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Analytic Atomic Wave Functions

By J. C. SLATER
Massachusetts Institute of Technology

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A method is suggested for setting up analytic atomic wave functions which form good approximations to Hartree's functions. These functions are of the form $\Sigma c r^n e^{-ar}$, where the exponent a as well as c and n vary from one term to another. The constants are determined for 1, 2, and 3-quantum electrons by fitting Hartree's values numerically for five selected atoms, and interpolation methods are presented for dealing with the intermediate atoms. A method is suggested for setting up exactly orthogonal functions, with no loss of accuracy. It is shown that the analytic wave functions are the solutions of central field problems in which the field is slightly different for different quantum numbers, on account of the inaccuracy in the function, but a table shows that the discrepancy between this and the correct field is small over the region where the wave function is large. Suggestions are made for future work, on the one hand in extending the tables, on the other in using the wave functions in investigating atomic energies, exchange integrals, etc.

FOR any detailed calculations dealing with atomic or molecular structure, good approximations to the atomic wave functions are essential. The most satisfactory method, in general, for building up such functions seems to be by the use of one-electron functions which are solutions of the problem of an electron moving in a central field, setting up sums of products of such functions, antisymmetric in the electrons. But no completely satisfactory set of one-electron functions has been developed. It is the purpose of this paper to suggest a considerable improvement in such functions.

The best one-electron functions which we have are those of Hartree.[1] It is to be regretted that these functions are not in more accessible form; but they have been computed, by Hartree or his collaborators, for the atoms He, Li$^+$, Be^{++}, Be, B^{+++}, O^{+++}, O^{++}, O$^+$, O, F$^-$, Ne, Na$^+$, Al^{+++}, Al$^+$, Si^{+4}, Cl$^-$, A, K$^+$, Ca^{++}, Cu$^+$, Rb$^+$, Cs$^+$. It has been shown by the writer and by Fock[2] that these are the best one-electron functions which can be set up, if we neglect exchange terms, and it is to be presumed that the corrections made by introducing exchange would be small. We should state at the outset that the functions suggested in this paper are no improvement on Hartree's in the matter of accuracy; they are in fact somewhat inferior, but are much more convenient. For there are two important points in which Hartree's functions are far from satisfactory. First, and most important, they exist only as tables of values, and as such cannot be used for any analytical calculations. Second, the functions for different quantum numbers with the same atom are not exactly orthogonal to each other, and this introduces great complications when

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[1] D. R. Hartree, Proc. Camb. Phil. Soc. **24,** 89, 111 (1928) and later papers by Hartree and others. For Si^{+4}, J. McDougall, Proc. Roy. Soc., to appear shortly. I am much indebted to Dr. Hartree for the list of atoms whose structure has been investigated, and for tables of values of wave functions.

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

calculations using antisymmetric combinations are made. Our present functions are analytical approximations to Hartree's functions, modified to make them orthogonal.

Among analytic wave functions, two types may be mentioned as extreme examples. First, Pauling[3] has used hydrogen-like functions of the form $e^{-Zr/n}$ times polynomial in r, the coefficients of the polynomial being given as for a hydrogen problem with nuclear charge Z. He has set up a set of screening constants, giving Z for each electron of each atom. By comparison of one of Pauling's functions with the corresponding one of Hartree's (see Fig. 1), we see that the nodes in Pauling's functions lie at too large values of r. The reason is that the nodes get closer together for large Z. Now the nodes lie in any case at smaller values of r than the principal, outer maximum of the function, and in an actual atom this region near the nucleus has a larger effective Z than the range around the maximum, compressing the nodes; while Pauling uses a constant Z all over the wave function. On account of this behavior of the nodes, Pauling's functions are rather badly in error.

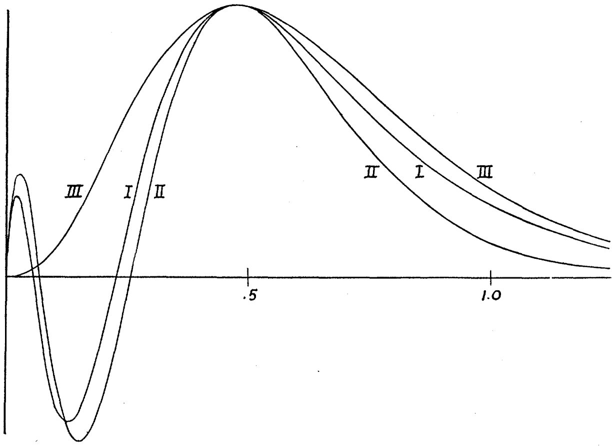

Fig. 1. Wave functions for Rb$^+$ 3s. I. Present wave function. On this scale, Hartree's curve departs from this by negligible amounts. II. Hydrogen-like curve. III. Single term r^3e^{-ar}. Constants for II and III are chosen so as to make all curves coincide at the maximum, rather than to agree with the screening constants of Pauling and the writer, respectively.

The other extreme in the way of wave functions was suggested by the writer.[4] These functions were of the form $r^{n-1}e^{Zr/n}$, without any nodes at all. It is plain that the correct wave functions, having nodes larger than in the writer's functions, but smaller than in Pauling's, lie between these two sets. In all these sets of functions, the maxima are so adjusted that they approximately agree in position.

ANALYTICAL EXPRESSION FOR WAVE FUNCTIONS

As a method of improving these functions, one may proceed according to the following line of thought. A 3s function for instance, has a wave function

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[3] L. Pauling, Proc. Roy. Soc. **A114**, 181 (1927).

[4] J. C. Slater, Phys. Rev. **36**, 57 (1931).

in hydrogen (multiplied by r) of the form $e^{-Zr/3}(r^3-ar^2+br)$, where a and b are definitely determined. The three terms of this correspond roughly to the outer, middle, and inner maxima of the function: $e^{-Zr/3}\, r^3$ has its maximum at $9/Z$; the next term has its maximum at $6/Z$, and the inner one at $3/Z$. But now really the middle maximum lies in a range of larger Z then the outer one, and the inner maximum has still higher Z. Let us then use different Z's for each maximum, taking a function of the form $r^3e^{-Z_1r/3}-a'r^2e^{-Z_2r/3}+b're^{-Z_3r/3}$, where a', b' are no longer the same as a and b. The maxima will then lie at $9/Z_1$, $6/Z_2$, $3/Z_3$, and if Z_2, Z_3 are much larger than Z_1, the inner maxima, and hence the nodes, will lie much further in than with the hydrogen-like function of Pauling. It is now actually found that functions of this form, as for example $c_1re^{-a_1r}-c_2r^2e^{-a_2r}+c_3r^3e^{-a_3r}$, can form good representations of Hartree's functions, by proper choice of constants.

One further refinement of these functions proves to be necessary, if we are to get really satisfactory agreement with Hartree's functions. This can be seen most clearly from the $3d$ function, for which our method would give

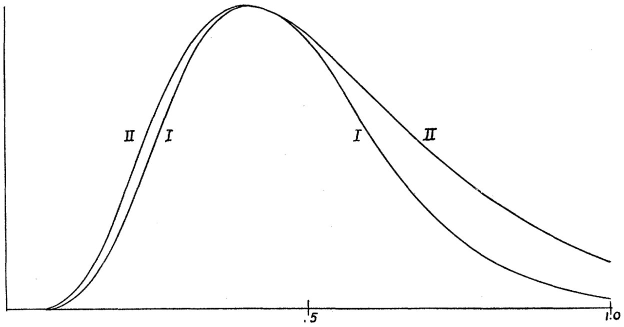

Fig. 2. Wave functions for Rb$^+$ $3d$. I. Hydrogen-like curve. II. Present wave function, agreeing with Hartree's curve.

r^3e^{-ar}. This has but one parameter, a, and if it is chosen to make the maximum agree with that of Hartree's curve, the general form of the curve is evidently wrong, as we may see from Fig. 2. Hartree's function falls off much more slowly for large r. The reason is clear; in the outer part of the orbit, the effective Z is smaller, resulting in a more gradual change of the function. This can be remedied by using two exponentials connected with the same power of r, as $r^3(c_1e^{-a_1r}+c_2e^{-a_2r})$, the smaller exponent giving the outer part of the function, the larger one the inner part. It is found that this gives a good representation, except for Cu$^+$, where the $3d$ electrons lie at the outside of the atom. There the effect is so pronounced that three exponentials are necessary, and it was found that even as far along as Rb three exponentials improve the agreement, though they are not so necessary. Now the $3d$ is an extreme case, but for the other orbits as well it was found helpful to use two exponentials for the outer maximum, though not for the inner ones. The only wave functions represented sufficiently well without this were the $1s$ and $2s$. Thus for $3s$ we should use a function $c_1re^{-a_1r}-c_2r^2e^{-a_2r}+r^3(c_3e^{-a_3r}+c_4e^{-a_4r})$. Such a function is capable of representing Hartree's solutions with very good accuracy. We give in Table I three examples of agreement between such analytical functions and Hartree's tables of values.

TABLE I. *Comparison of analytic functions with Hartree's for 2s, 3s, and 3d electrons of* Rb^+.

r	2s		3s		3d	
	Hartree	*Anal.*	*Hartree*	*Anal.*	*Hartree*	*Anal.*
0.01	0.679	0.695	0.678	0.637	0.001	0.001
0.02	0.882	0.896	0.874	0.846	0.006	0.005
0.03	0.796	0.795	0.772	0.736	0.019	0.014
0.04	0.546	0.538	0.504	0.480	0.040	0.031
0.06	−0.138	−0.156	−0.211	−0.209	0.108	0.088
0.08	−0.795	−0.825	−0.867	−0.854	0.207	0.176
0.10	−1.290	−1.300	−1.308	−1.292	0.329	0.289
0.12	−1.601	−1.602	−1.492	−1.495	0.466	0.420
0.14	−1.752	−1.747	−1.476	−1.478	0.623	0.562
0.16	−1.777	−1.773	−1.276	−1.282	0.752	0.709
0.18	−1.715	−1.709	−0.954	−0.965	0.889	0.853
0.20	−1.597	−1.597	−0.557	−0.574	1.017	0.989
0.25		−1.213	0.540	0.519	1.284	1.278
0.30	−0.827	−0.842	1.508	1.496	1.462	1.468
0.35	−0.535	−0.546	2.198	2.199	1.556	1.575
0.40	−0.333	−0.340	2.600	2.611	1.583	1.601
0.45	−0.202	−0.205	2.763	2.786		1.570
0.5	−0.120	−0.121	2.750	2.778	1.505	1.498
0.6	−0.041	−0.039	2.416	2.441	1.335	1.316
0.7	−0.013	−0.012	1.927	1.950	1.138	1.107
0.8	−0.004	−0.004	1.449	1.472	0.944	0.915
0.9	−0.001	−0.001	1.052	1.070	0.767	0.748
1.0			0.742	0.762	0.614	0.606
1.2			0.350	0.364	0.382	0.386
1.4			0.160	0.165	0.230	0.235
1.6			0.072	0.071	0.137	0.139
1.8			0.032	0.030	0.080	0.079
2.0			0.014	0.012	0.047	0.045

METHOD OF DETERMINING CONSTANTS

After choosing a form of analytical wave function, at least two methods are available for determining the constants. One would be to construct a wave function for the whole atom from such functions, and determine the constants by the variation method, minimizing the whole energy. This would be a very interesting method, essentially that which Zener[5] has used on the light atoms, except that Zener did not use our wave functions with the adjustable exponents. The second method, however, is simpler and more available, and that is to choose the functions to fit Hartree's curves as well as possible. This was the method adopted. Dr. Hartree very kindly supplied the complete tables of wave functions of the five atoms Si^{+4}, K^+, Cu^+, Rb^+, Cs^+, and these were fitted by numerical methods. The two schemes should, of course, arrive at substantially the same results. In the present paper, the coefficients and exponents are given for the 1, 2, and 3 quantum electrons of these atoms. They are tabulated in Table II, and plotted in Fig. 3.

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[5] C. Zener, Phys. Rev. **36**, 51 (1930); Guillemin and Zener, Zeits. f. Physik **61**, 199 (1930).

TABLE II. *Exponents in analytic wave functions for five atoms.*

Explanation: The wave function for a 1s electron (multiplied by r) is re^{-ar}, where a is tabulated. For a 2s, it is $re^{-ar}-cr^2e^{-br}$ where a and b are tabulated (for example, for Si^{+4}, $a=12.25$, $b=4.53$). For a 3s, it is $re^{-ar}-cr^2e^{-br}+r^3(de^{-fr}+ge^{-hr})$, where for example in K^+, $a=15.35$, $b=5.89$, $f=3.27$, $h=2.30$. The coefficients are determined for orthogonal functions as follows: c in the 2s is determined to make 2s orthogonal to 1s; in 3s, d and g are related by the condition that $de^{-fr}=ge^{-hr}$ for $r=3/2.67$ (where 2.67 is in the column "3s intersection," and c, and d, are determined to make the 3s orthogonal to 1s and 2s.

For a 2p, the function is $r^2(ae^{-br}+ce^{-dr})$, where the exponents are given by the entries "2p inner" and "2p outer," and the relation between coefficients is such that the terms are equal when $r=2/$"2p intersection." For 3p, we have $r^2e^{-ar}-r^3(be^{-cr}+de^{-fr})$. For 3$d$, in Cu^+ and Rb^+, the functions are $r^3(ae^{-br}+ce^{-dr}+fe^{-gr})$, where the exponents are tabulated, and also the values "3d inner intersection" and "3d outer intersection" from which the corresponding r's are the values where the first two, or last two, exponentials are equal.

The curves are sufficiently straight so that linear interpolations between adjacent atoms should be fairly good. But extrapolations are dangerous, since the curves break at the completion of shells of electrons.

The constants as given do not suffice to describe the functions agreeing with Hartree's curves, but only the slightly different orthogonal functions.

Power of r	Orbit	Si^{+4}	K^+	Cu^+	Rb^+	Cs^+
r	1s	13.70	18.70	28.70	36.70	54.70
	2s	12.25	16.00		30.00	44.02
	3s		15.35	21.62	25.30	31.70
r^2	2s	4.53	6.67		14.80	23.03
	3s		5.89	10.35	13.40	19.92
	2p inner	6.00	8.98	14.69	18.80	27.95
	2p intersection	4.56	7.12	12.11	16.10	24.41
	2p outer	3.59	5.77	10.10	13.67	21.85
	3p		7.05	12.32	15.78	23.00
r^3	3s inner		3.27	6.62	9.17	15.76
	3s intersection		2.67	4.68	6.40	11.27
	3s outer		2.30	4.19	6.02	11.10
	3p inner		2.99	5.84	8.21	14.25
	3p intersection		1.72	3.55	5.43	10.66
	3p outer		1.72	3.57	5.54	10.60
	3d inner			6.29	9.20	15.46
	3d inner intersection			3.78	5.55	10.62
	3d middle			2.65	4.74	10.10
	3d outer intersection			1.15	1.12	
	3d outer			1.28	2.60	

The actual methods used for fitting Hartree's functions may be of interest. Suppose we wish to fit a 3s function, and that by interpolation or otherwise we can get first, rough estimates of the terms. Then first we subtract the estimated values of the terms in r and r^2 from Hartree's function, leaving approximately the term which should be represented by r^3 times the sum of two exponentials. We divide the difference by r^3, take the logarithm to base two exponentials. We divide the difference by r^3, take the logarithm to base 10, for convenience. The result would give a straight line if one exponential were enough. As it is, however, the line is likely to be bent sharply at small r's, on account of inaccurate estimates of the terms in r and r^2; this can be disregarded. But more important, the line as a whole is curved, and must be represented, not by one term a^{-br}, but by two, in the form $\log_{10}(10^{a-br}+10^{c-dr})$. The graph of this function has two asymptotes, the straight lines $a-br$ and $c-dr$; at the point where these lines cross, the graph lies a distance $\log_{10} 2$ above the intersection. We can make a further useful set of observations: where one line is, for example, 0.1 above the other, the graph lies a distance $\log_{10}(1+10^{-0.1})=0.2539$ above the upper straight line, and 0.3539 above the lower. Using a table constructed according to this model, making use of the positions of the asymptotes, and making a few trials, we may readily get the constants a, b, c, d. Then we compute the term $r^3(10^{a-br}+10^{c-dr})$, subtract it and the approximate first term from Hartree's curve, and get the term which should be represented by $r^2\,10^{e-fr}$. Dividing by r^2 and plotting the logarithm, we find a straight line, from which e and f are determined. Finally we subtract the difference of the correct second and third terms from Hartree's function, divide by r and take the logarithm, and read off from this straight line the coefficient and exponent of the term in r. If the original estimates were far wrong, the process can be repeated, yielding good results fairly rapidly. The final straight lines turn out in all cases to be remarkably straight. The same method can be used on all the functions. It was found in many cases that the constants were by no means uniquely determined. It was possible to choose sets of constants varying over quite a wide range, giving equally good agreement with the curve. In these cases, constants were chosen to give smooth curves of exponents against atomic number, as described in the next section.

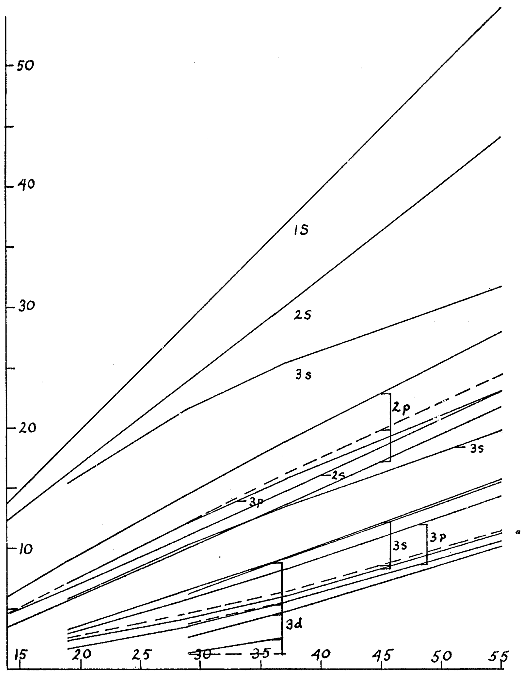

Fig. 3. Diagram of exponents and coefficients as function of atomic number. Drawn from the data of Table II, with linear interpolation. See Table II for explanation. The curves for intersections are drawn with dotted lines.

INTERPOLATION METHODS; ORTHOGONALITY OF WAVE FUNCTIONS

The wave functions for five isolated atoms would be of small value; the real use of the present method is that it provides a means of interpolation, by which wave functions of intermediate atoms can be found. The interpolation can be thrown into a form suggesting Moseley curves of x-ray term values. The reason is that the exponent Z/n, is of the same form as the square root of an x-ray term, which is plotted in those diagrams. In Fig. 3 we show the exponents as functions of atomic number, giving approximately straight lines, but breaking for the outer electrons when shells are completed, as in x-ray diagrams. Not only the exponents, but some of the coefficients as well, can be put in this form. Thus in an expression $r^n(ce^{-ar}+de^{-br})$, which we have in the outer parts of the wave functions, we may compute the value r_0 for which the two exponentials are equal: $c\,e^{-ar_0}=de^{-br_0}$. This point generally proves to be between the maxima of the two exponentials. Now these maxima come for $r=n/a$, and n/b, respectively. Thus we can define a quantity, analogous to a and b, equal to n/r_0, which will lie generally between a and b, and will fall on the interpolation diagram just as the exponents themselves do. These quantities are plotted in Fig. 3. We discuss the other coefficients in the next paragraph.

The functions of Hartree, which we approximate, are not exactly orthogonal, as we mentioned above. Thus if we use our analytical expressions for Hartree's functions, we find that $(1s, 2s)$ (meaning by this the integral of the product of the functions) for Rb^+ is 0.0072, $(1s, 3s)$ is -0.0078, $(2s, 3s)$ is -0.0015, showing that the departure from orthogonality is of the order of a percent. Now when one constructs antisymmetric wave functions in the form of determinants, one has a certain freedom in choosing the one-electron functions entering into it. The reason is that the determinant has the same value, apart from a constant factor, if the elements of each row (or column) are replaced by arbitrary linear combinations of the corresponding elements of the other rows. For example, the determinant

$$\begin{vmatrix} 1s(1) & 1s(2) & 1s(3) \\ 2s(1) & 2s(2) & 2s(3) \\ 3s(1) & 3s(2) & 3s(3) \end{vmatrix}$$

has the same value as

$$\begin{vmatrix} 1s(1) & 1s(2) & 1s(3) \\ 2s(1)+a1s(1) & 2s(2)+a1s(2) & 2s(3)+a1s(3) \\ 3s(1)+b2s(1)+c1s(1) & 3s(2)+b2s(2)+c1s(2) & 3s(3)+b2s(3)+c1s(3) \end{vmatrix}$$

except for a constant factor which drops out on normalizing. As a result, we shall have the same wave function for an atom if, instead of using Hartree's one-electron wave functions, we use a set constructed after the following model: For $1s$: Hartree's $1s$; for $2s$: Hartree's $2s+$constant times his $1s$; for $3s$: Hartree's $3s+$constant times $2s+$constant times $1s$, and so on. And here the constants can be so chosen as to make the resulting functions orthogonal. Thus a set of orthogonal functions can be set up, similar to Hartree's, and giving just the same atomic wave function as Hartree's.

From our analytic functions, we can proceed in a very similar way to set up orthogonal functions. For the correct $2s$, we should subtract some of our $1s$ from the $2s$ as determined from Hartree's function. But the $1s$ is so nearly the same as the inner term of the $2s$, that we can subtract some of that instead. In other words, we merely change the coefficient of the term in r, to make the function orthogonal to $1s$. Similarly, in the $3s$ function, we can change the coefficients of the terms in r, r^2 to get orthogonality with both $1s$ and $2s$. It is easily seen that conditions of this sort give just enough equations to determine all the coefficients of our final orthogonal functions. We thus have the following rule: we use orthogonal wave functions of the form $c_1 r e^{-a_1 r} - c_2 r^2 e^{-a_2 r} + \cdots$, where the coefficients are so chosen that the functions are all orthogonal (and of course normalized). The exponents are taken from our interpolation graph. In this process, the sum of exponentials occurring in the outer maximum is treated as a single term. Of course, this rule applies to the part of the wave function which is a function of r; it is to be multiplied by the proper spherical harmonic of the angle.

As an example, let us choose the s states of Rb. For $1s$ the exponent from the graph is 36.70. Thus the function is $cre^{-36.70r}$, and if we normalize to unity, we have $c^2\int r^2 e^{-73.40r}dr = 1 = c^2\, 2!/(73.40)^3$, $c = 444.7$. Next, for the $2s$, we have $c_1 r e^{-30.00r} - c_2 r^2 e^{-14.80r}$. For orthogonality, the integral of the product of this with $re^{-36.70r}$ must be zero:

$$c_1\int r^2 e^{-66.70r}dr - c_2\int r^3 e^{-51.50r}dr = 0,\ c_2/c_1 = (51.5)^4/3(66.7)^3 = 7.903.$$

Finally for normalization we have

$$c_1^2\int r^2 e^{-60.0r}dr - 2c_1c_2\int r^3 e^{-44.8r}dr + c_2^2\int r^4 e^{-29.6r}dr$$
$$= 1,\ c_1^2\{2/(60.0)^3 - 2c_1c_2 6/(44.8)^4 + c_2^2 24/(29.6)^5\} = 1.$$

Solving these simultaneously gives $c_1 = 139.1$, $c_2 = 1099$. Lastly, for the $3s$ we have $c_1 r e^{-25.30r} - c_2 r^2 e^{-13.40r} + r^3(c_3 e^{-8.97r} + c_4 e^{-6.02r})$. The value giving the intersection of the last two is 6.40, so that $c_3 e^{-8.97\times 3/6.40} = c_4 e^{-6.02\times 3/6.40}$, giving $c_4 = 0.2512\ c_3$. Then applying the conditions of orthogonality with $1s$ and $2s$, and normalizing, we find $c_1 = 49.65$, $c_2 = 534.8$, $c_3 = 572.5$, $c_4 = 143.8$, determining the function completely.

Differential Equation Satisfied by the Wave Function

It is interesting to consider what differential equation is satisfied by our analytical wave functions. Let us write the function $u = \Sigma u_n = \Sigma c_n r^n e^{-a_n r}$, times function of angle, where we may have more than one term for a given exponent n. This can be written as the solution of an equation $Hu = Eu$, where $H = -\nabla^2 - 2Z(r)/r$, provided $Z(r)$ is properly chosen; for to get it we need only set $Z(r)=-(r/2)\ (\nabla^2 u/u+E)$. Computing the derivatives, we have $\nabla^2 u=\Sigma([n(n-1)-l(l+1)]/r^2-2a_n n/r+a_n^2)u_n$, where l is the azimuthal quantum number, from which $Z(r)$ can be at once computed, if we assume a value of E. Since our functions are essentially the same as Hartree's, and since his are solutions of central field problems for which he has found the energy values, we take those values for E. We give in Table III for illustration the resulting values of $Z(r)$ for the 3-quantum orbits of Rb, computed for each wave function. We see that they are all different, as they naturally would be since we have not a real solution of a single central field problem. On the other hand, the curves agree with each other over wide ranges of variables, in fact over the whole range where the individual wave functions are large. Not only that, but they agree well with what we should expect from Hartree's calculations. We give also in Table III the values calculated from Hartree's field, representing the $Z(r)$ which, divided by r, gives the potential in which a 3-quantum electron moves (strictly different for $3s$, $3p$, $3d$, but nearly enough the same so that we can use a sort of average).

TABLE III. *Effective nuclear charge for 3-quantum electrons of Rb, compared with Hartree's value.***

r	Z Hartree	Z $3s$	Z $3p$	Z $3d$
0.01	35.14	34.94		
0.02	33.56	32.97	31.49	
0.03	32.16	32.86		
0.04	30.89	32.75*	29.99	
0.06	28.65	23.47	28.38	
0.08	26.69	25.59	26.84	
0.10	24.92	24.56	25.34	22.40
0.15	21.41	21.57	22.09	
0.2	18.73	19.62*	— —*	18.59
0.3	14.64	14.44	14.56	15.04
0.4	11.66	11.70	11.60	11.95
0.5	9.55	9.63	9.54	9.53
0.6	8.06	8.12	8.10	7.78
0.7	7.05	7.22	7.05	6.64
0.8	6.29	6.30	6.26	5.97
0.9	5.66	5.80	5.68	5.68
1.0	5.12	5.38	5.16	5.32
1.2	4.25	4.71	4.35	4.77
1.4	3.60	4.07	3.61	4.00
1.6	3.12	3.27	2.84	3.15
1.8	2.77	2.23	1.93	2.34
2.0	2.52	1.34	0.96	1.71
2.5	2.19	−1.96	−2.00	1.60
3.0	2.07	−5.41	−5.26	4.09

** An electron moving in the field of potential $-2Z/r$, where Z has the tabulated value, would have just the analytic wave functions we have found. Asterisks mark the nodes, at which particularly large errors of Z are found.

On a graph of $Z(r)$ it is easily shown that a hydrogen-like curve, as used by Pauling, is represented by a straight line, and a single exponential term, as used by the writer, by a parabola-like curve opening downward. Obviously both of these are far less accurate than the functions of the present paper. The principal inaccuracies in our present values come at the nodes of the functions (where, since u appears in the denominator, a very small error in the position of the node can result in a behavior of the Z curve resembling anomalous dispersion), and at large r's , where the curves approach straight lines which generally are not horizontal, as they should be. Both these inaccuracies come in regions where the wave function is small, showing that at all points where it is large it satisfies rather accurately the differential equation which it should.

SUGGESTIONS REGARDING FURTHER WORK

It seems that the present wave functions are accurate enough to form good approximations, and at the same time are as simple as they could possibly be—they are scarcely more complicated than hydrogen wave functions. They should be useful, in the first place, in further calculations of atomic structure by Hartree's method. For by interpolation, a decidedly accurate approximation to the wave function can be obtained, to use as a starting point for the method of self-consistent fields. Of course, the curves of constants given in the present paper are far from satisfactory. No doubt they are not even the best approximations for the five atoms which have been computed. They cover only a few of the atoms for which calculations have been made, and not all the wave functions even of those. It is hoped that further work may improve and extend these curves, as the Moseley x-ray term diagrams have been continuously improved. In particular, attention is called to the fact that almost all the atoms which have been calculated by Hartree's method, except for a few light atoms, consist entirely of closed shells. If a few atoms were worked out containing uncompleted shells, as for instance in the iron group, it would be possible to extend the curves to the outer, optical electrons, adding greatly to their usefulness. Fairly reliable extrapolations can be easily made, though they are not indicated in this paper. The wave functions of the present paper should be useful, then, both in stimulating and in guiding further calculations by the method of self-consistent fields, and it is to be hoped that those who make such calculations will at the same time find analytical approximations to their results, so as to improve the curves.

The wave functions themselves are good enough so that a number of calculations become possible which could not be done before. These deal principally with applications of the perturbation theory to atomic structure; for here we have a really good set of orthogonal functions, which can be used as a starting point for perturbation calculations. It will be possible to compute the total energy of atoms, by integration of the energy operator over the orbits, as Zener has done for the light atoms. Further, the exchange integrals coming into the theory of atomic spectra can be calculated from these wave functions, if they are extended to the optical levels. Other interesting applications would be to the effect on the wave function of the perturbations produced by relativity in heavy atoms, and by exchange. The wave functions would be useful in the theory of hyperfine structure. Still another use, of course, is in forming atomic approximations to use with Heitler and London's method of treating molecular structure. Most of these applications demand rather definitely the order of accuracy, as well as the analytical convenience, attained in the present wave functions, and which have been impossible before. In addition, there are other calculations which can be made better with these functions, but were possible before, as diamagnetism, polarizability, atomic diameters, etc., previously studied with less accurate analytic functions, and atomic scattering, etc., studied with Hartree's or the Thomas-Fermi functions. In conclusion, the writer wishes again to acknowledge his gratitude to Dr. Hartree for his kindness in providing the tables of wave functions, and for many useful suggestions.