from the discrepancy between the theoretical curve and the experimental results that the plane-wave Born approximation is not applicable at low bombarding energies. At higher energies (between 1.5 and 4.0 MeV) this approximation works quite well.[13] To explain the low-energy data it is probably necessary to include effects due to the Coulomb deflection of the bombarding particle by the nuclear field. It has already been shown[14] that this must be done to fit the K x-ray ionization cross sections at low bombarding energies. No theoretical expressions for M-shell ionization cross sections are available so that no quantitative comparison can be made.

ACKNOWLEDGMENTS

The authors would like to thank Roy Cedarlund, Bruce Burford, and Al Horn for their help during the course of these experiments.

PHYSICAL REVIEW VOLUME 127, NUMBER 5 SEPTEMBER 1, 1962

Accurate Analytical Self-Consistent Field Functions for Atoms. II. Lowest Configurations of the Neutral First Row Atoms

E. Clementi
Research Laboratory, International Business Machines Corporation, San Jose, California
AND
C. C. J. Roothaan and M. Yoshimine*
Laboratory of Molecular Structure and Spectra, Department of Physics, University of Chicago, Chicago, Illinois

(Received April 23, 1962)

Self-consistent field wavefunctions have been obtained for the ground states of the first row atoms and for the excited states belonging to the same configurations. They are the solution of the variational problem of finding the best orbitals for a given state, without any additional approximations except for those inherent in the expansion method.

INTRODUCTION

ANALYTICAL self-consistent field (SCF) functions for the $1s^2$, $1s^2 2s$, and $1s^2 2s^2$ atomic configurations were published recently.[1] These calculations, which we shall now consider (I) in a series of papers,[2] differ from other recent work[3–5] in, among other things, that a great deal of effort has been put into obtaining *accurate representations* of the Hartree-Fock functions with

TABLE I. Orbital exponents of the basis function.

	Li(^2S)	Be(^1S)	B(^2P)	C(^3P)	C(^1D)	C(^1S)	N(^4S)
$1s$	2.4803	3.4703	4.4661	5.4125	5.4300	5.3842	6.4595
$1s$	4.7071	6.3681	7.8500	9.2863	9.1500	9.0600	10.8389
$2s$	0.3500	0.7516	0.8320	1.0311	1.2255	1.2100	1.4699
$2s$	0.6600	0.9084	1.1565	1.5020	1.6142	1.5929	1.9161
$2s$	1.0000	1.4236	1.9120	2.5897	2.6990	2.5964	3.1560
$2s$	1.7350	2.7616	3.5213	4.2595	4.2131	4.2500	5.0338
$2p$			0.8783	0.9554	0.9372	1.1060	1.1937
$2p$			1.3543	1.4209	1.4147	0.5074	1.7124
$2p$			2.2296	2.5873	2.5545	2.3590	3.0112
$2p$			5.3665	6.3438	6.3021	6.2000	7.1018
	N(^2D)	N(^2P)	O(^3P)	O(^1D)	O(^1S)	F(^2P)	Ne(^1S)
$1s$	6.4730	6.5035	7.6160	7.6105	7.5333	8.5126	9.5735
$1s$	10.9700	1.1318	13.3243	13.2681	12.7015	14.4130	15.4496
$2s$	1.2745	1.2721	1.7582	1.7582	1.7098	1.8599	1.9550
$2s$	1.8034	1.8038	2.5627	2.5630	2.4512	2.7056	2.8462
$2s$	3.1159	3.0120	4.2832	4.2754	4.0761	4.9019	4.7746
$2s$	5.0338	5.2338	5.9445	5.9445	5.9445	6.4440	7.7131
$2p$	1.0906	1.0580	1.1536	1.0626	1.0555	1.2655	1.4700
$2p$	1.6446	1.6279	1.7960	1.7405	1.6985	2.0301	2.3717
$2p$	3.0200	3.0243	3.4379	3.4198	3.3517	3.9106	4.4545
$2p$	7.1650	7.2029	7.9070	7.8890	7.6690	8.6363	9.4550

---

* Present address: Argonne National Laboratory, Argonne, Illinois.

[1] C. C. J. Roothaan, L. M. Sachs, A. W. Weiss, Revs. Modern Phys. **32**, 186 (1960).

[2] In reference 1, we referred tothe paper describing the general theory (here reference 6, as I). We hereby specifically withdraw this and we shall use the Roman numerals to indicate the various practical applications which are now under way or planned for the near future.

[3] L. C. Allen, J. Chem. Phys. **34**, 1156 (1960).

[4] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 521 (1961); **124**, 1117 (1961).

[5] L. M. Sachs, Phys. Rev. **124**, 1283 (1961).

TABLE II. Total energy, orbital energies, cusps, and expansion coefficients.[a]

Li(^2S) −7.432726	Be(^1S) −14.57302	B(^2P) −24.52905	C(^3P) −37.68861	C(^1D) −37.63132	C(^1S) −37.54954	N(^4S) −54.40091	N(^2D) −54.29615	N(^2P) −54.22809	O(^3P) −74.80936	O(^1D) −74.72921	O(^1S) −74.61095	F(^2P) −99.40929	Ne(^1S) −128.5470
1*s*	1*s*	1*s*	1*s*	1*s*	1*s*	1*s*	1*s*	1*s*	1*s*	1*s*	1*s*	1*s*	1*s*
−2.47773	−4.73267	−7.69528	−11.32552	−11.35144	−11.39112	−15.62891	−15.66635	−15.69151	−20.66864	−20.69318	−20.73039	−26.38294	−32.77276
−3.01720	−4.01874	−5.01179	−6.01404	−6.00540	−6.00682	−7.00949	−7.01199	−7.01475	−8.01920	−8.01843	−8.01252	−9.01863	−10.00493
0.89778	0.91792	0.92109	0.92695	0.91966	0.91962	0.92787	0.93112	0.93232	0.93835	0.93800	0.93397	0.94205	0.93093
0.11031	0.08742	0.07847	0.07665	0.07951	0.08620	0.06535	0.06148	0.05675	0.03825	0.03909	0.05014	0.04499	0.04610
−0.00006	0.00147	−0.00036	−0.00073	−0.00090	0.00068	−0.00067	−0.00033	−0.00020	−0.00097	−0.00097	−0.00071	−0.00010	−0.00085
0.00109	−0.00267	0.00085	0.00167	0.00220	−0.00137	0.00188	0.00122	0.00092	0.00439	0.00440	0.00313	0.00153	0.00321
−0.00144	0.00222	0.00002	0.00639	−0.00042	0.00466	0.00017	0.00048	0.00095	−0.00829	0.00820	−0.00316	−0.00075	−0.00180
0.00937	0.00597	0.01146	0.00210	0.01067	−0.00019	0.01665	0.01732	0.02105	0.04171	0.04100	0.02882	0.02388	0.03537
2*s*	2*s*	2*s*	2*s*	2*s*	2*s*	2*s*	2*s*	2*s*	2*s*	2*s*	2*s*	2*s*	2*s*
−0.19632	−0.30927	−0.49468	−0.70563	−0.71867	−0.73936	−0.94523	−0.96364	−0.97627	−1.24428	−1.25646	−1.27512	−1.57255	−1.93048
−3.04216	−4.04641	−5.02680	−6.02743	−6.02394	−6.02121	−7.01319	−7.01711	−7.02527	−8.03678	−8.03626	−8.02955	−9.02646	−10.00520
−0.14426	0.17066	−0.19401	−0.20786	−0.20727	−0.20998	−0.21744	−0.21838	−0.21658	−0.21979	−0.22033	−0.22210	−0.22924	−0.23171
−0.01584	0.01468	−0.01243	−0.01175	−0.01235	−0.01333	−0.00843	−0.00809	−0.00841	−0.00573	−0.00588	−0.00738	−0.00534	0.00442
0.00195	−0.11550	0.01800	0.06495	0.23681	0.19886	0.27744	0.08811	0.08958	0.42123	0.41542	0.33802	0.27178	0.18201
0.97901	−0.67835	0.71580	0.74109	0.61238	0.61835	0.54807	0.70830	0.68904	0.54368	0.54890	0.58982	0.65367	0.66106
0.09084	−0.30265	0.38903	0.34626	0.31624	0.33657	0.33901	0.36978	0.36685	0.23061	0.23101	0.25682	0.33031	0.32372
−0.08967	0.09232	−0.11029	−0.13208	−0.14709	−0.13361	−0.14212	−0.14451	−0.12646	−0.17856	−0.17837	−0.16495	−0.23130	−0.14244
		2*p*	2*p*	2*p*	2*p*	2*p*	2*p*	2*p*	2*p*	2*p*	2*p*	2*p*	2*p*
		−0.30987	−0.43334	−0.38134	−0.30984	−0.56753	−0.50864	−0.47125	−0.63186	−0.60066	−0.55549	−0.73001	−0.85048
		−2.49899	−3.00014	−2.99993	−3.03499	−3.49996	−3.50003	−3.50005	−4.00010	−4.00007	−3.99956	−4.50005	−5.00003
		0.54005	0.24756	0.31916	0.68350	0.29731	0.25796	0.27164	0.16371	0.13324	0.15046	0.17003	0.22430
		0.38244	0.57773	0.50063	0.05445	0.48388	0.52425	0.51301	0.57600	0.60066	0.56886	0.55982	0.51826
		0.13208	0.23563	0.25045	0.35041	0.28079	0.28935	0.29307	0.33392	0.34397	0.36196	0.34875	0.33902
		0.00957	0.01090	0.01097	0.01237	0.01352	0.01260	0.01208	0.01495	0.01500	0.01715	0.01691	0.01765

---

[a] The total energy is given immediately below the state designation. The first entry in each column is the orbital energy, the second is the computed cusp value, and the following are the expansion coefficients corresponding to the basis set given in Table I.

short expansions. We believe we have generally succeeded in obtaining three decimal place accuracy for the orbitals or better.

The calculations in (I) were based on a formulation of the SCF problem[6] which handles configurations with one open shell correctly as to the off-diagonal Lagrangian multipliers. An extension of this method to two open shells was given by Huzinaga.[7] More recently a modification which can conveniently handle any number of open shells, except that no two shells may be of the same symmetry. This was worked out in detail.[8] Thus the SCF problem for configuration like sp^n, $sp^nd^{n'}$, etc., is solved in the sense that the best orbitals are determined for a particular individual case; for instance, for the oxygen atom in the state $1s^22s2p^5$, ^3P. The IBM 7090 program based on this analysis[8] has the following important features which are rather essential to successful calculations:

(1) automatic optimization of the basis functions, so that satisfactory *short expansions* can be tracked down systematically;

(2) automatic adjustment of convergence thresholds, guaranteeing the greatest accuracy obtainable in a particular case;

(3) elaborate error and diagnostic facilities.

RESULTS AND DISCUSSION

The SCF functions were determined for all the states associated with the ground state configurations of Li, Be, B, C, N, O, F, Ne. The basis functions are Slater-type functions (STO's) with integer principal quantum numbers, but flexible exponents. Note that the notation $1s$, $2s$, $2p$, etc., is used in two different ways. Namely, a $2s$ STO means the basis function $re^{-\zeta r}$, whereas a $2s$ occupied orbital means an s function with one radial node.

In Table I we give the optimized basis functions; they were obtained in each case as the best of many SCF calculations. We believe that we have thus obtained functions which represent to three decimal places or better the solutions of the Hartree-Fock integro-differential equations. A necessary, but not at all sufficient, criterion for having obtained the Hartree-Fock functions is that the virial theorem should be satisfied; for our best expansions we found $V/E = 2.00000 \pm 0.00002$. Another test on the orbitals is the "cusp value" which can be used as a rough indication of the quality of the orbitals near the origin.[1]

In Table II are given the total energies, orbital energies, cusps, and expansion coefficients; numerical tabulations of the radial functions $P(r)$ are computed. Tabulations of these wavefunctions for different grids are available upon request of the authors.[9]

ACKNOWLEDGMENTS

We are indebted to Lockheed Missiles and Space Company and to Argonne National Laboratory for providing the facilities to develop the IBM 7090 program with which these calculations were carried out at the IBM Research Laboratory in San Jose. During the final stages of the design and construction of this program, we were ably assisted by W. S. Worley, whose cooperation is hereby gratefully acknowledged.

---

[6] C. C. J. Roothaan, Revs. Modern Phys. **32**, 179 (1960).

[7] S. Huzinaga, Phys. Rev. **120**, 866 (1960); **122**, 131 (1961).

[8] C. C. J. Roothaan and P. S. Bagus, *Methods in Computational Physics* (Pergamon Press, New York, 1962), Vol. 1 (to be published).

[9] These tables have also been deposited as Document No. 7217 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.