Hartree-Fock Wave Functions for the 4*p*-Shell Atoms

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Conventional (or restricted) Hartree-Fock wave functions have been obtained for Ga^+, Ge^{++}, Br^-, Rb^+, and the neutral atoms Zn, Ga, Ge, As, Se, Br, and Kr. Analytic Hartree-Fock methods utilizing a version of Nesbet's symmetry and equivalence restrictions were used to obtain the solutions in analytic form (sums of powers of r times exponentials). Results are given in the form of wave functions, one-electron energies, and total energies. Comparison is made with the earlier results for Zn and Kr, the only atoms in this group for which Hartree-Fock solutions exist.

I. INTRODUCTION

It has become increasingly apparent that Hartree-Fock wave functions for free atoms and ions can play a vital role in providing approximate descriptions of molecular and solid state phenomenon. A striking example of this, and one which was quite unexpected, is the successful use[1] of free-ion Hartree-Fock wave functions to describe the recent data on isomeric shifts (i.e., total s-electron density at the nucleus) which have been determined by Mössbauer experiments. It goes without saying that basic to any such applications is not only the existence of such functions but their availability in a form suitable for computation. In some of our own studies involving the $4p$ atoms the complete lack of H-F wave functions, for this part of the periodic table, was only too obvious. In order to overcome this difficulty, we have determined Hartree-Fock solutions for Ga^+, Ge^{++}, Br^-, Rb^+, and the neutral atoms Zn, Ga, Ge, As, Se, Br, and Kr. Of these, Hartree-Fock (H-F) results have been previously available for only Zn[2] and Kr.[3] These are conventional or restricted Hartree-Fock solutions in that one-electron functions of the same shell are constrained to have the same radial dependence.[4]

As we have said, aside from their own inherent interest as a description of the electronic structure of free atoms, a major purpose of such calculations is to supply a starting point for further investigations. The spherical ion results have been used to obtain the Sternheimer quadrupole antishielding factors[5] (γ_∞'s) as these extend our knowledge of theoretical values of γ_∞ to ions for which only estimates could be made previously[6] (except for Rb^+ for which Hartree calculations exist). The H-F results have been utilized in several other investigations. Atomic scattering factors have been obtained,[7] and the Ge results have supplied a starting point in an effort to improve on core and valence electron self-consistency in orthogonalized plane wave calculations[8] for germanium.

Analytic H-F methods,[9] utilizing a version of Nesbet's symmetry and equivalence restrictions,[10] have been used to obtain the wave functions. Some details of the method are discussed in Sec. II. A fuller discussion has been given previously[11] where H-F results for $3p$-shell atoms were reported. The H-F results appear in Sec. III along with comparisons of the previously available Zn and Kr functions.

II. DESCRIPTION OF THE CALCULATION

Six of the eleven atoms and ions, for which H-F results will be reported, are closed-shell ions. These can be

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[1] L. R. Walker, G. K. Wertheim, and V. Jaccarino, Phys. Rev. Letters **6**, 98 (1961); S. DeBenedetti, G. Lang, and R. Ingalls, *ibid.* **6**, 60 (1961).

[2] R. E. Watson, Phys. Rev. **118**, 1036 (1960).

[3] B. H. Worsley, Proc. Roy. Soc. (London) **A247**, 390 (1958).

[4] Among recent discussions see: R. E. Watson and A. J. Freeman, Phys. Rev. **120**, 1125 (1960) and R. K. Nesbet, Revs. Modern Phys. **33**, 28 (1961).

[5] R. M. Sternheimer, Phys. Rev. **80**, 102 (1950); **84**, 244 (1951); **86**, 316 (1953); and **95**, 736 (1954).

[6] R. M. Sternheimer and H. M. Foley, Phys. Rev. **102**, 731 (1956); E. G. Wikner and T. P. Das, *ibid.* **109**, 360 (1958).

[7] A. J. Freeman and R. E. Watson (to be published).

[8] F. Quelle (to be published).

[9] C. A. Coulson [Proc. Cambridge Phil. Soc. **34**, 204 (1938)] appears to have been the first to have used an expansion technique in a molecular problem, while C. C. J. Roothaan [Revs. Modern Phys. **23**, 69 (1951)] presented the approach in a particularly desirable form for closed-shell molecules. Nesbet, with his symmetry and equivalence restrictions, extended the method to nonclosed shells and emphasized its use for atomic cases [see reference 10 and also Quarterly Progress Reports No. 15, January, 1955, p. 10; No. 16, April, 1955, p. 38 and p. 41; No. 18, October, 1955, p. 4, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Massachusetts (unpublished)]. Recently C. C. J. Roothaan [Revs. Modern Phys. **32**, 179 (1960)] has extended his formalism to cover the nonclosed shell case for the conventional restricted Hartree-Fock method where nonzero off-diagonal Lagrange multipliers occur. S. Huzinaga [Phys. Rev. **120**, 866 (1960); **122**, 131 (1961)] has extended Roothaan's formalism further.

[10] R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955).

[11] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 521 (1961); Sec. II and the Appendix of this paper supply sufficient information for the reader to construct the Hartree-Fock equations solved in the present paper.

straightforwardly handled,[12] but the remaining five ions with their unfilled $4p$ and filled $2p$ and $3p$ shells raise a problem of maintaining orthogonality between p orbitals. We have discussed this matter at length when reporting[11] $3p$-atom solutions and the reader is referred there for a discussion of this. We have utilized the same version of Nesbet's symmetry and equivalence restrictions[10] as was used in the $3p$-atom investigation.[11] This procedure does not yield the best possible H-F results but it has been our experience,[13] and that[14] of investigators who have used the numerical H-F method, that the H-F eigenfunctions are insensitive to the way in which the orthogonality "problem" is treated. Because of this, application of the symmetry and equivalence restrictions yields results which are only negligibly inferior to the "best results." The discrepancies introduced are far smaller than the difference between the Hartree-Fock and the "true" many-electron wave functions. It is our opinion that if one requires superior many-electron eigenfunctions or eigenvalues one should be prepared to obtain these by going beyond the conventional Hartree-Fock formalism.

As already noted, we have utilized the analytic Hartree-Fock method to obtain our results. This method uses standard matrix techniques to obtain orthonormal analytic Hartree-Fock radial orbitals, $U_i(r)$, of the form

$$U_i(r)=\sum_j C_{ij}R_j(r). \tag{1}$$

Their normalization condition is

$$\int_0^\infty |U_i(r)|^2dr=1, \tag{2}$$

and the basis functions, R_j, are of the form

$$R_j(r)\equiv N_j r^{(l+A_j+1)}e^{-Z_j r}, \tag{3}$$

where l is the one-electron angular momentum quantum number appropriate for the one-electron orbital of which $U_i(r)$ is the radial part. The N_j is a normalization constant and is expressible in terms of the other parameters, i.e.,

$$N_j=[(2Z_j)^{2l+2A_j+3}/(2l+2A_j+2)!]^{\frac{1}{2}}. \tag{4}$$

$U_i(r)$'s of common l value are constructed from a common set of $R_j(r)$'s. Given the basis sets, i.e., the $R_j(r)$'s, the problem is reduced to solving the Hartree-Fock integro-differential equations for the eigenvectors (the C_{ij}'s) and their eigenvalues. This is done by straightforward matrix diagonalization and manipulation and avoids the problems of numerical accuracy inherent in the integrations of the numerical H-F method.

Recently[3,15,16] several workers have overcome the problem of numerical integration accuracy. In particular, Mayers[15] has not only obtained highly accurate numerical H-F solutions but he has also accurately evaluated (a not easy task) the one- and two-electron integrals making up the total energy. This will allow detailed comparisons to be made for the first time between numerical and analytic results.

In general the two approaches are complementary; sometimes one and sometimes the other provides (a) the more suitable method of computation and/or (b) results in a more convenient form. We have found the analytic approach to be very useful[17] when going beyond the conventional free-atom H-F formalism. We have also found it convenient to have the resultant wave functions in analytic form.

In using the analytic approach we have replaced the problem of accuracy of numerical integration by the problem of choosing adequate basis sets. Let us consider this matter now. First there is the question of the size of the set. A small set is desirable because of economy in computer time and retains the advantages of wave functions of analytic form. These advantages come from the ease, accuracy, and convenience with which matrix elements can be obtained if the functions are in analytic form. Large basis sets allow greater accuracy of solution (*provided* that we maintain sufficient linear independence among the basis set, otherwise errors accumulate during matrix diagonalization). Having made the choice of the size of the basis set, there is then the problem of choosing the individual R_j's. In the present work we have relied heavily on earlier[2,18] H-F investigations for the iron series ions and so we will review these briefly. The first investigation[18] involved obtaining H-F solutions for iron series ions in $3d^n$ (i.e., no $4s$ electrons) configurations. The basis sets were the largest that could be fitted onto the computer that was

[12] See D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957) for details concerning the conventional Hartree-Fock formalism and for the derivation of Hartree-Fock equations.

[13] This observation is based on the work reported in reference 11 and in R. K. Nesbet and R. E. Watson, Ann. Phys. **9**, 260 (1960).

[14] In two cases [D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A193**, 299 (1948); W. Hartree, D. R. Hartree, and M. Manning, Phys. Rev. **60**, 857 (1948)] small "off-diagonal" Lagrange multipliers were included for orthogonality; otherwise [D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A164**, 167 (1938); D. A. Goodings (to be published); and unpublished work of D. F. Mayers (1958)] the problem was ignored, i.e., the multipliers were set equal to zero and orthogonality was reasonably maintained.

[15] D. F. Mayers (to be published) has obtained, among others, numerical Hartree-Fock results for Zn, but at the time of writing these results were in a preliminary stage and thus were not available for comparison.

[16] D. A. Goodings (to be published) has obtained accurate numerical "unrestricted" Hartree-Fock solutions for a number of low Z atoms.

[17] For example, the analytic method was used to obtain Hartree-Fock solutions (1) for ions in external "crystalline" fields [R. E. Watson, Phys. Rev. **117**, 742 (1960) and R. E. Watson and A. J. Freeman, Phys. Rev. **120**, 1134 (1960)]; (2) for a nonmagnetic ion in the "exchange field" of neighboring magnetic ions [A. J. Freeman and R. E. Watson, Bull. Am. Phys. Soc. **6**, 234 (1961)]; and (3) to obtain one-electron orbitals which are not separable into a product of a radial and an angular function [C. Sonnenschein (to be published)]. In (2) and (3) the analytic method has several advantages in making the computations possible.

[18] R. E. Watson, Phys. Rev. **119**, 1934 (1960).

TABLE I. Parameters (A_j and Z_j) which define the basis orbitals (R_j's).

R_j's used for the construction of	j	A_j	Z_j for Zn($4s^2,{}^1S$)	Ga$^+$($4s^2,{}^1S$)	Ga($4s^24p,{}^2P$)	Ge^{++}($4s^2,{}^1S$)	Ge($4s^24p^2,{}^3P$)	As($4s^24p^3,{}^4S$)	Se($4s^24p^4,{}^3P$)	Br($4s^24p^5,{}^2P$)	Br$^-$($4s^24p^6,{}^1S$)	Kr($4s^24p^6,{}^1S$)	Rb$^+$($4s^24p^6,{}^1S$)
s orbitals ($l=0$)	1	0	31.6557	32.7951	32.7951	33.9345	33.9345	35.0739	36.2133	37.3527	37.3527	38.4921	39.6315
	2	1	27.9415	28.9818	28.9818	30.0221	30.0221	31.0624	32.1027	33.1430	33.1430	34.1833	35.2236
	3	1	14.4013	14.9772	14.9772	15.5531	15.5531	16.1290	16.7049	17.2808	17.2808	17.8567	18.4326
	4	2	13.6516	14.1895	14.1895	14.7273	14.7273	15.2651	15.8029	16.3407	16.3407	16.8785	17.4163
	5	2	6.8235	7.1430	7.1430	7.4622	7.4622	7.7814	8.1006	8.4198	8.4198	8.7390	9.0582
	6	2	5.1970	5.4823	5.4823	5.7676	5.7676	6.0529	6.3382	6.6235	6.6235	6.9088	7.1941
	7	3	5.4626	5.7224	5.7224	5.9822	5.9822	6.2420	6.5018	6.7616	6.6182	7.0214	7.2812
	8	3	2.3494	2.6961	2.6049	3.0892	2.8604	3.1159	3.3714	3.6269	3.4730	3.8824	4.1379
	9	3	1.3648	1.6592	1.5507	2.0145	1.7366	1.9225	2.1084	2.2943	2.1970	2.4802	2.6661
	10	3	0.8829	1.0954	1.0237	1.3508	1.1645	1.3053	1.4461	1.5869	1.4859	1.7277	1.9464
p orbitals ($l=1$)	1	0	19.6637	20.3930	20.3930	21.1223	21.1223	21.8516	22.5809	23.3102	23.3102	24.0396	24.7689
	2	0	12.3337	12.9976	12.9976	13.6615	13.6615	14.3254	14.9893	15.6532	15.6532	16.3171	16.9810
	3	1	11.7281	12.3476	12.3476	12.9671	12.9671	13.5866	14.2061	14.8256	14.8256	15.4451	16.0646
	4	1	7.4809	7.9029	7.9029	8.3249	8.3249	8.7469	9.1689	9.5909	9.5909	10.0129	10.4349
	5	1	4.6219	4.9255	4.9255	5.2291	5.2291	5.5327	5.8363	6.1399	6.1399	6.4435	6.7471
	6	2	4.3975	4.5067	4.5067	4.7359	4.7359	4.9651	5.1943	5.4235	5.3085	5.6527	5.8819
	7	2	1.9142	2.0473	2.0473	2.2704	2.2704	2.4935	2.7166	2.9397	2.8150	3.1628	3.3859
	8	2	1.0264	1.0911	1.0911	1.2458	1.2458	1.4005	1.5552	1.7099	1.6374	1.8646	2.1006
	9	2	0.6758	0.7335	0.7335	0.8512	0.8512	0.9689	1.0866	1.2043	1.1277	1.3220	1.4893
d orbitals ($l=2$)	1	0	1.8017	2.0478	2.0478	2.2939	2.2939	2.5400	2.7861	3.0322	2.9679	3.2783	3.5244
	2	0	2.9851	3.3364	3.3364	3.6877	3.6877	4.0390	4.3903	4.7416	4.7416	5.0929	5.4442
	3	0	5.3914	5.7709	5.7709	6.1504	6.1504	6.5299	6.9094	7.2889	7.2889	7.6684	8.0479
	4	0	7.9320	8.3627	8.3627	8.7934	8.7934	9.2241	9.6548	10.0855	10.0855	10.5162	10.9469
	5	0	13.5738	14.0706	14.0706	14.5674	14.5674	15.0642	15.5610	16.0578	16.0578	16.5546	17.0514

TABLE II. The eigenvectors (C_{ij}) defining the Hartree-Fock radial functions (U_i) in terms of the basis sets (R_j).

	j	$Zn(4s^2,{}^1S)$	$Ga^+(4s^2,{}^1S)$	$Ga(4s^24p,{}^2P)$	$Ge^{++}(4s^2,{}^1S)$	$Ge(4s^24p^2,{}^3P)$	$As(4s^24p^3,{}^4S)$	$Se(4s^24p^4,{}^3P)$	$Br(4s^24p^5,{}^2P)$	$Br^-(4s^24p^6,{}^1S)$	$Kr(4s^24p^6,{}^1S)$	$Rb^+(4s^24p^6,{}^1S)$
$i=1s$	1	0.90709748	0.90413465	0.90413367	0.90136614	0.90136591	0.89877456	0.89632411	0.89405941	0.89406192	0.89190601	0.88987625
	2	0.11641141	0.12062149	0.12059706	0.12455705	0.12448456	0.12810632	0.13169027	0.13465988	0.13465573	0.13765253	0.14047258
	3	−0.01055316	−0.01260815	−0.01252562	−0.01456509	−0.01432529	−0.01597817	−0.01809951	−0.01893064	−0.01747428	−0.02031053	−0.02162351
	4	0.00868203	0.01060202	0.01047949	0.01253253	0.01215612	0.01373670	0.01615916	0.01667612	0.01461559	0.01814546	0.01958976
	5	−0.01726706	−0.02315043	−0.02213661	−0.03038332	−0.02698088	−0.03191332	−0.04295477	−0.04224288	−0.03266752	−0.04836274	−0.05501380
	6	0.02909256	0.03837489	0.03641491	0.04995061	0.04346710	0.05050929	0.06789049	0.06502205	0.04673850	0.07373764	0.08327781
	7	−0.01528476	−0.01980595	−0.01866719	−0.02556854	−0.02180156	−0.02485716	−0.03320887	−0.03103815	−0.02107437	−0.03482123	−0.03903396
	8	0.00030244	0.00061449	0.00050201	0.00121533	0.00074852	0.00104629	0.00180540	0.00181172	0.00159735	0.00234621	0.00306864
	9	−0.00019724	−0.00038622	−0.00032001	−0.00071985	−0.00046289	−0.00062518	−0.00106868	−0.00100598	−0.00090279	−0.00125984	−0.00172477
	10	0.00008165	0.00014541	0.00012890	0.00023725	0.00018120	0.00023787	0.00040031	0.00036230	0.00031786	0.00044276	0.00065053
$i=2s$	1	−0.27981497	−0.27986383	−0.27985348	−0.27991606	−0.27989444	−0.27993746	−0.27996963	−0.28003250	−0.27994219	−0.28007968	−0.28013752
	2	−0.16563476	−0.16678269	−0.16676161	−0.16779003	−0.16777153	−0.16864884	−0.16962121	−0.17014316	−0.17249767	−0.17075739	−0.17131092
	3	0.67545985	0.66811921	0.66803160	0.66112272	0.66102808	0.65431295	0.64856880	0.64192396	0.60013676	0.63611581	0.63059776
	4	0.45229459	0.46030181	0.46033996	0.46805722	0.46798376	0.47539660	0.48136252	0.48925636	0.54378769	0.49584938	0.50227173
	5	0.14904477	0.13825694	0.13828769	0.12627758	0.12802690	0.11706234	0.11505374	0.09495210	0.05184964	0.08286656	0.06920842
	6	−0.19567300	−0.16900390	−0.16892698	−0.14212278	−0.14523889	−0.12193749	−0.11564016	−0.07885577	−0.01577214	−0.05694830	−0.03317976
	7	0.09582943	0.07862839	0.07853960	0.06203650	0.06377211	0.04987885	0.04546751	0.02544879	−0.00341365	0.01358279	0.00098203
	8	−0.00063612	0.00051434	−0.00051174	0.00003458	−0.00024728	0.00021044	0.00011532	0.00156438	0.00284058	0.00254607	0.00396587
	9	0.00035545	0.00019249	0.00022111	−0.00027554	−0.00000801	−0.00035554	−0.00030383	−0.00124117	−0.00195256	−0.00181966	−0.00282945
	10	−0.00013818	−0.00005129	−0.00007456	0.00013323	0.00002372	0.00016390	0.00013692	0.00048914	0.00072679	0.00068879	0.00113678
$i=3s$	1	0.10598677	0.10702338	0.10702374	0.10813854	0.10813368	0.10926361	0.11040375	0.11150294	0.11146347	0.11256998	0.11362859
	2	0.05959651	0.06119108	0.06097027	0.06272518	0.06228110	0.06352238	0.06450933	0.06576739	0.06655214	0.06677341	0.06772936
	3	−0.24825317	−0.24974526	−0.24895014	−0.25129423	−0.24969232	−0.25040727	−0.25043030	−0.25155304	−0.23475783	−0.25195062	−0.25231847
	4	−0.34366733	−0.34701174	−0.34854156	−0.35081615	−0.35393374	−0.35956495	−0.36661198	−0.37138991	−0.39329055	−0.37728707	−0.38328364
	5	0.73912139	0.64432040	0.66737595	0.55154568	0.60073391	0.53802877	0.49214037	0.42560703	0.41883164	0.37398855	0.32463808
	6	−0.08520175	0.10378904	0.05620145	0.28491788	0.18532109	0.30413184	0.38992937	0.51090294	0.54188295	0.60272698	0.68996185
	7	0.53641260	0.43044605	0.45988350	0.33007863	0.39169562	0.33068296	0.28882767	0.22874180	0.21053722	0.18525767	0.14437383
	8	0.03048772	0.03446115	0.03092930	0.03951374	0.03091084	0.03085439	0.02954984	0.03092025	0.02480334	0.03146733	0.03261221
	9	−0.01676536	−0.01793408	−0.01636989	−0.01898579	−0.01546846	−0.01443464	−0.01249665	−0.01244238	−0.01012664	−0.01167423	−0.01233601
	10	0.00678473	0.00655008	0.00646920	0.00601189	0.00597458	0.00546188	0.00462019	0.00458575	0.00373252	0.00428437	0.00478593
$i=4s$	1	−0.02116275	−0.02657713	−0.02487901	−0.03089578	−0.02774082	−0.03012110	−0.03230841	−0.03420874	−0.03330359	−0.03589367	−0.03840633
	2	−0.01228875	−0.01503131	−0.01409084	−0.01748191	−0.01563894	−0.01700713	−0.01831023	−0.01947774	−0.01946686	−0.02058588	−0.02210015
	3	0.05101164	0.06143794	0.05759839	0.07020964	0.06283842	0.06720989	0.07120779	0.07462571	0.06874398	0.07775195	0.08238557
	4	0.06996675	0.09334884	0.08700354	0.11105925	0.09983625	0.11036951	0.12015399	0.12863010	0.12924824	0.13592181	0.14692594
	5	−0.06269363	−0.15760614	−0.13446812	−0.20641348	−0.17852820	−0.20283058	−0.22339614	−0.23155680	−0.16206355	−0.23182777	−0.23857743
	6	−0.22885257	−0.10694237	−0.12854594	−0.06583725	−0.07461864	−0.05524901	−0.04097520	−0.04750869	−0.17826355	−0.06523353	−0.08366013
	7	0.04751508	−0.06864891	−0.04347880	−0.13267354	−0.10279938	−0.13877892	−0.17171638	−0.19067388	−0.09919678	−0.20277922	−0.22089864
	8	0.40669291	0.42372176	0.44960946	0.37269557	0.47173308	0.48213845	0.49397419	0.49966946	0.54486003	0.50286503	0.52412702
	9	0.59138808	0.64785939	0.59011613	0.70560098	0.58289441	0.57986312	0.57503311	0.57378512	0.49587107	0.57320774	0.60184584
	10	0.12181579	0.02950113	0.07764199	0.02523804	0.06878168	0.06993423	0.07411869	0.08093770	0.11299232	0.09000001	0.04580513

TABLE II (*continued*).

	j	Zn($4s^2$,^1S)	Ga^+($4s^2$,^1S)	Ga($4s^24p$,^2P)	Ge^{++}($4s^2$,^1S)	Ge($4s^24p^2$,^3P)	As($4s^24p^3$,^4S)	Se($4s^24p^4$,^3P)	Br($4s^24p^5$,^2P)	Br^-($4s^24p^6$,^1S)	Kr($4s^24p^6$,^1S)	Rb^+($4s^24p^6$,^1S)
$i=2p$	1	0.13632108	0.13205013	0.13203146	0.12820957	0.12818694	0.12471123	0.12161700	0.11885621	0.11884028	0.11631155	0.11405529
	2	0.81190588	0.79207890	0.79218268	0.77397963	0.77408561	0.75749233	0.74206901	0.72773761	0.72773755	0.71452355	0.70216821
	3	0.05963430	0.08506727	0.08496014	0.10771998	0.10761908	0.12790288	0.14635841	0.16312389	0.16308735	0.17819787	0.19202635
	4	0.02804937	0.02760269	0.02762653	0.02803246	0.02804390	0.02907437	0.03037509	0.03193413	0.03206215	0.03398562	0.03602158
	5	−0.00617375	−0.00431952	−0.00434653	−0.00349905	−0.00350803	−0.00315002	−0.00304190	−0.00311412	−0.00323128	−0.00357807	−0.00398609
	6	0.00288420	0.00178174	0.00179663	0.00127725	0.00127813	0.00098768	0.00082227	0.00072998	0.00083492	0.00083640	0.00087301
	7	−0.00001924	0.00000615	0.00000683	0.00006832	0.00007395	0.00012503	0.00017096	0.00020924	0.00011885	0.00019560	0.00024083
	8	−0.00000309	−0.00002724	−0.00002745	−0.00007918	−0.00008345	−0.00012712	−0.00016601	−0.00019733	−0.00013120	−0.00019686	−0.00024620
	9	0.00000381	0.00001631	0.00001628	0.00004243	0.00004436	0.00006533	0.00008365	0.00009697	0.00006494	0.00009637	0.00011282
$i=3p$	1	−0.05431937	−0.05341600	−0.05338908	−0.05255531	−0.05259611	−0.05198741	−0.05131172	−0.05086990	−0.05080062	−0.05053151	−0.05027371
	2	−0.29604653	−0.29302738	−0.29361617	−0.29096502	−0.29143936	−0.28934424	−0.28780357	−0.28601688	−0.28605059	−0.28413488	−0.28246208
	3	−0.12925735	−0.13777294	−0.13754547	−0.14554676	−0.14564100	−0.15344400	−0.16008110	−0.16683777	−0.16638357	−0.17325791	−0.17932574
	4	0.45044380	0.41717707	0.41689984	0.38950036	0.38955493	0.36457256	0.34045512	0.31866779	0.31670662	0.29820784	0.27896436
	5	0.60799336	0.65315311	0.65614098	0.68538043	0.68869754	0.71898211	0.74784057	0.77422733	0.77835143	0.79857614	0.82244622
	6	0.12919068	0.11556996	0.11248089	0.10715093	0.10308129	0.09384425	0.08553410	0.07767760	0.07761614	0.07051512	0.06240623
	7	0.02651500	0.02101822	0.02085233	0.01966771	0.02074593	0.02093698	0.01976050	0.01929407	0.01603307	0.01944683	0.02075060
	8	−0.01402794	−0.01120365	−0.01112124	−0.01039622	−0.01067466	−0.01026878	−0.00952648	−0.00900867	−0.00764718	−0.00873055	−0.00955913
	9	0.00662338	0.00539764	0.00540078	0.00486827	0.00507145	0.00477444	0.00433325	0.00401448	0.00336516	0.00382104	0.00379283
$i=4p$	1			0.00851157		0.01050560	0.01198709	0.01214282	0.01258977	0.01065810	0.01307891	0.01335865
	2			0.04821793		0.05687705	0.06342685	0.06982584	0.07479640	0.07205327	0.07881708	0.08867493
	3			0.02336514		0.03189312	0.03904179	0.04113315	0.04475386	0.03712509	0.04871024	0.05203390
	4			−0.07211494		−0.08632606	−0.09469433	−0.09074191	−0.08883384	−0.07257493	−0.08695068	−0.08205795
	5			−0.13014302		−0.15697729	−0.18169817	−0.21495730	−0.24263505	−0.24214166	−0.26704517	−0.31704766
	6			0.01093182		0.00330906	−0.00320120	0.00406558	0.00642446	0.03040386	0.00625232	0.01868629
	7			0.41869593		0.48403755	0.52368131	0.53513573	0.54683306	0.54776493	0.55603453	0.57780436
	8			0.63959741		0.61165694	0.58340596	0.54004030	0.51388790	0.39752275	0.49831427	0.50500149
	9			0.05944962		0.01455123	0.00217450	0.04275167	0.06244276	0.19739924	0.07318112	0.02673810
$i=3d$	1	0.13359702	0.10872067	0.11394008	0.09039209	0.10292151	0.09693210	0.09313190	0.09117469	0.08748007	0.09088797	0.08865689
	2	0.42930368	0.44511438	0.44001041	0.45940041	0.44673035	0.45186644	0.45720985	0.46209809	0.46866733	0.46687663	0.47505279
	3	0.39516908	0.37788834	0.38050777	0.36135244	0.36801378	0.35664626	0.34560852	0.33544523	0.33199635	0.32567254	0.31397852
	4	0.17950968	0.18580394	0.18411731	0.19057043	0.18650855	0.18742602	0.18762404	0.18710998	0.18842290	0.18592421	0.18576618
	5	0.03080699	0.03079098	0.03097435	0.03079474	0.03122981	0.03149040	0.03170923	0.03192129	0.03173741	0.03210521	0.03211207

TABLE III. Hartree-Fock one-electron energies (ϵ_i), one-electron nuclear potential+kinetic energies (K_i), total energies, and two-electron $F^k(4p,4p)$ integrals. All energies are in atomic units (1 a.u.=2 ry).

	$Zn(4s^2,{}^1S)$	$Ga^+(4s^2,{}^1S)$	$Ga(4s^24p,{}^2P)$	$Ge^{++}(4s^2,{}^1S)$	$Ge(4s^24p^2,{}^3P)$	$As(4s^24p^3,{}^4S)$	$Se(4s^24p^4,{}^3P)$	$Br(4s^24p^5,{}^2P)$	$Br^-(4s^24p^6,{}^1S)$	$Kr(4s^24p^6,{}^1S)$	$Rb^+(4s^24p^6,{}^1S)$
ϵ_{1s}	−353.299	−379.120	−378.811	−405.988	−405.235	−432.578	−460.862	−490.052	−489.719	−520.167	−551.658
ϵ_{2s}	−44.358	−48.469	−48.165	−52.887	−52.145	−56.306	−60.666	−65.194	−64.858	−69.904	−75.250
ϵ_{3s}	−5.635	−6.697	−6.394	−7.926	−7.189	−8.029	−8.931	−9.869	−9.530	−10.850	−12.333
ϵ_{4s}	−0.291	−0.688	−0.424	−1.175	−0.553	−0.686	−0.837	−0.992	−0.684	−1.153	−1.721
ϵ_{2p}	−38.921	−42.795	−42.490	−46.973	−46.231	−50.150	−54.266	−58.548	−58.214	−63.011	−68.107
ϵ_{3p}	−3.837	−4.783	−4.482	−5.893	−5.160	−5.880	−6.661	−7.476	−7.138	−8.332	−9.688
ϵ_{4p}			−0.208		−0.287	−0.370	−0.403	−0.457	−0.137	−0.524	−1.009
ϵ_{3d}	−0.780	−1.494	−1.192	−2.368	−1.633	−2.112	−2.649	−3.218	−2.880	−3.826	−4.933
K_{1s}	−449.848	−480.346	−480.346	−511.845	−511.845	−544.343	−577.841	−621.339	−621.339	−647.838	−684.336
K_{2s}	−110.571	−118.164	−118.163	−126.007	−126.005	−134.098	−142.441	−151.035	−151.033	−159.878	−168.973
K_{3s}	−43.155	−46.384	−46.381	−49.754	−49.746	−53.241	−56.860	−60.602	−60.598	−64.457	−68.438
K_{4s}	−12.218	−15.140	−14.470	−17.748	−16.531	−18.540	−20.586	−22.631	−22.216	−24.695	−27.247
K_{2p}	−109.913	−117.508	−117.509	−125.353	−125.351	−133.449	−141.795	−150.391	−150.391	−159.238	−168.336
K_{3p}	−40.981	−44.206	−44.233	−47.584	−47.613	−51.123	−54.760	−58.518	−58.508	−62.386	−66.384
K_{4p}			−10.749		−13.056	−15.198	−17.068	−19.035	−17.976	−21.052	−23.954
K_{3d}	−34.722	−38.541	−38.505	−42.390	−42.304	−46.140	−50.042	−54.022	−54.014	−58.071	−62.233
$F^0(4p,4p)$			0.2650		0.3162	0.3605	0.3942	0.4293	0.3975	0.4643	0.5229
$F^2(4p,4p)$			0.1340		0.1623	0.1867	0.2038	0.2221	0.2005	0.2406	0.2750
Total energy	−1777.841	−1923.059	−1923.260	−2074.529	−2075.354	−2234.239	−2399.867	−2572.443	−2581.539	−2752.056	−2938.220

used.[19] Their size fixed, they were obtained by an extensive series of computations where the basis functions were varied. This search concentrated on obtaining good basis functions for V through Ni. This investigation was followed by a series of H-F calculations for the neutral $3d^{n-2}4s^2$ iron series atoms. These were done on a computer of larger capacity, and the basis sets were obtained by adding additional s-like R_j's (for the construction of the outer loop of the $4s$ orbitals) to the otherwise unmodified basis sets of the first investigation. An extensive basis function search was thus avoided at the cost of building in the shortcomings of the first effort. Subsequently, more accurate analytic H-F calculations were done for Zn ($3d^{10}4s^2,{}^1S$), which are reported here, and for Fe ($3d^64s^2,{}^5D$), Mn^{++} ($3d^5,{}^6S$), and Cu^+ ($3d^{10},{}^1S$), which appear elsewhere.[20] The greatest discrepancies between calculations for the same state occur for Cu^+ and Zn, which lie outside the group emphasized in the first basis-function search.

The present computations were done on the IBM 704 computer at Avco whose capacity (32 000 words) allowed the use of larger basis sets and we have taken advantage of this capability. In fact, the choice of R_j's is based on the iron series R_j's and on an extensive basis-function search for Kr followed by tests on the resultant sets for other atoms. As a result the H-F functions appearing in this paper are more accurate than the earlier[2,18] iron series solutions. The parameters defining the R_j's appear in Table I. We have reported (and used) screening constants (Z_j's) with four digits after the decimal point. This does not mean that Z_j's were uniquely established to this many digits. The investigations varying the Z_j's carried this many digits, and since these were kept in the final calculations they are reported here.

III. RESULTS

The eigenvectors (C_{ij}) which define the $U_i(R)$ in terms of the $R_j(r)$ appear in Table II. Note that the C_{ij}'s are given for *normalized* $R_j(r)$'s. The C_{ij}'s have not been uniquely established to the number of digits quoted, but with these digits they provide well-orthonormalized, well-defined Hartree-Fock orbitals. Total energies, one-electron energies (ϵ_i), one-electron kinetic plus nuclear potential energies (K_i), and two-electron $F^k(4p,4p)$ integrals[21] are listed in Table III. The quantities appearing there are accurately evaluated for the functions defined in Table II. The Hartree-Fock one-electron and total energies have not been rigorously

[19] The Massachusetts Institute of Technology Whirlwind I computer was used.

[20] For definitions see E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1953), p. 177.

[21] The Mn^{++} results appear in an investigation [R. E. Watson and A. J. Freeman (to be published)] of hyperfine effects, those for Cu^+ in an investigation of quadrupole polarizabilities [A. J. Freeman and R. E. Watson, Bull. Am. Phys. Soc. 6, 166 (1961)], and the Fe results are unpublished.

TABLE IV. Kr one-electron energies (in atomic units) for the present calculation and as obtained by Worsley.[a]

	Worsley's results[a]	Present calculation
ϵ_{1s}	-520	-520.167
ϵ_{2s}	-69.9	-69.904
ϵ_{3s}	-10.8_5	-10.850
ϵ_{4s}	-1.151_5	-1.153
ϵ_{2p}	-63.1	-63.011
ϵ_{3p}	-8.33_5	-8.332
ϵ_{4p}	-0.53	-0.524
ϵ_{3d}	-3.80	-3.826

[a] See reference 3.

established to the number of digits quoted. More accurate solution of the Hartree-Fock equations (e.g., through the use of larger improved basis sets) will affect the last one or two digits of these quantities. Note that Hartree atomic units have been used (1 a.u.$=$2 ry).

The K_i's, which do not include interelectronic terms, offer a sensitive test of wave function behavior. For fixed Z, a contraction in a $U_i(r)$ causes an increase in the magnitude of its K_i. Inspection of the K_i's of Table III shows in general that the U_i's of any one element contract when going to a state of higher positive ionization. This is, of course, not surprising. Of greater interest is the exception to this rule which occurs for the $2p$ and $3p$ orbitals on going from a state with one or more $4p$ orbitals (such as Ga or Ge) to a state with none (such as Ga^+ or Ge^{++}). The requirements of obtaining three simultaneous (hence orthogonal) p-like eigenfunctions for the former state and the partial relaxation of this for the latter has caused a reverse trend in K_{2p} and K_{3p}. It should be noted that the resultant $2p$ and $3p$ orbital variations are small.

Let us now compare the present results with those previously available for Kr and Zn. Worsley's numerically obtained[8] ϵ_i's for Kr appear in Table IV. K_i's and the total energy were not obtained by her. We see that there is substantial agreement between the two sets of results. More detailed comparisons can be made with the earlier obtained[2] analytic Zn results where K_i's, ϵ_i's, and the total energy are available. These appear in Table V. Comparison of ϵ_i's show larger discrepancies than were seen for Kr. This is due to the previously discussed deficiencies in the basis set of the earlier calculation. If one chose to inspect the ϵ_i's to learn of orbital variation as has often been done (out of necessity) in the past, one would conclude that the $4s$ orbitals have changed least (the ϵ_{4s}'s being in best agreement between calculations) and that the $3d$ orbital of the present calculation is the more contracted (since its ϵ_{3d} is more negative). On the other hand, inspection of the K_i's shows that neither conclusion is correct. The $4s$ orbitals show the greatest, not the least, modification and the present calculation's $3d$ orbital is expanded and not contracted relative to the earlier results. In addition to inspecting individual ϵ_i's, sums[22] of ϵ_i's (which also appear in Table V) have in the past been used to estimate the variation in total energy. Such sums suggest that there has been a 1 a.u. change in total energy when in reality a change of one fiftieth that size has occurred. In other words the one-electron energies supply an often misleading "yardstick" to wave-function behavior.

TABLE V. Zn one-electron energies (ϵ_i), one-electron kinetic +nuclear potential energy integrals (K_i), sums of one-electron energies, and total energies for the present and earlier[a] analytic Hartree-Fock calculations, in atomic units.

	Earlier calculation[a]	Present calculation
ϵ_{1s}	-353.261	-353.299
ϵ_{2s}	-44.319	-44.358
ϵ_{3s}	-5.600	-5.635
ϵ_{4s}	-0.286	-0.291
ϵ_{2p}	-38.882	-38.921
ϵ_{3p}	-3.804	-3.837
ϵ_{3d}	-0.751	-0.780
K_{1s}	-449.849	-449.848
K_{2s}	-110.569	-110.571
K_{3s}	-43.136	-43.155
K_{4s}	-12.060	-12.218
K_{2p}	-109.912	-109.913
K_{3p}	-40.996	-40.981
K_{3d}	-34.842	-34.722
Total energy	-1777.823	-1777.843
$\sum_{i=1}^{30} \epsilon_i$	-1070.558	-1071.514

[a] See reference 2.

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[22] Such a sum counts interelectronic interaction term twice and so is not the correct expression for total energy.