Studies of Atomic Self-Consistent Fields. I. Calculation of Slater Functions*

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A refined technique is described for approximating the numerically given radial part of atomic wave functions associated with self-consistent fields with exchange by means of Slater's analytical functions obtained by replacing each exponential in a hydrogen-like wave function by the sum of one, two, three, or more exponentials. Exponents and coefficients of these exponentials are calculated for the $3p$-function of Cl^-, corresponding to an accuracy of 0.0015 for the normalized radial part, and, with slightly less accuracy, for all the functions of two closed-shell ions, F^- (without exchange) and Na^+, and for some neutral first-row atoms, $C(^1D)$, $N(^2P)$, and $O(^1S)$. The interpolation problem is discussed, and a new interpolation rule for the coefficients is stated, which gives excellent agreement (0.001) in the examples chosen, namely the $1s$-functions of the He-like ions and the $2p$-functions of Na^+, Mg^{+2}, and Si^{+4}.

IN the quantum-mechanical treatment of many-electron atoms, the total antisymmetric wave functions describing the different atomic states are usually approximated by the sum of one, two, three or more determinants[1] of one-electron wave functions, each being a product of an atomic orbital (AO) and a spin function. The atomic orbitals are determined from the basic Schrödinger equation for the atom by means of the variation principle[2] as products of radial parts and spherical harmonics, and the best expressions for the former are obtained *numerically* by step-by-step integration of the Hartree-Fock equations by using the self-consistent-field technique developed by Hartree.[3]

For some purposes, it has been found desirable to use also *analytic* forms of these atomic orbitals. Here we will not discuss the question whether it is better to base applications of the atomic theory on the analytical wave functions rather than on the numerical tables. It has often been said that the analytic expressions would be better for use, e.g., in the theory of molecules and crystals, but our experience is that it is often just as convenient to use numerical computations as analytical calculations and that many times the former are simpler and quicker. However, considering the fact that many physicists are more accustomed to analytical work than to numerical computations, we think that both methods should be developed simultaneously without giving priority to anyone of them. This series of papers will be devoted to a study of the atomic self-consistent fields with exchange, and various problems will be discussed both from the analytical and the numerical points of view.

Analytic expressions for the radial wave functions can be derived in two ways, either directly by fixing

parameters in given analytic functions, for instance, of the hydrogen-like type by means of the variation principle as described by Zener[4] and others,[5] or indirectly by approximating the numerically given Hartree-Fock functions in some way analytically, as was proposed by Slater.[6] Except for the simplest cases, the former method leads to rather formidable calculations, whereas the latter is simple but based on the assumption that the self-consistent-field functions are given in advance. An investigation of the accuracy of these analytic atomic orbitals shows that the Zener and Morse-Young-Haurwitz functions[4,5] containing only a few exponentials represent rather poor approximations of the self-consistent fields[7] and hence also of the true charge distributions,[8] and that the deviations are appreciable, particularly at large distances. The last fact is of essential importance in the theory of molecules and crystals, and the simplest way of obtaining good analytical orbitals for applications in this field seems therefore to be to use Slater's approach.[6] Part I of this series of papers will be devoted to a study of a refinement of Slater's method, giving analytic atomic wave functions with almost the same accuracy as the numerical functions themselves.

I. CALCULATION OF SLATER-FUNCTIONS

An atomic orbital with the quantum numbers n, l, m is the product of a radial wave function $f_{nl}(r)/r$ and a

[1] J. C. Slater, Phys. Rev. 34, 1293 (1929).
[2] J. C. Slater, Phys. Rev. 35, 210 (1930), and V. Fock, Z. Physik 61, 126 (1930).
[3] For an excellent survey of this field, see D. R. Hartree, Rep. Prog. Phys. 11, 113 (1946).

[4] V. Guillemin and C. Zener, Z. Physik 61, 199 (1930); C. Zener, Phys. Rev. 36, 51 (1930); J. C. Slater, Phys. Rev. 36, 57 (1930).
[5] Extensive tables have been given by Morse, Young, and Haurwitz, Phys. Rev. 48, 948 (1935); for improvements and corrections, see also L. Goldberg and A. M. Clogston, Phys. Rev. 56, 696 (1939), and W. E. Duncanson and C. A. Coulson, Proc. Roy. Soc. (Edinburgh) 62, 37 (1944).
[6] J. C. Slater, Phys. Rev. 42, 33 (1932); F. W. Brown, Phys. Rev. 44, 214 (1933).
[7] Only in a few cases have Zener-type functions been used as starting functions for self-consistent-field calculations; see, e.g., V. Fock and M. J. Petrashen, Physik. Z. Sowjetunion 6, 368 (1934); 8, 359 (1935).
[8] H. Bethe, Z. Physik 55, 431 (1929); 57, 815 (1929), has given a survey of different approximations of the charge distribution of He and He-like ions in comparison to the "true" distributions given by Hylleraas.

normalized spherical harmonic $Y_{lm}(\theta, \varphi)$. The best expressions for the functions $f_{nl}(r)$ are now given numerically for many atoms and ions by Hartree and Hartree, Fock, and others.[3] In order to express $f_{nl}(r)$ analytically, we will now slightly generalize Slater's original idea[9] and try to approximate these tables by functions obtained by replacing each exponential in the corresponding hydrogen-like functions by a sum of one, two, three or more exponentials. For the lowest functions, this gives the following expansions:

$$f_{1s}(r) = r\sum_k A_k \exp(-a_k r),$$
$$f_{2s}(r) = r\sum_k A_k \exp(-a_k r) - r^2\sum_k B_k \exp(-b_k r),$$
$$f_{2p}(r) = r^2\sum_k B_k \exp(-b_k r),$$
$$f_{3s}(r) = r\sum_k A_k \exp(-a_k r) - r^2\sum_k B_k \exp(-b_k r) \quad (1)$$
$$\qquad\qquad + r^3\sum_k C_k \exp(-c_k r),$$
$$f_{3p}(r) = r^2\sum_k B_k \exp(-b_k r) - r^3\sum_k C_k \exp(-c_k r),$$
$$\cdots \text{etc.}$$

where the exponents a_k, b_k, $\cdots$ and the coefficients A_k, B_k, $\cdots$ may be different for each orbital. We will here determine the values of these parameters by a numerical method, which is a simple development of the graphical method described by Slater.[6]

The exponentials involved in the expansions (1) may be calculated by means of a method of successive approximations[10] going inwards from $r \approx \infty$ to $r = 0$. The computations are based on the fact that in the outer region ($r \approx \infty$) only a single exponential is important, in the next inner region two terms are important, in the following region three terms, etc. The numerically given function $f(r)$, divided by the highest power r^p of r according to (1), is considered in equidistant points; a *quotient series* is then formed for the outer region by successive divisions, and from this series a trial exponential function is determined as a geometrical series. This function is now subtracted from $f(r)/r^p$, and the difference is investigated in the next inner region, where a new quotient series is formed, giving a new trial exponential function. This second function is now subtracted from $f(r)/r^p$, and the outer region is considered a second time with a still better result for the first term, etc. In most cases, this process is quite straightforward, and special care must be taken only in regions where the power of r has to be changed according to (1).

We note that here the quotient series have taken the place of Slater's logarithmic graphs. The success of the method depends partly on the fact that these quotient series and the trial exponentials, i.e., the geometrical series, can be computed so quickly by means of the modern electric desk machines.

A few words may be said about the fixing of the first trial functions for each region. It is easily seen that if a

TABLE I. Survey of the maximum errors in different intervals in the analytic SCF-functions for Rb^+ (without exchange) given by Slater (reference 6) as an example of the accuracy of his graphical method.

r-interval	Maximum error in units of 10^{-3}		
	Rb^+_{2s}	Rb^+_{3s}	Rb^+_{3p}
0.00			
	14	−41	−9
0.04			
	−30	±17	−46
0.20			
	−15	±28	14
0.50			
	2	25	−31
1.00			
	14		5

function g_n is the sum of two geometric series,

$$g_n = a k_1{}^n + b k_2{}^n, \quad (2)$$

of which the first is dominating, then the quotient g_{n+1}/g_n is slowly varying according to the formula

$$g_{n+1}/g_n = k_1 - (b/a)(k_1 - k_2)(k_2/k_1)^n + \cdots. \quad (3)$$

From the quotient series, considered in a region where g_n still has enough significant figures, it is therefore possible to get an approximate value of k_1 and estimates of k_2 and $b k_2{}^n/a k_1{}^n$, of which the latter are usually too rough to be of real value for determining an *initial* term $a k_1{}^n$ somewhere in the first geometrical series. After fixing a suitable value of k_1, we form instead the auxiliary function

$$h_n = k_1 g_n - g_{n+1} \approx b k_2{}^n(k_1 - k_2) \quad (4)$$

and its quotient series h_{n+1}/h_n, from which we get a much better estimate of k_2, $b k_2{}^n$, and finally of $a k_1{}^n = g_n - b k_2{}^n$. After choosing a specific initial term of the first geometric series, we can then form our first trial exponential by repeated multiplication with constant factors, different for the various interval lengths. The method of successive approximations, as described above, is now started.

The accuracy of the analytic self-consistent-field (SCF) functions obtained by Slater's graphical method may be illustrated by his own example for Rb^+ in Table I; even if the maximum error is of the order 45×10^{-3}, the approximation is certainly good for many applications. The analytic SCF-functions, calculated from Slater's exponents[6] for other atoms of the periodic system, have also errors of about the same order of magnitude. In treating F, F^-, and Ne, Brown[6] reports errors of the order 20×10^{-3}.

In our investigation of the alkali chlorides,[11] we needed the $3p$-function of Cl^- with exchange, given numerically by Hartree and Hartree,[12] with a very high accuracy and most of the technique described in this

[9] According to Slater (reference 6) only the exponential multiplied with the highest power in r should eventually be replaced by a sum of exponentials, but our generalization is obvious.

[10] A preliminary report of this method was given at the Shelter Island Conference, 1951.

[11] P. O. Löwdin, *A Theoretical Investigation into some Properties of Ionic Crystals* (Almqvist and Wiksells, Uppsala, 1948), thesis.

[12] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A156**, 45 (1936).

TABLE II. Exponents and coefficients in an analytic SCF-function of the form (1) for Cl⁻(3p) with exchange (reference 12). Maximum error$=1.5\times10^{-3}$.

AO		$k=$	1	2	3	$k=$	1	2	3
Cl⁻(3p)	b_k		4.2435	8.4758	22.314	c_k	0.92426	1.6658	2.9859
	B_k		9.0441	26.493	2.49	C_k	0.07099	1.3955	8.4236

TABLE III. Exponents and coefficients in analytic SCF-functions of the form (1) for F⁻ without exchange (reference 13) and for Na⁺ with exchange according to Fock and Petrashen (reference 14). For maximum errors, see Table IV.

AO		$k=$	1	2	$k=$	1	2	3	4
F⁻(1s)	a_k		8.1890	12.187					
	A_k		40.285	9.5770					
F⁻(2s)	a_k		7.1485	...	b_k	1.6465	2.7178	4.1211	...
	A_k		11.755	...	B_k	1.3054	8.7816	6.6845	...
F⁻(2p)					b_k	0.64417	1.4357	3.0759	5.9696
					B_k	0.080948	1.3016	8.6449	7.0549
Na⁺(1s)	a_k		8.1093	11.577					
	A_k		12.835	57.640					
Na⁺(2s)	a_k		9.1285	...	b_k	2.3650	3.9031	...	
	A_k		16.895	...	B_k	3.6178	25.462	...	
Na⁺(2p)					b_k	2.3718	3.8934	6.5076	
					B_k	5.1958	14.024	18.128	

paper was actually developed for the investigation of this function. Our final result is given in Table II, and, by using six exponentials (three in the C-group and three in the B-group), we could obtain a fit as good as 1.5×10^{-3}, i.e., the analytic SCF-function had about the same accuracy as the numerical function itself. With slightly less accuracy, we treated then two other closed-shell ions in the same way, namely, F⁻ without exchange[13] and Na⁺ with exchange.[14] The results in a somewhat improved form are condensed in Table III and the maximum errors for different intervals in Table IV. In tabulating the errors, we are always giving the quantity $(f_{\text{analytical}}-f_{\text{numerical}})$ for the normalized functions in units of 10^{-3}.

TABLE IV. Maximum errors of the analytic SCF-functions for F⁻ and Na⁺ in Table III, in units of 10^{-3}.

r-interval	F⁻₁ₛ	F⁻₂ₛ	F⁻₂ₚ	r-interval	Na⁺₁ₛ	Na⁺₂ₛ	Na⁺₂ₚ
0.00				0.0			
	1	8	0		±7	3	−5
0.08				0.2			
	−1	±10	1		8	±1	−1
0.3				0.4			
	−1	−10	−5		−3	±2	2
0.6				1.0			
	1	4	±1			2	−1
1.2				2.0			
		−1	−1			±1	0
3.0							
		0	±1				
6.0							
		0	1				
10.0							
			−1				

In the theory of molecules, some first row atoms are of particular importance, and we have therefore tried to obtain analytic SCF-functions for neutral carbon (¹D-state), neutral nitrogen (²P-state), and neutral oxygen (¹S-state), all given numerically with exchange by different authors.[15] The results are condensed in Table V, and the maximum errors are given in Table VI. We note that all the functions in Tables III and V are of orthodox Slater-type,[6] having only their highest-power exponential developed in a sum. The accuracy is essentially higher than in Slater's original functions, but this improvement is gained by adding at least one more exponential, which will again increase the work in the applications.

As was already pointed out by Slater,[6] all these expansions are not uniquely determined at all, and the exponents and the coefficients may vary over considerable ranges. A drastic example of this phenomenon is obtained by comparing our 2p-function for carbon (¹D)

TABLE V. Exponents and coefficients in analytic SCF-functions of the form (1) for neutral carbon (reference 15), ¹D ($\beta=0.04$), for neutral nitrogen (reference 15), ²P state ($\beta=0$), and for neutral oxygen (reference 15), ¹S state ($\beta=0$), all with exchange. For maximum errors, see Table VI.

State	AO		$k=$	1	2	$k=$	1	2	3
¹D	C(1s)	a_k		4.9840	7.0411				
		A_k		14.881	12.811				
	C(2s)	a_k		3.9471	...	b_k	1.4784	2.8493	7.7990
		A_k		5.9095	...	B_k	2.5829	5.2230	4.5676
	C(2p)					b_k	1.0789	2.1444	5.9216
						B_k	0.87935	3.3336	2.1226
²P	N(1s)	a_k		6.2736	10.920				
		A_k		28.744	6.8632				
	N(2s)	a_k		4.1749	...	b_k	1.7123	3.4424	8.8037
		A_k		7.8400	...	B_k	3.5175	11.832	8.4171
	N(2p)					b_k	1.2210	2.4466	5.6236
						B_k	1.0755	5.2350	3.4611
¹S	O(1s)	a_k		7.2052	12.523				
		A_k		35.267	8.6933				
	O(2s)	a_k		5.9096	...	b_k	1.9764	3.6744	13.931
		A_k		9.8450	...	B_k	4.9049	11.246	5.5364
	O(2p)					b_k	1.3632	2.7487	5.9169
						B_k	1.3284	7.3218	6.0887

in Table V with the 2p-function in Table VII given previously by Mulliken and others;[16] it is impossible to see directly that these functions with essentially different parameters approximate the same numerical function, but this is actually the case. The respective errors may be found in Table VI, and a closer investigation shows that the two error functions have opposite signs almost everywhere. In general, the order of magnitude and the sign of the errors will determine how much the different parameters in the functions (1) may vary.

The different *states* of a specific electronic configuration of an atom (or ion) may be characterized by Slater's[17] parameter β, and Hartree and others[15] have found by experience that the corresponding radial

[13] D. R. Hartree, Proc. Roy. Soc. (London) A151, 96 (1935).

[14] V. Fock and M. Petrashen, Physik. Z. Sowjetunion 6, 368 (1934). The slightly improved tables for Na⁺ given by D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) A193, 299 (1948), were not available in Uppsala at the time of these first calculations.

[15] C: A. Jucys, Proc. Roy. Soc. (London) A173, 59 (1939). N: D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) A193, 299 (1948). O: Hartree, Hartree, and Swirles, Trans. Roy. Soc. (London) A238, 229 (1939).

[16] Mulliken, Rieke, Orloff, and Orloff, J. Chem. Phys. 17, 1248 (1949); the function in their Eq. (76) is transformed to our form (1).

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

functions $f_{nl}(r)$ vary almost linearly in this parameter. In order to investigate whether this simple linearity in β could be transferred, e.g., to the coefficients in the analytic SCF-functions, we have treated neutral oxygen in two of its states, namely the ^1S-state ($\beta=0$) and the ^3P-state ($\beta=-0.6$). As may be seen from a comparison between Tables V and VII, the preliminary result was negative, and the problem is therefore still under investigation.

II. INTERPOLATION OF SLATER-FUNCTIONS

The purpose of the original Slater-functions[6] was not only to describe numerically given SCF-functions analytically, but even to permit interpolations to atoms for which these self-consistent fields had not yet been prepared. This interpolation was based on the rule that the exponents should vary linearly for similar electron configurations and different atomic numbers. The coefficients in the last group were interpolated by means of an auxiliary "intermediate" exponent, also varying linearly, which gave the ratio between the

TABLE VI. Maximum errors of the analytic SCF-functions for C, N, and O given in Tables V and VII, in units of 10^{-3}.

r-inter-val	^1D		Mulli-ken		r-inter-val	^2P			^1S			^3P
	C_{1s}	C_{2s}	C_{2p}	C_{2p}		N_{1s}	N_{2s}	N_{2p}	O_{1s}	O_{2s}	O_{2p}	O_{2p}
0.0					0.0							
	6	4	3	-3		8	-2	0	12	-1	0	0
0.2					0.04							
	±3	8	±3	12		8	-2	1	10	1	3	±1
0.8					0.2							
	3	-4	3	±8		±4	2	2	±4	-12	4	±1
2.4					0.5							
	0	-4	±1	±3		±2	±4	±3	±2	±6	±3	-6
4.0					1.2							
		4	-2	2		-1	±6	±3	-1	-9	±2	±6
8.0					4.0							
			-2	2			2	1		2	-3	±2
					7.0							
								-1			-1	0

coefficients; the absolute values were then determined by the normality and orthogonality conditions.

The interpolation problem can, of course, be treated rigorously by investigating the effect of variations of the atomic number Z in the basic Hartree-Fock equations,[18] but, with the present mathematical methods, the error margins seem to be too large to render really useful results. For the moment, it seems therefore to be better to work intuitively by using the hypothesis that the SCF-functions are closely analogous to the hydrogen-like functions, but that they just have more general exponents replacing the atomic number Z. The interpolation rule for the exponents seems very plausible from this point of view,[19] but, in order to obtain full accuracy also in the interpolated functions, we must modify the interpolation rule for the coefficients.

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[18] Compare also D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A166**, 450 (1938), and reference 3.

[19] Compare also the exponents in the analytic wave functions for Be-like atoms and ions, calculated directly from the variational principle by V. Fock and M. Petrashen, Physik. Z. Sowjetunion **8**, 359 (1935), Table IV.

TABLE VII. Exponents and coefficients in an analytic $2p$-function of the form (1) for the ^3P-state of neutral oxygen (reference 15), and in Mulliken's (reference 16) $2p$-function for the ^1D-state of neutral carbon (reference 15).

State	AO	$k =$	1	2	3
^3P	$O(2p)$	b_k	1.4107	2.8500	6.5935
		B_k	1.4384	8.3557	4.7562
^1D	$C(2p)$	b_k	0.898	1.416	2.694
Mulliken:		B_k	0.2727	1.427	3.576

Let us consider the simplest SCF-functions, namely the $1s$-functions of the He-like ions, which we will express in the following form:

$$f_{1s}(r) = A_1 r \exp(-a_1 r) + A_2 r \exp(-a_2 r). \quad (4a)$$

The numerical functions for $Li^+(Z=3)$ and $C^{+4}(Z=6)$ are given by Fock and Petrashen[20] and by Jucys,[15] respectively, and the corresponding values of our parameters in (4a) are condensed in Table VIII; the maximum errors are in both cases below 1.0×10^{-3}. By using these data, we will then try to make interpolations and extrapolations in the series of the He-like ions.

The exponents a_1 and a_2 are easily determined as linear functions of Z from the fixed values for $Z=3$ and $Z=6$. For the coefficients A_1 and A_2, the normalization condition for f_{1s} gives one relation, but, in order to carry out the interpolation, we need one more equation for them. However, we note that, for a pure hydrogen-like $1s$-function, we would have the relations

$$f_{1s}(r) = 2Z^{\frac{3}{2}} r \exp(-Zr), \quad [f_{1s}(r)/2r]_{r=0}^{\frac{2}{3}} = Z, \quad (5)$$

and, according to our analogy rule, the last relation indicates that, also for the SCF-functions, the quantity

$$K_{1s} = [f_{1s}(r)/2r]_{r=0}^{\frac{2}{3}} \quad (6)$$

will vary linearly with Z. We have tested this rule on some numerical SCF-functions calculated by Hartree and others,[3] and the results in Table IX show that the "linearity rule" holds with excellent accuracy. Similar quantities K_{2s}, K_{2p}, K_{3s}, $\cdots$ may be constructed also for the $2s$-, $2p$-, $3s$-, $\cdots$ functions, and a closer investigation shows that they are approximately linear in Z, too. Complete results also for the higher functions will be given in a later paper in this series. We note that all these quantities are important in the calculations of self-consistent fields with exchange, since they char-

TABLE VIII. Analytic SCF-functions of the form (1) for $Li^+(1s)$ and for $C^{+4}(1s)$; the maximum error is below 1.0×10^{-3}.

AO	$k =$	1	2
$Li^+(1s)$	a_k	2.4346	4.4250
	A_k	6.6641	2.5618
$C^{+4}(1s)$	a_k	5.4523	9.5935
	A_k	23.919	4.0324

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[20] V. Fock and M. Petrashen, Physik. Z. Sowjetunion **8**, 547 (1935).

Z	Atom	K_{1s}	Z	Atom	K_{1s}
6	C	5.760	17	Cl⁻	16.70
7	N	6.757	18	Ar	17.69
8	O	7.751	19	K⁺	18.70
			20	Ca⁺²	19.69
11	Na⁺	10.73			
14	Si⁺⁴	13.73			

acterize the behavior of the normalized wave functions in the neighborhood of the point $r=0$.

If the K_{1s}-rule is applied also to the He-series, we get a second relation for the coefficients A_1 and A_2, which then may be determined. The results of the interpolation are condensed in Table X, and it may be of some interest to test its accuracy. The 1s-function for Be⁺² is numerically given by Hartree and Hartree,[21] and a comparison shows that our analytic functions reproduces the numerical table with full accuracy. We may suppose that the same will be true also for B⁺³. In the extrapolations, the accuracy can certainly not be so high, but we note that our analytic function will give the same charge distribution for He as was once numerically given by Hartree.[22] Even for H⁻ our analytic function is comparatively good, since it gives a much better fit to Hylleraas's charge distribution[8] than the best hydrogen-like wave function.

The calculations involved in the application of the K_{1s}-rule are somewhat clumsy, and we have therefore tried to derive a simpler interpolation rule for the coefficients, which could be generalized also to functions containing more exponentials. Using the analogy principle, we will make the assumption that each coefficient A_k as a function of Z has the form

$$A_k(Z)=\kappa_k\{a_k(Z)\}^{p_k},\qquad(7)$$

where the parameters κ_k and p_k are independent of Z. This means that $\log_{10}A_k$ is a *linear* function of $\log_{10}a_k$:

$$\log_{10}A_k(Z)=\log_{10}\kappa_k+p_k\log_{10}a_k(Z),\qquad(8)$$

Table X. Interpolated and extrapolated SCF-functions of the form (1) for some He-like ions, obtained by using the linearity of the quantity K_{1s}. The star * indicates the given quantities, taken from Table VIII.

Z	Atom	K_{1s}	a_1	a_2	A_1	A_2
1	H⁻	0.7505	0.4228	0.9794	0.30025	1.0001
2	He	1.7608	1.4287	2.7022	2.7626	1.9104
3	Li⁺	2.7711*	2.4346*	4.4250*	6.6641*	2.5618*
4	Be⁺²	3.7814	3.4405	6.1478	11.601	3.1057
5	B⁺³	4.7917	4.4464	7.8706	17.387	3.5909
6	C⁺⁴	5.8021*	5.4523*	9.5935*	23.919*	4.0324*
7	N⁺⁵	6.8124	6.4582	11.316	31.101	4.4604
8	O⁺⁶	7.8227	7.4641	13.039	38.897	4.8621
Difference:		1.0103	1.0059	1.7228		

[21] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) A149, 210 (1935).
[22] D. R. Hartree, Proc. Cambridge Phil. Soc. 24, 111 (1928).

Table XI. Coefficients in interpolated and extrapolated SCF-functions for some He-like ions. The exponents are the same as in Table X, but, this time, the coefficients are obtained by using the simple rule (8). The star * indicates given quantities, taken from Table VIII.

Z	Atom	Unnormalized coefficients		Normalized coefficients	
		A_1	A_2	A_1	A_2
1	H⁻	0.41560	1.0585	0.3385	0.8622
2	He	2.8631	1.9269	2.7772	1.8691
3	Li⁺	6.6641*	2.5618*	6.6641	2.5618
4	Be⁺²	11.529	3.1064	11.593	3.1236
5	B⁺³	17.312	3.5905	17.382	3.6049
6	C⁺⁴	23.919*	4.0324*	23.919	4.0324
7	N⁺⁵	31.281	4.4422	31.117	4.4189
8	O⁺⁶	39.349	4.8271	38.930	4.7759
	$\kappa=$	1.6265	1.0713		
	$p=$	1.5850	0.5862		

and the coefficients A_k are therefore easily determined, e.g., by using divided differences. However, these preliminary values of the coefficients A_k are usually not representing a function which is fully normalized, and, in the last step of the interpolation, they should therefore be given revised values by using the normalization condition.

The results of the application of the rule (8) to the He-series are given in Table XI, and we note that, for the interpolated ions Be⁺² and B⁺³, the coefficients are practically the same as in Table X.

The interpolation rule (8) may be directly generalized also to the other groups of coefficients $(B, C, \cdots)$. As another example, let us consider the 2p-functions of some Ne-like ions. The functions for Na⁺$(Z=11)$ and Si⁺⁴$(Z=14)$ are numerically given by Hartree and others,[23] and our parameters for the corresponding analytic functions (1) are listed in Table XII and the maximum error (0.002) in Table XIII. From these fixed data, the interpolations for Mg⁺²$(Z=12)$ and Al⁺³$(Z=13)$ were carried out by using the simple rule (8) and the normalization condition. Our analytic 2p-function for Mg⁺² may be checked against the SCF-function given numerically by Yost,[24] which is almost fully reproduced with an error below 0.0016; it is somewhat surprising that the error in the interpolated function is even lower than in one of the fixed functions (Na⁺), see Table XIII.

The net result of our investigation seems to be that it is possible to interpolate analytic SCF-functions with about the same accuracy as in the fixed functions by using Slater's rule for the exponents and the simple rule (8) and the normalization condition for the coefficients. The results already obtained are somewhat encouraging, and further work on this problem is now in progress.

[23] Na⁺: D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) A193, 299 (1948). Si⁺⁴: Hartree, Hartree, and Manning, Phys. Rev. 60, 857 (1941).
[24] W. J. Yost, Phys. Rev. 58, 557 (1940).

TABLE XII. Analytic SCF-functions for $Na^+(2p)$ and $Si^{+4}(2p)$ with exchange calculated from the numerical tables (reference 23), and interpolated functions for $Mg^{+2}(2p)$ and $Al^{+3}(2p)$ with the coefficients determined by the simple rule (8). For maximum errors, see Table XIII.

Z	Atom	b_1	b_2	b_3	Unnormalized coefficients			Normalized coefficients		
					B_1	B_2	B_3	B_1	B_2	B_3
11	Na^+	2.1880	3.7288	6.8864				3.6164	15.660	18.729
12	Mg^{+2}	2.7226	4.4808	7.9907	6.9728	22.590	21.156	7.0360	22.795	21.348
13	Al^{+3}	3.2572	5.2327	9.0950	11.952	30.781	23.524	12.043	31.016	23.704
14	Si^{+4}	3.7918	5.9847	10.1993				18.870	40.231	25.840
Diff:		0.5346	0.7520	1.1043						
					$\kappa=$ 0.34400	1.1348	3.8533			
					$p=$ 3.0046	1.9943	0.81944			

CONCLUSIONS

In the theory of molecules and crystals, which is based on the use of atomic orbitals in one or other form, the SCF-functions take a selected and most important place, since they represent the *best* one-electron AO which are available. The problem of calculating analytic SCF-functions has become particularly important during the last few years, since most of the extensive molecular tables under preparation in Chicago under Mulliken, in Oxford under Coulson, and in Tokyo under Kotani, are based on the use of single exponential functions.[25] In order to make all these tables applicable even to the best atomic orbitals, it would be desirable to have the exponents and the coefficients in the analytic functions (1) calculated for all self-consistent-fields which are numerically available, and to carry out interpolations to atoms which have not yet been treated by the Hartree-Fock technique.[26] In addition to the best fits, it would also be of interest to have fairly accurate analytic SCF-functions containing as few exponentials as possible.

By the generalized Slater method described in this paper, it is possible to calculate analytic SCF-functions from the numerically given tables with any desired accuracy, but, even if the technique is simple, the computations are still time-consuming and rather tedious. It is felt that, if the periodic system should be investigated on a large-scale basis in order to obtain analytic SCF-functions having errors of the order of magnitude (0.001–0.002) examplified in Tables II, VIII, and XIII, then it would be worthwhile to re-examine the basic method for further improvements, if possible. Work on this program is now in progress, and the results will be reported in a later paper in this series.

[25] Molecular tables for particular atoms may also be prepared directly from the numerically given SCF-functions; see, e.g., reference 11, Method I.

[26] It seems probable that the interpolated analytic functions would give very good initial functions for self-consistent-field calculations.

TABLE XIII. Maximum errors of the analytic SCF-functions given in Table XII in units of 10^{-3}; note that Mg^{+2} is interpolated between Na^+ and Si^{+4}.

r-interval	$Na^+{}_{2p}$	$Mg^{+2}{}_{2p}$	$Si^{+4}{}_{2p}$
0			
	−0.6	−0.7	−0.9
0.04			
	2.0	1.6	1.1
0.20			
	−2.1	−1.3	0.7
0.50			
	2.1	±1.1	−0.9
1.2			
	−2.1	±1.4	−0.8
4.0			
	−0.6	±0.4	
6.0			