)^3}$$

$$+\frac{12288}{g^3h^4(g+2\kappa)^3}+\frac{147456}{g^6h^4(2+h)^3}+\frac{442368}{g^6h^4(2+h)^4}+\frac{221184}{g^3h^8(2+g)^2}+\frac{442368}{g^3h^8(2+g)^3}$$

$$+\frac{3}{\zeta^3\eta^4}-\frac{3}{16\zeta^3\kappa^4}-\frac{768}{\zeta^3h^7}-\frac{3}{16\zeta^2\kappa^5}+\frac{768}{\zeta^3h^4(h+2\zeta)^3}+\frac{2304}{\zeta^2h^4(h+2\zeta)^4}+\frac{24576}{g^3h^3(h+2\kappa)^4}$$

$$+\frac{24576}{g^3h^2(h+2\kappa)^5}+\frac{18432}{g^2h^4(g+2\kappa)^4}\Big]+\alpha\Big[-\frac{30720}{g^9h^4}-\frac{16384}{g^9h^3}-\frac{16384}{g^9(2+h)^3}-\frac{49152}{g^9(2+h)^4}$$

$$+\frac{4096}{g^9t^3}+\frac{3072}{g^8t^4}+\frac{43008}{g^8h^4}+\frac{768}{g^6h^4}+\frac{256}{g^6\kappa^3}+\frac{384}{g^6t^4}+\frac{256}{g^6t^3}-\frac{4096}{g^6(g+2\kappa)^3}$$

$$+\frac{768}{g^5h^4}-\frac{6144}{g^5(g+2\kappa)^4}-\frac{73728}{g^6h^4(2+g)^2}-\frac{147456}{g^6h^4(2+g)^3}-\frac{4}{\zeta^3\kappa^3}+\frac{4}{\zeta^3(\zeta+\kappa)^3}+\frac{6}{\zeta^2(\zeta+\kappa)^4}$$

$$+\frac{256}{g^3\zeta^3h^3}-\frac{256}{g^3\zeta^3(h+2\zeta)^3}-\frac{768}{g^3\zeta^2(h+2\zeta)^4}-\frac{3072}{g^3h^4(g+2\zeta)^2}-\frac{3072}{g^2h^4(g+2\zeta)^3}\Big]$$

$$+\Big[\frac{5}{8\zeta^5}+\frac{2560}{g^{12}}-\frac{3072}{g^{11}}-\frac{128}{g^9}+\frac{8192}{g^9(2+g)^2}+\frac{16384}{g^9(2+g)^3}-\frac{128}{g^8}-\frac{128}{g^6\zeta^2}$$

$$+\frac{1024}{g^6(1+3\zeta)^2}+\frac{1024}{g^5(1+3\zeta)^3}\Big]\Big\}$$

Second Type: $a = e^{-r}$

$b = \alpha r e^{-\eta r} + r e^{-\zeta r} + \beta e^{-r}$

$h = 1+\eta \qquad 2k = \eta + \zeta \qquad \beta = -24\left\{\frac{\alpha}{h^4} + \frac{1}{g^4}\right\}$

$g = 1+\zeta \qquad t = 1+k$

A, E', G, C' - p 59

$B = \pi\left\{\alpha^2 B''(\eta) + \alpha B'(\eta,\zeta) + B^{0}(\zeta)\right\}$ etc. for F, D

But $B''(x) = B^{0}(x)$; $B'(\eta,\zeta) = B'(\zeta,\eta)$

5- $B = \int b_1^2 \, d\tau_1$; $B''(\eta) = \frac{3}{\eta^5} - \frac{576}{h^8}$; $B'(\eta,\zeta) = \frac{6}{k^5} - \frac{1152}{h^4 g^4}$

6- $F = \int b_1^2 \frac{1}{r_1} \, d\tau_1$; $F''(\eta) = \frac{1.5}{\eta^4} - \frac{384}{h^7} + \frac{576}{h^8}$; $F'(\eta,\zeta) = \frac{3}{k^4} - \frac{384}{h^3 g^4} - \frac{384}{h^4 g^3} + \frac{1152}{g^4 h^4}$

7- $K = \int b_1^2 b_2^2 \frac{1}{r_{12}} \, d\tau_{1,2}$ see next page.

8- $D' = \int \left(\frac{\partial b_1}{\partial r_1}\right)^2 d\tau_1$; $D''(\eta) = \frac{1}{\eta^3} + \frac{960}{h^7} - \frac{1728\eta}{h^8}$; $D'(\eta,\zeta) = \frac{960}{h^3 g^4} - \frac{4}{k^3} + \frac{6\eta\zeta}{k^5} +$

$+ \frac{960}{h^4 g^3} - \frac{3456k}{h^4 g^4}$.

11- $\int a_1 b_1 \, d\tau_1 = 0$ $\quad\beta$ as above.

12- $H = \int a_1^2 b_2^2 \frac{1}{r_{12}} \, d\tau_{1,2} = \pi^2\left\{\alpha^2 H''(\eta) + \alpha H'(\eta,\zeta) + H''(\zeta)\right\}$

$H''(\eta) = \frac{1.5}{\eta^4} + \frac{360}{h^8} + \frac{384}{h^4(2+h)^3} + \frac{1152}{h^4(2+h)^4} - \frac{1.5}{h^4} - \frac{3}{h^5} - \frac{384}{h^7}$.

$H'(\eta,\zeta) = \frac{3}{k^4} + \frac{720}{h^4 g^4} + \frac{384}{h^4(2+g)^3} + \frac{384}{g^4(2+h)^3} + \frac{1152}{h^4(2+g)^4} +$

$\frac{1152}{g^4(2+h)^4} - \frac{3}{t^4} - \frac{6}{t^5} - \frac{384}{h^3 g^4} - \frac{384}{h^4 g^3}$.

13- $J = \int a_1 b_1 a_2 b_2 \frac{1}{r_{12}} \, d\tau_{1,2} = \pi^2\left\{\alpha^2 J''(\eta) + \alpha J'(\eta,\zeta) + J''(\zeta)\right\}$

$J''(\eta) = \frac{360}{h^8} - \frac{252}{h^7} + \frac{384}{h^4(2+h)^3} + \frac{1152}{h^4(2+h)^4}$.

$J'(\eta,\zeta) = -\frac{48}{g^4 t^3} - \frac{48}{g^3 t^4} - \frac{24}{g^2 t^5} + \frac{384}{g^4(2+h)^3} + \frac{1152}{g^4(2+h)^4}$

$- \frac{384}{h^4 g^3} + \frac{384}{h^4(2+g)^3} + \frac{1152}{h^4(2+g)^4} + \frac{720}{h^4 g^4}$.

$$7\text{-}\quad K = \int b_1^2 b_2^2 \frac{1}{r_{1,2}}\, d\tau_{1,2} = \pi^2\left\{\alpha^4 K''''(\eta) + \alpha^3 K'''(\eta,\xi) + \alpha^2 K''(\eta,\xi) + \alpha K' + K^{\circ}(\xi)\right\}$$

$$K''''(x) = K^{\circ}(x)\quad ; \quad K'''(\eta,\xi) = K'(\xi,\eta)\quad ; \quad K''(\eta,\xi) = K''(\xi,\eta)$$

$$K''''(\eta) = \Big[\frac{837}{256\cdot\eta^9} + \frac{207360}{h^{16}} - \frac{138240}{h^{15}} - \frac{3456}{h^{13}} - \frac{1728}{h^{12}}$$

$$+ \frac{1{,}327{,}104}{h^{12}(2+h)^4} + \frac{442{,}368}{h^{12}(2+h)^3} - \frac{1728}{h^8\eta^4} + \frac{55296}{h^8(1+3\eta)^4} + \frac{147456}{h^7(1+3\eta)^5}$$

$$+ \frac{184320}{h^6(1+3\eta)^6}\Big] = K^{\circ}(\eta)$$

$$K'''(\eta,\xi) = \frac{18}{\eta^5 k^4} - \frac{18}{\eta^5(\eta+k)^5} - \frac{54}{\eta^4(\eta+k)^5} - \frac{90}{\eta^3(\eta+k)^6} - \frac{90}{\eta^2(\eta+k)^7}$$

$$+ \frac{55296}{h^4 g^4(g+2\eta)^4} + \frac{147456}{h^4 g^3(g+2\eta)^5} + \frac{184320}{h^4 g^2(g+2\eta)^6} + \frac{55296}{h^4 g^4(h+2\eta)^4} + \frac{147456}{h^3 g^4(h+2\eta)^5}$$

$$+ \frac{184320}{h^2 g^4(h+2\eta)^6} + \frac{110592}{h^8(h+2k)^4} + \frac{294912}{h^7(h+2k)^5} + \frac{1327104}{h^8 g^4(2+h)^3} + \frac{3981312}{h^8 g^4(2+h)^4}$$

$$+ \frac{442368}{h^{12}\, g^3} + \frac{442368}{h^{12}(2+g)^3} + \frac{1327104}{h^{12}(2+g)^4} + \frac{829440}{h^{12} g^4} - \frac{3456}{\eta^4 h^4 g^4}$$

$$- \frac{3456}{g^4 h^8} - \frac{6912}{g^4 h^9} - \frac{3456}{h^8 k^4} - \frac{368640}{h^6(g+2\eta)^6} - \frac{110592}{h^{12} t^3}$$

$$- \frac{110592}{h^{11} t^4} - \frac{55296}{h^{10} t^5} - \frac{718848}{h^{11} g^4} - \frac{3456}{h^8 t^4} - \frac{6912}{h^8 t^5}\,.$$

$$K''(\eta,\xi) = K''(\xi,\eta) = 13.078125/k^9 + \frac{55296}{g^8(g+2\eta)^4} + \frac{9}{\eta^5\xi^4} + \frac{147456}{g^7(g+2\eta)^5}$$

$$+ \frac{184320}{g^6(g+2\eta)^6} + \frac{55296}{h^8(h+2\xi)^4} + \frac{147456}{h^7(h+2\xi)^5} + \frac{184320}{h^6(h+2\xi)^6} + \frac{1327104}{g^4 h^8(2+g)^3}$$

$$+ \frac{3981312}{g^4 h^8(2+g)^4} + \frac{1327104}{g^8 h^4(2+h)^3} + \frac{3981312}{g^8 h^4(2+h)^4} + \frac{1244160}{g^8 h^8} + \frac{110592}{g^4 h^4(g+2k)^4}$$

$$+ \frac{294912}{g^3 h^4(g+2k)^5} - \frac{138240}{g^7 h^8} + \frac{368640}{g^2 h^4(g+2k)^6} + \frac{110592}{g^4 h^4(h+2k)^4}$$

$$+ \frac{294912}{g^4 h^3(h+2k)^5} + \frac{368640}{g^4 h^2(h+2k)^6} - \frac{138240}{g^8 h^7} - \frac{0.5625}{\eta^5 k^4} - \frac{0.84375}{\eta^4 k^5}$$

$$- \frac{0.703125}{\eta^3 k^6} - \frac{0.3515625}{\eta^2 k^7} - \frac{1728}{\xi^4 h^8} - \frac{1728}{g^4 h^8} - \frac{3456}{g^5 h^8} - \frac{1728}{\eta^4 g^8}$$

$$- \frac{110592}{g^4 h^8 t^3} - \frac{110592}{g^4 h^7 t^4} - \frac{55296}{g^4 h^6 t^5} - \frac{1728}{g^8 h^4} - \frac{3456}{g^8 h^5} - \frac{6912}{g^4 h^4 k^4}$$

$$- \frac{6912}{g^4 h^4 t^4} - \frac{13824}{g^4 h^4 t^5} - \frac{110592}{g^8 h^4 t^3} - \frac{110592}{g^7 h^4 t^4} - \frac{55296}{g^6 h^4 t^5}\,.$$