Analytical Hartree-Fock Self-Consistent-Field Wave Functions for some $1s^1 2s^1 2p^6$ Configurations*†

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Analytical Hartree-Fock self-consistent-field solutions have been obtained by matrix methods for the ten-electron systems F^-, Ne, and Na^+. In addition, solutions have been obtained for the F^- and Na^+ ions in the presence of a superposed potential sphere. Tables of the two *goodness* functions, $f(r)=FR-\epsilon R$ and $g(r)=FR/\epsilon R$, and expectation values of r_i and r_i^2 are given. The diamagnetic susceptibility has been calculated for all the systems reported.

I. INTRODUCTION

In this paper we present self-consistent solutions of the Hartree-Fock (HF) equations for the ten-electron configuration $1s^2 2s^2 2p^6$. Solutions have been obtained for the isoelectronic sequence F^-, Ne, and Na^+. In addition to the free-ion solutions, self-consistent field (SCF) solutions have been obtained for the ions F^- and Na^+ in the presence of a superposed potential due to a charged spherical shell. A number of previous HF-SCF calculations on the ten-electron systems, of varying degrees of accuracy, have been reported in the literature.[1–7] It was the aim of this series of calculations to obtain approximate solutions of as great an accuracy as feasible.

In the second section we state our Hamiltonians, the assumed HF-SCF wave functions and the resulting HF equations. In the third section we discuss the method of solution employed and present some detail regarding the computational procedure in the following section. The fifth section contains a discussion of the results of the calculations and in the sixth section we examine the quality of the SCF solutions. The final section concludes with a short resume of the work.

II. HARTREE-FOCK EQUATIONS

The free-atom (or ion) Hamiltonian which we are concerned with may be written

$$\mathcal{H}=\sum_i(\tfrac{1}{2}p_i^2+Zr_i^{-1})+\sum_{i>j}r_{ij}^{-1}, \qquad (1)$$

where $\mathbf{p}_i$ is the momentum of the ith electron, Z is the nuclear charge, r_i is the distance of electron i from the nucleus, and r_{ij} is the distance between electrons i and j. We have chosen atomic units with the unit of energy $2R_\infty hc=27.21$ ev, the unit of length the first Bohr radius, and the mass and charge of the electron as unity. The superposed potential which we have utilized for the ion calculations is a charged spherical shell with the potential

$$V=q/a \quad \text{for } r\leqslant a, \qquad =q/r \quad \text{for } r\geqslant a, \qquad (2)$$

where q is the charge on the sphere and a is the radius of the sphere.

In the Hartree-Fock approximation the wave function is assumed to be an antisymmetrized product of one-electron orbitals. These orbitals are obtained as solutions of the set of simultaneous integro-differential equations obtained from applying the variational principle to the expectation value of the Hamiltonian. For a closed-shell configuration, such as $1s^2 2s^2 2p^6$, there exists no ambiguity in the form of the wave function as it may be represented as a single determinant which is invariant under the transformations of the symmetry group of the Hamiltonian (1). The wave function which we have computed may be written

$$\Psi=\mathcal{A}\{1s^2,2s^2,2p^6\}, \qquad (3)$$

where $\mathcal{A}$ is the well-known antisymmetrizing operator and Ψ is a determinant of order ten. When the variational principle is applied to the expectation value of the Hamiltonian, subject to an orthonormal constraint on the set of orbitals $\{\phi_i\}$, we obtain (after a suitable unitary transformation of the ϕ_i) the system of HF equations,

$$[H_i+\sum_j(2J_j-K_j)]\phi_i=\epsilon_i\phi_i, \qquad (4)$$

where

$$H_i=-\tfrac{1}{2}\Delta_i-Zr_i^{-1}+V_i, \qquad (5)$$

$$J_j\phi_i(1)=\int|\phi_j(2)|^2 r_{12}^{-1}dV_2\,\phi_i(1), \qquad (6)$$

$$K_j\phi_i(1)=\int\phi_j^*(2)\phi_i(2)r_{12}^{-1}dV_2\,\phi_j(1). \qquad (7)$$

V_i is any superposed one-electron potential (if present) and Z is the nuclear charge. To obtain the wave function (3), the set of equations (4) must be solved for the orbitals $\{\phi_i\}$.

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[1] F. W. Brown, Phys. Rev. 44, 214 (1933).
[2] D. R. Hartree, Proc. Roy. Soc. (London) A151, 96 (1935).
[3] C. Froese, Proc. Cambridge Phil. Soc. 53, 206 (1957).
[4] B. H. Worsley, Can. J. Phys. 36, 289 (1958).
[5] A. M. Karo and L. C. Allen, J. Chem. Phys. 31, 968 (1959).
[6] L. C. Allen, J. Chem. Phys., 34, 1156 (1961).
[7] V. Fock and M. J. Petrashen, Physik. Z. Sowjetunion 6, 368 (1934).

III. METHOD OF SOLUTION

It is customary to assume that a central electrostatic field exists about the nucleus so that each orbital may be expressed in the form

$$\phi_{nlm}(r,\theta,\varphi)=R_{nl}(r)Y_{lm}(\theta,\varphi)=r^{-1}P_{nl}(r)Y_{lm}(\theta,\varphi), \quad (8)$$

where $Y_{\ m}(\theta,\varphi)$ is a complex spherical harmonic. We further assume that all the radial functions $R_{nl}(r)$ of a given shell are equal so that the orbitals are either equal in pairs or mutually orthogonal. Equations (4) then become a system of one-dimensional equations for the radial functions.

There are two forms in which approximate SCF solutions may be obtained. If direct numerical integration is employed, the orbitals are obtained as numerical tables.[8] An analytic form for the orbitals may be obtained directly by assuming an expansion in terms of a set of analytical functions. The expansion coefficients may be obtained either by iteration of the density matrix of the wave function[9] or iteration of the matrix representation of the HF equations.[10–12] We have chosen the latter method to obtain our solutions of the HF equations.

The radial functions were expanded in terms of Slater-type functions, that is,

$$R_{nl}(r)=\sum_p c_{nl;\,p}\chi_{lp}(r), \quad (9)$$

where

$$\chi_{lp}(r)=(2\zeta_{lp})^{n_{lp}+\frac{1}{2}}[(2n_{lp})!]^{-\frac{1}{2}}r^{n_{lp}-1}e^{-\zeta_{lp}r}. \quad (10)$$

The matrix representation of the HF equations, (4), then assumed the form

$$\mathbf{F}\mathbf{c}_{nl}=\epsilon_{nl}\mathbf{S}\mathbf{c}_{nl}, \quad (11)$$

where $\mathbf{F}$ is the matrix HF Hamiltonian, $\mathbf{S}$ is the overlap matrix of the basic functions $\{\chi_{lp}\}$, $\mathbf{c}_{nl}$ is the vector of coefficients of the expansion (9), and ϵ_{nl} is the eigenvalue corresponding to $\mathbf{c}_{nl}$. Complete details on solution of (11) may be found in references 9, 10, and 11.

IV. DETAILS OF COMPUTATION

A computer program was constructed for the IBM-704 to solve the HF equations (11). This program allows complete freedom (within the floating-point range of the computer) on the values of the exponents ζ_{lp} and the (integral) powers n_{lp}, thus affording considerable flexibility in the choice of basis functions. The computer output consists of the basis function parameters, the expansion coefficients, the total energy, and the reduced logarithmic derivatives of the orbitals at the origin. The latter quantities should satisfy the relation

$$\tilde{R}\equiv(l+1)[R_1'/R_1]_{r=0}=-Z, \quad (12)$$

where

$$R_1=r^lR. \quad (13)$$

The relation (12) thus constitutes a test of the quality of the solution in the region near the origin.

Considerable experimentation was carried out with various combinations of the (Slater-type) basis functions before the author settled on the combination reported herein. [See Tables I–III.) It was found least difficult to minimize the total energy using basis sets

TABLE I. Parameters for the F^- SCF orbitals.

Charge on sphere (a.u.) ···				1.00		1.00		1.00		1.00	
Radius of sphere (a.u.) ···				2.40		2.57		2.70		3.789	
ζ	n	C_{1s}	C_{2s}	C_{1s}	C_{2s}	C_{1s}	C_{2s}	C_{1s}	C_{2s}	C_{1s}	C_{2s}
12.20	1	0.089611	−0.199570	0.089916	−0.239794	0.089840	−0.227944	0.089872	−0.221050	0.089711	−0.201754
8.20	1	0.938018	0.610790	0.937421	0.683005	0.937570	0.661599	0.937518	0.649161	0.937830	0.614562
10.80	2	−0.022939	−0.138830	−0.022742	−0.167362	−0.022792	−0.158977	−0.022764	−0.154093	−0.022869	−0.140392
4.10	2	−0.007729	−0.193139	−0.007380	−0.215606	−0.007465	−0.209390	−0.007473	−0.205678	−0.007649	−0.194646
2.66	2	−0.005912	−0.565973	−0.005722	−0.604434	−0.005762	−0.590389	−0.005762	−0.582818	−0.005860	−0.565947
1.68	2	0.001681	−0.300736	0.001627	−0.292119	0.001639	−0.296774	0.001640	−0.299086	0.001668	−0.302182
4.50	3	0.014018	−0.053758	0.013687	−0.005869	0.013763	−0.020377	0.013758	−0.028662	0.013928	−0.051227
		C_{2p}		C_{2p}		C_{2p}		C_{2p}		C_{2p}	
6.05	2	0.064814		0.050244		0.050460		0.051184		0.059712	
3.06	2	0.551546		0.635847		0.634463		0.630219		0.580765	
1.44	2	0.500480		0.557051		0.550004		0.544725		0.514525	
0.69	2	0.086499		0.019084		0.029166		0.036150		0.701605	
3.75	3	−0.058375		−0.144059		−0.141918		−0.137323		−0.087558	
8.00	3	−0.006756		−0.011877		−0.011830		−0.011581		−0.008525	
$-\epsilon_{1s}$(a.u.)		25.82956		26.18396		26.16936		26.15867		26.08340	
$-\epsilon_{2s}$(a.u.)		1.074662		1.450631		1.431042		1.417240		1.331305	
$-\epsilon_{2p}$(a.u.)		0.1810072		0.5591383		0.5395839		0.5257729		0.4386323	
$-\tilde{R}_{1s}$		8.9947		8.9947		8.9947		8.9947		8.9947	
$-\tilde{R}_{2s}$		9.0409		9.0672		9.0597		9.0553		9.0425	
$-\tilde{R}_{2p}$		10.1932		10.2401		10.2368		10.2332		10.2058	
$-E$(a.u.)		99.45921		103.5879		103.3235		103.1422		102.0955	

[8] D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).
[9] R. McWeeny, Proc. Roy. Soc. (London) **A235**, 496 (1956); **A237**, 355 (1956); **A241**, 239 (1957); Revs. Modern Phys. **32**, 335 (1960).
[10] G. G. Hall, Proc. Roy. Soc. (London) **A205**, 541 (1951).
[11] C. C. J. Roothaan, Revs. Modern Phys. **23**, 69 (1951).
[12] C. C. J. Roothaan, Revs. Modern Phys. **32**, 179 (1960).

TABLE II. Parameters for the Na^+ SCF orbitals.

Charge on sphere (a.u.)		···		−1.00		−1.00		−1.00	
Radius of sphere (a.u.)		···		1.79		1.7953		1.90	
ζ	n	C_{1s}	C_{2s}	C_{1s}	C_{2s}	C_{1s}	C_{2s}	C_{1s}	C_{2s}
15.00	1	0.118514	0.050484	0.118547	0.039100	0.118585	0.041607	0.118583	0.043908
10.30	1	0.854775	0.171023	0.854737	0.190950	0.854666	0.186576	0.854665	0.182553
11.00	2	0.031730	0.084504	0.031796	0.067772	0.031835	0.071497	0.031828	0.074895
5.40	2	0.008566	−0.115679	0.008415	−0.096180	0.008407	−0.100483	0.008433	−0.104426
3.10	2	−0.001522	−0.775681	−0.001564	−0.749297	−0.001567	−0.756084	−0.001559	−0.761746
2.00	2	0.000665	−0.050108	0.000686	−0.064375	0.000685	−0.060506	0.000681	−0.057363
6.00	3	0.000535	−0.144197	0.000640	−0.173150	0.000658	−0.166421	0.000641	−0.160464
		C_{2p}		C_{2p}		C_{2p}		C_{2p}	
6.60	2	0.135376		0.143044		0.142694		0.141979	
3.40	2	0.715241		0.707453		0.704154		0.702768	
2.30	2	0.362710		0.203736		0.228789		0.253752	
1.80	2	0.062804		0.168879		0.150446		0.132852	
4.00	3	0.202196		−0.139094		−0.143792		−0.150723	
9.60	3	−0.014961		−0.013097		−0.013064		−0.013162	
$-\epsilon_{1s}$(a.u.)		40.75973		40.20039		40.22343		40.24794	
$-\epsilon_{2s}$(a.u.)		3.073676		2.501944		2.528619		2.555828	
$-\epsilon_{2p}$(a.u.)		1.797188		1.226943		1.253062		1.279855	
$-\bar{R}_{1s}$		11.0025		11.0025		11.0025		11.0025	
$-\bar{R}_{2s}$		11.0537		11.0300		11.0350		11.0396	
$-\bar{R}_{2p}$		13.1688		13.0616		13.0767		13.0923	
$-E$(a.u.)		161.6769		155.8185		156.1229		156.4242	

of this composition. The parameters and basis size were varied until a trough of minimization was reached, i.e., the same energy value was obtained using different sets of exponents for the expansion functions. Attempts to use larger basis sets for the F^- and Ne expansions yielded energies 10^{-5} a.u. below those reported in Tables I and III, but the SCF runs failed to converge. The criterion for self-consistency of the orbitals was set at

$$|\{c_{nl;p}\}_{N+1}| - |\{c_{nl;p}\}_N| \leqslant 10^{-4},$$

i.e., we compared the eigenvectors of the Nth and $(N+1)$th iteration. Within this criterion of convergence, the larger basis sets (those which failed to converge) appeared to be linearly dependent.

V. DISCUSSION OF RESULTS

(a) Field-Free Systems

The qualitative features of the field-free orbitals have been known for some time so that further discussion is unnecessary. Lack of space prevents the publication of the extensive tables of the orbital properties. The free-ion F^- solution is very similar to that of Froese.[3] The minor discrepancies in the values of the orbitals may be attributed to the limited storage capacity of the computer with which she worked. This storage limitation applies also to the Ne calculation done by Worsley.[4] The Na^+ solution due to Hartree and Hartree agrees with the present one to three figures, the number of significant figures carried in their work.

The parameters applicable to the field-free SCF orbitals are given in Tables I and II. From these values we have calculated $\langle r_i \rangle$ and $\langle r_i^2 \rangle$ for each of the three orbitals of the series and these are listed in Table IV.

(b) Systems in the Presence of a Superposed Potential

For the interpretation of many solid-state phenomena it would be very advantageous to have true solid-state SCF wave functions. These are not yet available and may be many years in coming, so that it seems plausible in the interim to obtain atomic wave functions that in some manner reflect the environment of the crystal lattice. Electron density studies of some alkali-halide crystals have shown that the charge distribution about lattice sites remains essentially spherical and about the

TABLE III. Parameters for the Ne SCF orbitals.

ζ	n	C_{1s}	C_{2s}	ζ	n	C_{2p}
14.00	1	0.104781	−0.339010	6.60	2	0.071588
9.20	1	0.891761	0.891909	3.40	2	0.616462
				2.20	2	0.261474
12.00	2	0.006277	−0.270688	1.60	2	0.296791
4.50	2	0.008780	−0.289318			
2.80	2	−0.001525	−0.706866	4.00	3	−0.152330
1.80	2	0.000650	−0.127561	9.00	3	−0.010184
5.00	3	−0.000799	0.004109			
$-\epsilon$(a.u.)		32.77205	1.930050			0.8501921
$-\bar{R}$		10.0011	9.9808			11.4695
$-E$(a.u.)				128.5470		

TABLE IV. Expectation values of r_i and r_i^2 for the HF orbitals of ten-electron systems.

System	Superposed sphere Charge	Radius	1s $\langle r\rangle$	1s $\langle r^2\rangle$	2s $\langle r\rangle$	2s $\langle r^2\rangle$	2p $\langle r\rangle$	2p $\langle r^2\rangle$
F^-	...	...	0.17576	0.04162	1.03553	1.31873	1.25551	2.21064
Ne	...	...	0.15763	0.03347	0.89220	0.96764	0.96496	1.22655
Na^+	...	...	0.14286	0.02748	0.77911	0.73148	0.79625	0.81592
F^-	1.0	2.40	0.17578	0.04163	1.03822	1.32414	1.21517	1.99162
F^-	1.0	2.57	0.17577	0.04163	1.03816	1.32472	1.22166	2.02329
F^-	1.0	2.70	0.17577	0.04163	1.03802	1.32472	1.22597	2.04516
F^-	1.0	3.789	0.17576	0.04162	1.03643	1.32122	1.24692	2.15983
Na^+	−1.0	1.70	0.14286	0.02748	0.77999	0.73430	0.80237	0.83514
Na^+	−1.0	1.7953	0.14286	0.02748	0.77968	0.73338	0.80083	0.83050
Na^+	−1.0	1.90	0.14286	0.02748	0.77946	0.73270	0.79956	0.82662

negative ions it remains spherical for a considerable distance. Kristoffel[13] has carried out a calculation on the Cl^- ion of KCl in which he assumes, in each of three regions, a different form for the orbitals of the outer shell. These regions were chosen so as to reflect the relative importance of the ion central field and the crystal field. The orbital parameters were determined from continuity and normalization conditions. The resulting orbitals tailed off faster than in the free ion. Kristoffel found that the positive ion showed an opposite effect, but the magnitude of the change was not as great. Hurst[14] has shown that in the presence of a point-charge crystal field, the optimum effective nuclear charge for the H^- wave function increases, indicating a charge distribution of lesser extent than the free ion. This situation should also prevail for the F^- ion in a crystal environment.

If we consider a single ion in a crystal lattice, we find that in addition to the atomic potential there exists the Madelung potential due to Coulomb interaction between the ions. There is also a repulsive potential of unknown origin. These external potentials, collectively acting as a potential well, modify the charge distribution about the nucleus. A complete calculation of the effect of these potentials is a major task which remains to be done. For immediate use, it is desirable to investigate the effect on the orbitals of various types of superposed potential fields which fall within the scope of the central-field SCF scheme.[15]

We have chosen as our superposed field a hollow sphere of radius a carrying a charge q. Such a potential has the value q/a for $0\leqslant r\leqslant a$ and q/r for $r\geqslant a$. A positively charged sphere should contrast the charge cloud of a negative ion and a negatively charged sphere should swell the charge cloud of a positive ion. The charge q has been taken with magnitude one, corresponding to the net charge exclusive of the ion. The parameter which remained to be chosen was the sphere radius a.

The proper value for the radius of the charged sphere is a debatable point. On intuitive grounds, one can choose the ionic radius; another choice is the lattice constant. Neither of these values can be fully justified. A third approach can be made by setting the value of the potential inside the sphere to the value of the cohesive energy per ion. This prescription is as questionable as the first two proposed. Only experimentation can shed any light on the best choice for the radius.

A number of spheres of varying radii were superposed on the F^- and Na solutions reported in this paper. The same exponents utilized for the field-free calculations were used for this series after experimentation with the basis sets had indicated that the size of the basis sets used in the field-free cases was sufficient to yield good results for the superposed-field calculations. This is demonstrated in the goodness tests, which we discuss in a later section. The radii of the spheres were chosen less than, equal to, and greater than the ionic radii as given by Pauling.[16] For F^- an additional value was chosen equal to the LiF lattice constant. These spheres had the desired effect of changing the size of the ions. The Na^+ orbitals were only slightly affected by the spheres, but a good deal of change was produced in the $2s$ and $2p$ orbitals of F^-.

The parameters applicable to the orbitals in the superposed field environment are given in Tables I and II.[17]

(c) Diamagnetic Susceptibility

The diamagnetic susceptibility may be calculated from the Langevin-Pauli formula,[18]

$$\chi=-(Ne^2/6mc^2)\sum_i\langle r_i^2\rangle, \qquad (14)$$

The susceptibilities for the field-free systems and the ions in a superposed potential are listed in Table V.

[13] N. N. Kristoffel, Akad. Nauk Estonian SSR (Tartu) **7**, 112 (1958).
[14] R. P. Hurst, Phys. Rev. **114**, 746 (1959).
[15] For a different approach see the work on O^{-2} by R. E. Watson, Phys. Rev. **111**, 1108 (1958); see also R. E. Watson, Phys. Rev. **120**, 1254 (1960).
[16] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960), 3rd ed., p. 514.
[17] More details of these calculations are contained in Argonne National Laboratory Technical Report ANL-6310 (unpublished).
[18] W. Pauli, Z. Physik **2**, 201 (1920).

The precise experimental values of the susceptibility for these systems is difficult to obtain. Landolt-Börnstein[19] list a value for Ne of -7.2×10^{-6} emu/mole, so that the value listed in Table V is within the experimental error. The susceptibilities for the ionic systems are obtained from measurements on crystals or aqueous solutions. The values for the ionic systems F^- and Na^+ are known only approximately, and Landolt-Börnstein list the values obtained by the various methods. This range of data is discussed by Myers[20] who concludes that a more accurate experimental technique is needed and that none of the values is a standard. The values given in Table V fall within the accepted range as given by Landolt-Börnstein and Myers.

The experimentally determined susceptibility values for LiF and NaF are given as 10.1 and 15.5 (in units of -10^{-6} emu/mole).[20] Using the free-ion values of Table V, we obtain for χ the values $\chi_{\mathrm{LiF}}=13.74$ and $\chi_{\mathrm{NaF}}=17.75$. These values are too large. Use of the χ for the ions with the superposed spheres of ionic radii yields the values $\chi_{\mathrm{LiF}}=12.5$ and $\chi_{\mathrm{NaF}}=16.84$, where the susceptibility for Li^+ has been assumed constant at 0.7. These values are in better agreement with experiment, though still high, as the potential field has not caused very large changes in the charge distributions. The radii of the spheres might be chosen such that the susceptibility calculated would agree with the experimental value, although this procedure does not lead to a unique choice for each ion.

VI. QUALITY OF THE APPROXIMATE WAVE FUNCTIONS

(a) Reduced Logarithmic Derivatives

It is worth knowing to what accuracy an approximate wave function represents an SCF solution of the HF equations. Any comparison of the HF method with other methods assumes that the HF equations are solved exactly. While energy minimization is the strict criterion for the worth of the orbitals, one cannot say for certain that a particular solution is the best attainable without some investigation into the quality of the solution.

For each of the orbitals reported, the value of $-\tilde{R}$ was evaluated by the computer program using (12) and these values are listed along with the other parameters in Tables I–III. The values of $\tilde{R}$ for $1s$ and $2s$ orbitals are in satisfactory agreement with (12), but the $\tilde{R}$ values for the $2p$ orbitals are not. It has been found that there is a close correlation between good s approximate orbitals, that is those which minimize the energy, and the ability of the $\tilde{R}$ value to satisfy (12). This has not been the situation with the $2p$ orbitals. As the energy minimum is approached, the reduced logarithmic derivative varies widely without a predictable pattern. Due to this behavior we have not been able to use (12) as a computational guide for the $2p$ orbitals.

[19] Landolt-Börnstein, *Tabelln* (Springer-Verlag, Berlin, 1950), 6th ed.

[20] W. R. Myers, Revs. Modern Phys. 24, 15 (1952).

TABLE V. Diamagnetic susceptibility for ten-electron systems.

System	Superposed sphere Charge	Radius	$10^6\chi$[a]
F^-	...	...	−12.665
Ne	...	...	− 7.4175
Na^+	...	...	− 5.0816
F^-	1.0	2.40	−11.633
F^-	1.0	2.57	−11.784
F^-	1.0	2.70	−11.888
F^-	1.0	3.789	−12.428
Na^+	−1.0	1.70	− 5.1775
Na^+	−1.0	1.7953	− 5.1539
Na^+	−1.0	1.90	− 5.1344

[a] Units are emu/mole.

(b) The Goodness Test

A stringent test for self-consistency which can be applied to analytic orbitals is the *goodness* test which requires computation of the functions

$$f_\phi(r)=(F-\epsilon)\phi, \tag{15}$$

and

$$g_\phi(r)=F\phi/\epsilon\phi, \tag{16}$$

where we have rewritten (4) as

$$F\phi_i=\epsilon_i\phi_i.$$

To obtain $f_\phi(r)$ and $g_\phi(r)$ we must evaluate the functional $F\phi$ at each point of space (r,θ,φ). Since we are working within the central field approximation, which allowed the introduction of (8), it is not necessary to retain an angular dependence in our goodness functions. We may multiply (15) by $Y_{lm}^*(\theta,\varphi)$ and integrate over $d\Omega_1$. This integration coupled with the integration over $d\Omega_2$ reduces the equation to a one-dimensional equation in r. The evaluation of the terms proceeds in a straightforward manner.[17]

The radial goodness functions,

$$f(r)=F(r)R-\epsilon R \tag{17}$$

and

$$g(r)=F(r)R/\epsilon R, \tag{18}$$

have been tabulated in abbreviated form in Tables VI–VIII for the field-free HF-SCF solutions reported. These indicate that the orbitals are accurate to about four figures. [Recall that (11) determines $R(r)$.] In the region close to the origin the goodness appears poor for many orbitals. This is due to the limitation on the accuracy of the eigenvectors. The possibility exists for obtaining better agreement at the origin by choosing the basis set so that (12) is satisfied exactly. Such a procedure makes the energy minimization procedure very tedious. In addition, the quality of the orbitals

TABLE VI. Goodness functions for F^-.

r	$f_{1s}(r)$	$g_{1s}(r)$	$f_{2s}(r)$	$g_{2s}(r)$	$f_{2p}(r)$	$g_{2p}(r)$
0	...	...	...	...	...	...
0.01	−39.76698	1.03258	21.30934	−0.86010	−4.54128	141.52194
0.02	−16.90096	1.01515	3.32377	0.68181	−3.99146	65.47140
0.03	−6.99129	1.00685	−0.25827	1.02716	−3.42238	39.45916
0.04	−1.87902	1.00201	−0.97554	1.11285	−2.86463	26.18603
0.05	0.71474	0.99916	−0.92455	1.11789	−2.34324	18.18659
0.10	1.29619	0.99764	−0.01013	1.00219	−0.53984	3.42766
0.20	−0.45142	1.00195	0.02746	0.97018	0.21806	0.28074
0.30	0.06205	0.99937	−0.00795	0.98981	0.03394	0.89354
0.40	0.11179	0.99739	−0.00843	0.99432	−0.05371	1.17607
0.50	0.00700	0.99963	−0.00288	0.99830	−0.03972	1.14234
0.60	−0.03848	1.00464	0.00284	1.00171	−0.00625	1.02508
0.70	−0.03141	1.00843	0.00454	1.00297	0.01418	0.93542
0.80	−0.01053	1.00616	0.00281	1.00208	0.01914	0.90036
0.90	0.00487	0.99397	0.00018	1.00015	0.01489	0.91107
1.00	0.01129	0.97163	−0.00163	0.99837	0.00745	0.94888
1.20	0.00814	0.92742	−0.00183	0.99746	−0.00442	1.04000
1.40	0.00090	0.97655	−0.00021	0.99958	−0.00763	1.09037
1.60	−0.00292	1.19844	0.00079	1.00221	−0.00541	1.08293
1.80	−0.00351	1.56691	0.00090	1.00353	−0.00182	1.03574
2.00	−0.00258	1.81148	0.00055	1.00304	0.00097	0.97576
2.40	−0.00022	1.10992	−0.00018	0.99811	0.00269	0.89477
2.80	0.00087	0.53706	−0.00038	0.99220	0.00158	0.90557
3.20	0.00101	0.33778	−0.00025	0.99027	0.00022	0.98036
3.60	0.00079	0.26417	−0.00005	0.99615	−0.00052	1.06980
4.00	0.00053	0.23646	0.00009	1.01229	−0.00070	1.13718
5.00	0.00014	0.24462	0.00017	1.10616	−0.00027	1.12902
6.00	0.00003	0.32670	0.00010	1.29839	0.00005	0.94611
7.00	0.00000	0.52074	0.00005	1.66354	0.00011	0.75958
8.00	0.00000	0.94624	0.00002	2.39392	0.00009	0.65158
9.00	−0.00000	1.88109	0.00001	3.93777	0.00005	0.61761
10.00	−0.00000	3.96362	0.00000	7.32495	0.00003	0.62840
12.00					0.00001	0.69929
14.00					0.00000	0.77618
18.00					0.00000	0.89262

TABLE VII. Goodness functions for Ne.

r	$f_{1s}(r)$	$g_{1s}(r)$	$f_{2s}(r)$	$g_{2s}(r)$	$f_{2p}(r)$	$g_{2p}(r)$
0	...	...	...	...	...	...
0.01	−26.50537	1.01471	−19.19259	1.77116	−3.40765	16.19761
0.02	−14.15198	1.00868	−5.11143	1.22755	−3.11992	8.30352
0.03	−5.97820	1.00405	−0.91657	1.04530	−2.70681	5.43231
0.04	−1.31020	1.00098	0.61293	0.96629	−2.24716	3.89417
0.05	1.04999	0.99913	1.07706	0.93389	−1.79252	2.93592
0.10	0.93934	0.99874	0.13582	0.98473	−0.23544	1.15977
0.20	−0.34851	1.00123	−0.08322	1.09702	0.16108	0.91625
0.30	0.12368	0.99888	0.07988	1.03271	−0.02552	1.01312
0.40	0.05926	0.99864	−0.00649	0.99818	−0.04176	1.02329
0.50	−0.02697	1.00154	−0.03169	0.99146	−0.00813	1.00514
0.60	−0.03289	1.00462	−0.00759	0.99778	0.01049	0.99233
0.70	−0.01184	1.00399	0.01154	1.00385	0.01214	0.98959
0.80	0.00408	0.99682	0.01360	1.00534	0.00701	0.99292
0.90	0.00965	0.98329	0.00668	1.00315	0.00157	0.99812
1.00	0.00871	0.95835	−0.00080	0.99955	−0.00191	1.00271
1.20	0.00204	0.97306	−0.00628	0.99467	−0.00348	1.00688
1.40	−0.00185	1.07022	−0.00312	0.99601	−0.00188	1.00516
1.60	−0.00251	1.22936	0.00077	1.00148	−0.00015	1.00056
1.80	−0.00178	1.33038	0.00258	1.00754	0.00084	0.99567
2.00	−0.00082	1.25580	0.00260	1.01143	0.00112	0.99207
2.40	0.00037	0.79755	0.00069	1.00684	0.00067	0.99128
2.80	0.00064	0.47401	−0.00075	0.98358	0.00004	0.99897
3.20	0.00054	0.31814	−0.00114	0.94580	−0.00030	1.01281
3.60	0.00036	0.23997	−0.00098	0.90116	−0.00040	1.03014
4.00	0.00022	0.19659	−0.00069	0.85720	−0.00036	1.04891
5.00	0.00005	0.14654	−0.00019	0.77754	−0.00017	1.09497
6.00	0.00001	0.12637	−0.00004	0.74548	−0.00005	1.13570
7.00			−0.00001	0.74122	−0.00002	1.17118
8.00			−0.00000	0.74842	−0.00000	1.20231
9.00			−0.00000	0.75928	−0.00000	1.22959
10.00			−0.00000	0.77083	−0.00000	1.25341

TABLE VIII. Goodness functions for Na^+.

r	$f_{1s}(r)$	$g_{1s}(r)$	$f_{2s}(r)$	$g_{2s}(r)$	$f_{2p}(r)$	$g_{2p}(r)$
0	...	...	...	...	...	...
0.01	−25.12714	1.00979	33.30480	0.29460	−3.19990	5.84844
0.02	−13.29794	1.00578	2.28331	0.94582	−3.02384	3.41721
0.03	−4.64523	1.00225	−2.39078	1.06372	−2.61381	2.46892
0.04	0.00177	1.00000	−2.48842	1.07471	−2.11444	1.93926
0.05	2.01714	0.99878	−1.70399	1.05782	−1.61192	1.60337
0.10	0.44722	0.99954	0.30384	0.97943	−0.02626	1.00632
0.20	−0.19373	1.00058	−0.04746	0.79625	0.09404	0.98189
0.30	0.17457	0.99854	−0.01821	0.99680	−0.05682	1.01127
0.40	−0.00527	1.00012	0.01472	1.00208	−0.01583	1.00353
0.50	−0.05657	1.00359	0.00650	1.00095	0.01420	0.99628
0.60	−0.02251	1.00379	−0.00223	0.99963	0.01207	0.99620
0.70	0.00807	0.99651	−0.00338	0.99933	0.00217	0.99917
0.80	0.01716	0.98189	−0.00124	0.99970	−0.00351	1.00163
0.90	0.01350	0.96728	0.00045	1.00014	−0.00428	1.00244
1.00	0.00640	0.96673	0.00072	1.00028	−0.00270	1.00188
1.20	−0.00311	1.06121	−0.00055	0.99966	0.00052	0.99946
1.40	−0.00466	1.28322	−0.00080	0.99920	0.00119	0.99814
1.60	−0.00297	1.44320	0.00012	1.00019	0.00062	0.99856
1.80	−0.00101	1.26849	0.00092	1.00244	0.00002	0.99994
2.00	0.00031	0.88987	0.00106	1.00462	−0.00028	1.00144
2.40	0.00119	0.39256	0.00018	1.00208	−0.00026	1.00283
2.80	0.00101	0.21375	−0.00057	0.98252	−0.00004	1.00098
3.20	0.00065	0.14293	−0.00072	0.94345	0.00007	0.99614
3.60	0.00037	0.10943	−0.00056	0.88929	0.00010	0.98903
4.00	0.00020	0.09123	−0.00036	0.82845	0.00008	0.98033
5.00	0.00004	0.07065	−0.00008	0.69788	0.00003	0.95394
6.00			−0.00001	0.63053	0.00001	0.92422
7.00			−0.00000	0.60698	0.00000	0.89587
8.00			−0.00000	0.60239	0.00000	0.87291
9.00					0.00000	0.85690

cannot be improved at the origin without disturbing the quality of the orbitals over some other region of space. Again, this is due to the limitation of the accuracy of the SCF procedure.

The orbitals and goodness functions have also been tabulated for the solutions in the presence of the superposed field. These tables and tables of the orbitals may be obtained on request. (See footnote 17.)

VII. CONCLUSIONS

We have reported on the results of approximate Hartree-Fock solutions for the ten-electron field-free systems of F^-, Ne, and Na^+. These were obtained as finite expansions of Slater-type functions using a matrix SCF procedure. The results obtained appear more accurate than the previous calculations including those obtained by numerical calculation. This was ascertained through computation of the goodness functions, $f(r)=F(r)R-\epsilon R$ and $g(r)=F(r)R/\epsilon R$. It has been shown, therefore, that the matrix procedure is capable of high accuracy although the relative merits of the numerical method and the matrix method have not been discussed.[21]

Solutions have also been obtained for the ionic systems F^- and Na^+ when in the presence of superposed potential field created by a hollow sphere carrying a unit charge of polarity opposite to that of the ion. The radius of the sphere was varied in order to give a qualitative suggestion of the proper radius to use so as to best simulate a crystalline environment by this procedure. It was found that the charge density of the negative ion was altered much more by the presence of such a sphere than was the charge distribution of the positive ion.

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[21] A short discussion of this point will be contained in a future publication.