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Accurate Analytical Self-Consistent Field Functions for Atoms. IV. Ground States and Several Excited States for Atoms and Ions of Al and Cu†‡

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Self-consistent field calculations by the expansion method were carried out for the ground states and several excited states of atoms and ions of Al and Cu. The results for the total energies of the states computed represent very accurately the absolute Hartree-Fock solutions. The wave functions were calculated with the requirement to satisfy identically the cusp condition so that they can be considered to be particularly accurate in the immediate vicinity of the nucleus. Comparison with experiment is carried out in particular for the calculated energy levels.

INTRODUCTION

QUANTUM-MECHANICAL laws of nature permit the calculation of all properties of atoms and molecules from their wave functions. Therefore, the calculation of such wave functions has become of great importance. However, approximate methods are necessary for many-particle systems.

An important method which has wide applicability is the self-consistent field (SCF) method using the factorization of the total wave function into one-electron wave functions. This method was originally developed for atoms by Hartree and Fock using the numerical integration procedure.[1] In this paper we shall use the name Hartree-Fock orbitals for the solutions of the numerical Hartree-Fock equations. More recently another method has proved very successful, namely, the SCF expansion method.[2–4]

The present paper is the fourth in a series of applications of this method aimed at obtaining high accuracy.[5–7] The calculations were carried out with a program written for the IBM 7090 computer.[4]

THEORETICAL REMARKS

The n-electron wave functions are constructed from antisymmetrized products, which are built from one-electron wave functions called orbitals. For closed-shell configurations one antisymmetrized product is sufficient to represent the total wave function. For open-shell configurations the total wave functions are, in general, represented by linear combinations of antisymmetrized products. To a total wave function constructed in this way, the variational principle is applied and the self-consistent field equations for the orbitals are obtained.

The orbitals are denoted by $\varphi_{i\lambda\alpha}(r,\vartheta,\varphi)$, where λ and α stand for the symmetry species and subspecies, respectively, and i distinguishes occupied orbitals of the same symmetry. Each orbital $\varphi_{i\lambda\alpha}$ is expanded in terms of basis functions of the same symmetry. The expansion then reads

$$\varphi_{i\lambda\alpha}=\sum_{p}\chi_{p\lambda\alpha}C_{i\lambda p}\,, \tag{1}$$

where $C_{i\lambda p}$ are coefficients of the expansion. The basis functions used are given by

$$\chi_{p\lambda\alpha}(r,\vartheta,\varphi)=R_{\lambda p}(r)Y_{\lambda\alpha}(\vartheta,\varphi)\,, \tag{2}$$

where $R_{\lambda p}$ is a normalized Slater-type function

$$R_{\lambda p}(r)=[(2n_{\lambda p})!]^{-1/2}(2\zeta_{\lambda p})^{n_{\lambda p}+\frac{1}{2}}r^{n_{\lambda p}-1}e^{-\zeta_{\lambda p}r}; \tag{3}$$

$n_{\lambda p}$ is the principal quantum number, $\zeta_{\lambda p}$ is the orbital exponent, and $Y_{\lambda\alpha}$ is the usual normalized spherical harmonic. One can use other functions for the radial parts of the basis functions; however, Slater-type functions are sufficiently flexible and at the same time computationally manageable, and we see no merit in using more complicated radial functions.

It is well known that the Hartree-Fock orbitals satisfy the cusp condition[5]

$$(\lambda+1)\left(\frac{1}{f_{\lambda}}\frac{df_{\lambda}}{dr}\right)_{r=0}=-Z; \tag{4}$$

TABLE I. Comparison with other calculations.

Source of calculation Quantity		Other authors	This work
Al, $3s^23p$, ^2P;	E[au]	-241.8692[a]	-241.8762
Cu$^+$, $3d^{10}$, ^1S;	E[au]	-1638.7049[b]	-1638.7215
Cu, $3d^94s^2$, ^2D;	E[au]	-1638.9310[c]	-1638.9438
Al;	$R^2_{4s,3p}$	5.17[d]	5.27
Al;	$R^2_{3p,3d}$	10.85[d]	6.43

[a] See Ref. 12. [b] See Ref. 16. [c] See Ref. 18. [d] See Ref. 15.

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TABLE II. Optimized exponents ζ of the basis functions for Al^+, Al and its excited states.

Atom and state / Basis function	Al^+ $3s^2, {}^1S$	Al $3s^23p, {}^2P$	Al $3s^23d, {}^2D$	Al $3s^24s, {}^2S$	Al $3s^24p, {}^2P$	Al $3s^24f, {}^2F$	Al $3s3p^2, {}^4P$	Al $3s3p^2, {}^2D$	Al $3s3p^2, {}^2P$	Al $3s3p^2, {}^2S$	Al $3p^3, {}^4S$
1s	13.00000	13.00000	13.00000	13.00000	13.00000	13.00000	13.00000	13.00000	13.00000	13.00000	13.00000
3s	14.81882	14.81882	14.81882	14.81882	14.81882	14.81882	14.81882	14.81882	14.81882	14.81882	14.81882
3s	10.95967	10.95967	10.95967	10.95967	10.95967	10.95967	10.95967	10.95967	10.95967	10.95967	10.95967
3s	7.03850	7.03975	7.03975	7.03975	7.03850	7.03850	6.84073	6.84073	6.84073	6.84073	6.94000
3s	4.45427	4.45008	4.45008	4.45008	4.45427	4.45427	4.34600	4.34600	4.34600	4.34600	4.38000
3s	1.73891	1.74739	1.75275	1.75723	1.73891	1.73891	1.69500	1.72801	1.79372	1.74000	1.80276
3s	1.24151	1.09143	1.22688	1.22423	1.22988	1.22365	1.13585	1.12451	1.19261	1.13000	
3s	0.68000	0.44922	0.67199	0.86184[a]	0.68566	0.67841	0.47000	0.46000	0.49000	0.47000	
4s				0.56059							
4s				0.30586							
2p	6.50000	6.50000	6.50000	6.50000	6.50000	6.50000	6.50000	6.50000	6.50000	6.50000	6.50000
4p	15.62221	15.71772	15.62737	15.60893	15.62221	15.62221	15.80000	15.80000	15.80000	15.80000	15.80000
4p	7.01039	7.34587	7.01267	7.00440	7.01039	7.01039	7.38884	7.38884	7.38884	7.38884	7.43962
4p	4.36248	4.62878	4.36365	4.35712	4.36248	4.36248	4.65954	4.65954	4.65954	4.65954	4.77264
4p	1.70240	2.01378	1.70286	1.70031	2.92882	1.70240	2.04374	1.99006	1.96055	1.95787	2.27957
4p		1.52000			1.49395		1.57000	1.50000	1.45000	1.44000	1.56017
4p		1.05599			0.96361		1.14302	1.03570	0.97133	0.96276	1.04478
4p		0.50615			0.42256		0.55000	0.50000	0.47000	0.46000	0.53740
4p					0.21400						
3d			4.33333								
5d			2.78673								
5d			1.24807								
5d			0.61618								
5d			0.39284								
5d			0.21000								
4f						3.25000					
6f						1.50759					
6f						0.60985					
6f						0.33227					

[a] Corresponds to basis function 4s.

where $r^\lambda f_\lambda(r)$ is the radial part of the orbital, and Z is the nuclear charge. However, if we expand the orbitals $\varphi_{i\lambda\alpha}$ in terms of known basis functions, they would generally not satisfy the cusp condition. Nevertheless, for a special choice[7] of basis functions the cusp condition can be identically satisfied, namely, if

$$\begin{aligned} \zeta_{\lambda 1} &= Z/(\lambda+1), \\ n_{\lambda 1} &= \lambda+1, \\ n_{\lambda p} &\geqslant \lambda+3, \quad p>1. \end{aligned} \tag{5}$$

It is also well known that for the Hartree-Fock solution the virial theorem is satisfied, namely,

$$E_p/E_k=-2, \tag{6}$$

where E_p and E_k are the potential and kinetic energies, respectively. The total energy E is, of course, given by

$$E=E_p+E_k. \tag{7}$$

When the orbitals $\varphi_{i\lambda\alpha}$ are given by Eqs. (1)–(3), it can be shown that there exists a common scale factor by which all the orbital exponents can be multiplied so that the virial theorem (6) is identically satisfied.

Clearly the identical satisfaction of the cusp conditions by imposing the restrictions (5) is incompatible with adjusting the exponents by a common scale factor to satisfy the virial theorem. In this work we enforce the cusp conditions so that we can use the value of E_p/E_k as compared with -2 as a guide for the accuracy of the results obtained by the expansion method with respect to the Hartree-Fock solutions.

TABLE III. Optimized exponents ζ of the basis functions for Cu^+, Cu, and its excited states.

Atom and state / Basis function	Cu^+ $3d^{10}, {}^1S$	Cu $3d^{10}4s, {}^2S$	Cu $3d^{10}4p, {}^2P$	Cu $3d^94s^2, {}^2D$
1s	29.00000	29.00000	29.00000	29.00000
3s	35.96083	35.96083	35.96083	35.96083
3s	24.96766	24.96766	24.96766	24.96766
3s	16.50784	16.50784	16.50784	16.50784
3s	11.89243	11.89243	11.89243	11.89243
3s	6.40248	6.40248	6.40248	6.40248
3s	4.12887	4.12887	4.12887	4.12887
4s		2.10931		2.19823
4s		1.11020		1.17860
2p	14.50000	14.50000	14.50000	14.50000
4p	33.47662	33.47662	33.47662	33.47662
4p	15.81620	15.81620	15.81620	15.81620
4p	10.75110	10.75110	10.75110	10.75110
4p	6.82655	6.82655	6.82655	6.82655
4p	4.07204	4.06941	4.07204	4.07204
4p			1.42000	
4p			0.70134	
3d	9.66667	9.66667	9.66667	9.66667
5d	13.93533	13.88335	13.93533	14.23703
5d	7.87939	7.85000	7.87939	8.05000
5d	4.28000	4.25312	4.28000	4.42710
5d	3.68321	3.72000	3.68321	3.91000
5d	2.28675	2.18421	2.28675	2.42755

TABLE IV. Eigenvectors of coefficients $C_{i\lambda p}$ for Al$^+$, Al, and its excited states.

Atom and state / Basis function	Al$^+$ $3s^2$, ^1S	Al $3s^23p$, ^2P	Al $3s^23d$, ^2D	Al $3s^24s$, ^2S	Al $3s^24p$, ^2P	Al $3s^24f$, ^2F	Al $3s3p^2$, ^4P	Al $3s3p^2$, ^2D	Al $3s3p^2$, ^2P	Al $3s3p^2$, ^2S	Al $3p^3$, ^4S
	1s	1s	1s	1s	1s	1s	1s	1s	1s	1s	1s
1s	0.96745	0.96744	0.96745	0.96745	0.96745	0.96745	0.96741	0.96742	0.96743	0.96742	0.96739
3s	0.03196	0.03193	0.03196	0.03197	0.03196	0.03196	0.03186	0.03186	0.03188	0.03186	0.03183
3s	0.01650	0.01658	0.01650	0.01648	0.01651	0.01650	0.01697	0.01677	0.01673	0.01676	0.01685
3s	0.00149	0.00147	0.00149	0.00151	0.00149	0.00149	0.00143	0.00144	0.00145	0.00144	0.00141
3s	0.00021	0.00023	0.00021	0.00020	0.00021	0.00021	0.00018	0.00018	0.00018	0.00018	0.00023
3s	0.00008	0.00004	0.00008	0.00011	0.00008	0.00008	0.00004	0.00003	0.00002	0.00003	−0.00001
3s	−0.00007	−0.00003	−0.00006	−0.00011	−0.00007	−0.00007	−0.00002	−0.00003	−0.00005	−0.00003	
3s	0.00002	0.00001	0.00002	0.00006[a]	0.00002	0.00002	0.00001	0.00001	0.00001	0.00001	
4s				−0.00003							
4s				0.00001							
	2s	2s	2s	2s	2s	2s	2s	2s	2s	2s	2s
1s	−0.25149	−0.25130	−0.25149	−0.25150	−0.25146	−0.25149	−0.25096	−0.25097	−0.25100	−0.25100	−0.25079
3s	−0.01036	−0.01031	−0.01012	−0.01007	−0.01038	−0.01037	−0.01317	−0.01315	−0.01311	−0.01314	−0.01086
3s	0.08624	0.08597	0.08549	0.08533	0.08629	0.08626	0.09932	0.09926	0.09917	0.09925	0.09014
3s	0.49005	0.48970	0.49144	0.49172	0.48979	0.49002	0.52205	0.52236	0.52290	0.52250	0.50908
3s	0.51903	0.51986	0.51844	0.51809	0.51925	0.51906	0.47956	0.47911	0.47830	0.47899	0.49895
3s	0.00935	0.00743	0.00831	0.00916	0.00926	0.00914	0.00348	0.00354	0.00366	0.00339	0.00370
3s	−0.00506	−0.00265	−0.00416	−0.00519	−0.00495	−0.00491	−0.00063	0.00001	0.00095	0.00011	
3s	0.00083	0.00043	0.00069	0.00158[a]	0.00085	0.00087	0.00002	0.00000	−0.00010	−0.00001	
4s				−0.00062							
4s				0.00012							
	3s	3s	3s	3s	3s	3s	3s	3s	3s	3s	
1s	0.06254	0.05799	0.06234	0.06241	0.06219	0.06254	0.05901	0.06100	0.06649	0.06153	
3s	0.00340	0.00361	0.00376	0.00391	0.00336	0.00365	0.00408	0.00459	0.00655	0.00513	
3s	−0.02517	−0.02459	−0.02613	−0.02654	−0.02497	−0.02589	−0.02734	−0.02935	−0.03634	−0.03095	
3s	−0.12841	−0.11661	−0.12616	−0.12564	−0.12775	−0.12715	−0.12967	−0.13168	−0.13490	−0.13032	
3s	−0.17457	−0.16482	−0.17707	−0.17826	−0.17338	−0.17629	−0.15390	−0.16438	−0.19548	−0.16975	
3s	0.58538	0.56879	0.58215	0.58034	0.58209	0.60115	0.61266	0.64007	0.68597	0.64470	
3s	0.48636	0.52051	0.49330	0.49968	0.49260	0.47633	0.46461	0.44612	0.41452	0.44385	
3s	0.00078	0.00095	0.00094	−0.00730[a]	−0.00260	−0.00435	0.00041	0.00110	−0.01173	0.00116	
4s				0.00521							
4s				−0.00048							
	2p	2p	2p	2p	2p	2p	2p	2p	2p	2p	2p
2p	0.53784	0.53907	0.53785	0.53773	0.53823	0.53784	0.53968	0.53972	0.53980	0.53975	0.54072
4p	0.00624	0.00400	0.00622	0.00629	0.00623	0.00624	0.00374	0.00375	0.00377	0.00376	0.00405
4p	0.27219	0.21919	0.27191	0.27315	0.27008	0.27219	0.21339	0.21322	0.21308	0.21304	0.19860
4p	0.32703	0.36920	0.32730	0.32628	0.33292	0.32703	0.37372	0.37402	0.37424	0.37439	0.37832
4p	0.00558	0.03045	0.00561	0.00556	−0.00674	0.00558	0.03169	0.03248	0.03203	0.03165	0.03902
4p		−0.01722			0.01314		−0.01949	−0.02105	−0.02090	−0.02046	−0.02175
4p		0.00418			−0.00683		0.00435	0.00599	0.00682	0.00656	0.00780
4p		−0.00031			0.00179		−0.00022	−0.00057	−0.00075	−0.00075	−0.00135
4p					−0.00068						
		3p	3d	4s	4p	4f	3p	3p	3p	3p	3p
		2p −0.09649	3d 0.00464	1s −0.01708	2p 0.03385	4f 0.00018	2p −0.10567	2p −0.09907	2p −0.08440	2p −0.09651	2p −0.10481
		4p −0.00038	5d 0.03428	3s −0.00089	4p 0.00054	6f 0.00973	4p −0.00045	4p −0.00029	4p −0.00014	4p −0.00019	4p −0.00057
		4p −0.04149	5d 0.17653	3s 0.00680	4p 0.01303	6f 0.21953	4p −0.04336	4p −0.04246	4p −0.03748	4p −0.04269	4p −0.03902
		4p −0.03076	5d 0.59782	3s 0.03535	4p 0.02719	6f 0.86057	4p −0.03720	4p −0.02960	4p −0.02124	4p −0.02536	4p −0.04306
		4p 0.39807	5d 0.36928	3s 0.04877	4p −0.06157		4p 0.43003	4p 0.44019	4p 0.35966	4p 0.45573	4p 0.25043
		4p 0.06282	5d 0.00052	3s −0.15745	4p −0.22004		4p 0.05066	4p 0.05247	4p 0.06123	4p 0.06128	4p 0.39933
		4p 0.62389		3s −0.18874	4p −0.12829		4p 0.59788	4p 0.59911	4p 0.66773	4p 0.58426	4p 0.44559
		4p 0.03384		4s 0.14620	4p 1.03517		4p 0.02108	4p 0.03079	4p 0.04101	4p 0.04452	4p 0.01173
				4s 0.91553	4p 0.01017						
				4s 0.02922							

[a] Corresponds to basis function 4s.

For an open-shell configuration of an atom, the total energy E depends upon so-called vector-coupling coefficients $J_{\lambda\mu\nu}$ and $K_{\lambda\mu\nu}$ which characterize the particular state.[4,8] For all the states treated in this paper $J_{\lambda\mu\nu}\equiv 0$.

COMPUTATIONAL PROCEDURE

The radial part of an SCF orbital is characterized by $i-\lambda-1$ nodes; the $i-\lambda$ regions separated by the nodes we call loops. Usually two to three basis functions are adequate to describe such a loop, *if the exponents are properly adjusted.* For a particular orbital we shall call the loop closest to the origin the first one, and continue numbering them in outward direction. For two functions of the same symmetry, the nth loops cover approximately the same region of r, and can usually be described by the same basis functions. In view of these facts the total number of basis functions necessary is about two to three times the number of occupied orbitals.

The optimum values of the exponents are, of course, dependent on the electron occupation, that is, on the configuration, and to a lesser extent, on the state. For instance, the optimum exponents for the states of the configuration $1s^2 2s^2 2p^2$ of C are significantly different from those for the configuration $1s^2 2s^2 2p$ of C^+, while the best exponents for the ^3P, ^1D, and ^1S states of the first configuration do not differ significantly.

It is, of course, desirable to subject *all* the exponents of a basis set to a simultaneous optimization. Such a procedure, however, would be very time consuming even for the fastest computers currently available. Furthermore, it was found that strong "coupling" exists only between those basis functions which cover the same region of r, and which have also sizeable expansion coefficients for at least one of the occupied orbitals. Therefore, it is usually possible to reach optimization of the basis set by optimizing only two or three exponents simultaneously.

When the Hartree-Fock energy has been approached within a few units in the last significant figure of the computation, further optimization would be meaningless because of masking by the round-off error. Further improvements can be obtained by using additional basis functions. These additional functions are inserted one at a time, and are retained if they yield a small improvement. A final saturation computation is performed with all those additional functions which gave a contribution. This procedure works well for ground states and such excited states where orbitals have no more nodes than required by orthogonality.

The initial vectors should always describe orbitals which are reasonable approximations to the orbitals sought, and in particular they should have the required number of nodes. Even so, the program we used did not prevent a highly excited orbital from "plunging down" to an orbital with less nodes, and often rather accurate

TABLE V. Eigenvectors of coefficients $C_{i\lambda p}$ for Cu^+, Cu, and its excited states.

Atom and state / Basis function	Cu^+ $3d^{10}$, ^1S	Cu $3d^{10}4s$, ^2S	Cu $3d^{10}4p$, ^2P	Cu $3d^9 4s^2$, ^2D
	1s	1s	1s	1s
1s	0.98283	0.98283	0.98283	0.98282
3s	0.00970	0.00967	0.00970	0.00967
3s	0.01990	0.02000	0.01991	0.02003
3s	−0.00517	−0.00537	−0.00518	−0.00539
3s	0.00279	0.00298	0.00279	0.00301
3s	−0.00079	−0.00095	−0.00079	−0.00098
3s	0.00025	0.00038	0.00025	0.00040
4s		−0.00008		−0.00009
4s		0.00003		0.00003
	2s	2s	2s	2s
1s	−0.30216	−0.30218	−0.30216	−0.30217
3s	−0.00553	−0.00547	−0.00553	−0.00545
3s	0.10201	0.10180	0.10200	0.10171
3s	0.58900	0.58952	0.58900	0.58960
3s	0.38813	0.38758	0.38813	0.38754
3s	0.01014	0.01060	0.01014	0.01071
3s	−0.00048	−0.00090	−0.00048	−0.00105
4s		0.00029		0.00032
4s		−0.00011		−0.00012
	3s	3s	3s	3s
1s	0.11288	0.11302	0.11291	0.11366
3s	0.00259	0.00263	0.00260	0.00311
3s	−0.04277	−0.04301	−0.04285	−0.04514
3s	−0.23336	−0.23304	−0.23319	−0.22908
3s	−0.31494	−0.31635	−0.31533	−0.32592
3s	0.69371	0.69708	0.69445	0.71432
3s	0.51423	0.51178	0.51367	0.50085
4s		−0.00079		−0.00653
4s		0.00129		0.00285
	2p	2p	2p	2p
2p	0.76443	0.76441	0.76443	0.76430
4p	0.00314	0.00314	0.00315	0.00314
4p	0.20244	0.20248	0.20233	0.20261
4p	0.10609	0.10606	0.10636	0.10607
4p	−0.00869	−0.00869	−0.00906	−0.00869
4p	0.00321	0.00319	0.00353	0.00308
4p			−0.00047	
4p			0.00020	
	3p	3p	3p	3p
2p	−0.28156	−0.28176	−0.28162	−0.28379
4p	−0.00035	−0.00034	−0.00037	−0.00049
4p	−0.06730	−0.06739	−0.06699	−0.06627
4p	0.12789	0.12799	0.12704	0.12407
4p	0.63988	0.64119	0.64163	0.65697
4p	0.36590	0.36458	0.36383	0.34954
4p			0.00370	
4p			−0.00072	
	3d	3d	3d	3d
3d	0.19927	0.19852	0.19900	0.20875
5d	0.05283	0.05390	0.05302	0.04744
5d	0.43087	0.43272	0.42980	0.43166
5d	0.44391	0.43276	0.45224	0.47494
5d	−0.00859	0.00697	−0.02102	−0.04022
5d	0.19472	0.19726	0.20192	0.16843
		4s	4p	4s
		1s −0.01960	2p 0.02610	1s −0.02318
		3s −0.00095	4p 0.00022	3s −0.00084
		3s 0.00963	4p 0.00405	3s 0.01022
		3s 0.03413	4p −0.00685	3s 0.04354
		3s 0.06984	4p −0.07911	3s 0.07861
		3s −0.16445	4p −0.00216	3s −0.18875
		3s −0.06445	4p 0.38918	3s −0.08744
		4s 0.42003	4p 0.72314	4s 0.50926
		4s 0.69249		4s 0.61378

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[8] G. L. Malli and C. C. J. Roothaan (to be published).

TABLE VI. Comparison of calculated energies with experimental energies.[a]

Atom or ion	State	Calculated total energy	Energies relative to ground state Calculated	Experimental	Calculated minus experimental
Al^+	$3s^2$, ^1S	−241.67379	0.20244	0.21972	−0.01728
Al	$3s^23p$, ^2P	−241.87623	0	0	0
	$3s^23d$, ^2D	−241.73174	0.14449	0.14753	−0.00304
	$3s^24s$, ^2S	−241.77080	0.10543	0.11524	−0.00981
	$3s^24p$, ^2P	−241.73947	0.13676	0.14991	−0.01315
	$3s^24f$, ^2F	−241.70504	0.17119	0.18801	−0.01682
	$3s3p^2$, ^4P	−241.79037	0.08586	0.13223	−0.04637
	$3s3p^2$, ^2D	−241.69111	0.18512	···	···
	$3s3p^2$, ^2P	−241.60543	0.27080	0.25802[b]	0.01278[b]
	$3s3p^2$, ^2S	−241.64455	0.23168	0.23555[b]	−0.00387[b]
	$3p^3$, ^4S	−241.52175	0.35448	···	···
Cu^+	$3d^{10}$, ^1S	−1638.7215	0.2347	0.2839	−0.0492
Cu	$3d^{10}4s$, ^2S	−1638.9562	0	0	0
	$3d^{10}4p$, ^2P	−1638.8445	0.1117	0.1397	−0.0280
	$3d^94s^2$, ^2D	−1638.9438	0.0124	0.0557	−0.0433

[a] See Ref. 19.
[b] Experimental energies are not certain.

approximations to the answers sought were necessary in order to make the run converge.

As an example, let us consider the excited configuration $3s^24p$ of Al. We constructed a trial $4p$ orbital by selecting basis functions and expansion coefficients as follows:

(1) For the first two loops: (a) the same basis functions and ratios of vector components as they were found for the $3p$ orbital in the ground state; (b) the magnitudes of vector components reduced by a factor of 3 or 4 with respect to those for the $3p$ orbital.

(2) For the outer loop: only one basis function with initial exponent 0.25, and expansion coefficient unity. The initial exponent is taken 0.25 because the outer loop of the excited $4p$ orbital is expected to be hydrogen-like. Further refinement may be obtained by adding one additional basis function at a time for the outer loop of such an excited orbital.

RESULTS AND DISCUSSION

The units used are the atomic units of Hartree.[1] According to Cohen, Crowe, and DuMond,[9] our atomic units for length and energy are 0.529172 Å and 27.20976 eV, respectively.

Some of the important results are presented in Tables I–VIII of this article. Some other results are deposited elsewhere.[10] The eigenvalues, sometimes called orbital energies, are denoted by ϵ. The radial

TABLE VII. Orbital energies ϵ.

	Al^+ $3s^2$, ^1S	Al $3s^23p$, ^2P	Al $3s^23d$, ^2D	Al $3s^24s$, ^2S	Al $3s^24p$, ^2P
$1s$	−58.81417	−58.50242	−58.69293	−58.66459	−58.69726
$2s$	−5.21853	−4.91139	−5.09697	−5.07045	−5.10301
$3s$	−0.65231	−0.39347	−0.53100	−0.51208	−0.54317
$4s$				−0.09704	
$2p$	−3.52340	−3.21890	−3.40194	−3.37481	−3.40840
$3p$		−0.20991			
$4p$					−0.06558
$3d$			−0.05797		

	Al $3s^24f$, ^2F	Al $3s3p^2$, ^4P	Al $3s3p^2$, ^2D	Al $3s3p^2$, ^2P	Al $3s3p^2$, ^2S	Al $3p^3$, ^4S
$1s$	−58.75153	−58.53783	−58.57792	−58.62849	−58.60015	−58.62686
$2s$	−5.15591	−4.94320	−4.98043	−5.02798	−5.00161	−5.02400
$3s$	−0.58970	−0.51928	−0.47296	−0.40245	−0.48656	
$2p$	−3.46078	−3.25808	−3.28483	−3.34103	−3.31582	−3.34678
$3p$		−0.25995	−0.20142	−0.18182	−0.16129	−0.25250
$4f$	−0.03124					

	Cu^+ $3d^{10}$, ^1S	Cu $3d^{10}4s$, ^2S	Cu $3d^{10}4p$, ^2P	Cu $3d^94s^2$, ^2D
$1s$	−329.10962	−328.79186	−328.88714	−329.03747
$2s$	−41.12940	−40.81754	−40.90846	−41.08758
$3s$	−5.32560	−5.00999	−5.10331	−5.26250
$4s$		−0.23774		−0.28499
$2p$	−35.92971	−35.61628	−35.70865	−35.88168
$3p$	−3.64229	−3.32286	−3.41975	−3.55875
$4p$			−0.12302	
$3d$	−0.81002	−0.48885	−0.58692	−0.74196

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[9] E. R. Cohen, K. M. Crowe, J. W. M. DuMond, *Fundamental Constants of Physics* (Interscience Publishers, Inc., New York, 1957).

[10] Tables IX–XIII and Figs. 1–5 are deposited as Document No. 7583 with the American Documentation Institute, Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. These tables and figures contain some numerical tabulations and graphs of the orbital wave functions.

part of the orbital $\varphi_{i\lambda\alpha}(r,\vartheta,\varphi)$ multiplied by r is denoted by $P_{i\lambda}(r)$. For each orbital of the states computed, the cusp condition is exactly satisfied so that it is not necessary to present the cusp values in the tables. In the numerical tabulations[10] of the orbital wave functions only representative cases are included, although such tables were computed for all the states considered in this work.

As to the accuracy of the results, it is believed that the values computed represent the Hartree-Fock values to six significant figures for total energies, and to three decimal places for the radial functions $P_{i\lambda}(r)$.

We compared our results with other SCF calculations wherever possible; the comparisons are summarized in Table I.

The ground state of Al$^+$ was calculated by Biermann and Harting[11] using a numerical procedure. Their orbitals disagree with ours in the second decimal place. Clearly, their numerical scheme must have been quite different from the customary Hartree-Fock method.

Analytic (i.e., expansion method) Hartree-Fock wave functions for the ground state of Al were calculated by Watson and Freeman.[12] These authors used approximations based upon the methods of Nesbet[13] for treating open shells.

Some excited orbitals and the $3p$ orbital of Al were calculated by Biermann,[14] and Biermann and Lübeck,[15] who used a numerical procedure. Comparing the tabulation, e.g., for $3p$, $4s$, and $3d$, presented by these authors[15] with ours, considerable differences were found. The squares of some transition integrals

$$R_{i\lambda,j\mu}=\int_0^\infty P_{i\lambda}(r)\, r\, P_{j\mu}(r)dr, \tag{9}$$

also yielded considerable discrepancies (see Table I).

Analytic Hartree-Fock functions for the ground state of Cu$^+$ were computed by Watson.[16] We recalculated Watson's results with our program, so that we obtained numerically tabulated functions to compare with ours. Generally, the orbitals agreed to about three decimal places, except for the $3d$ orbitals, which agreed to about two decimal places.

TABLE VIII. Virial theorem. (Values of E_p/E_k.)

Atom or ion	State	E_p/E_k
Al$^+$	$3s^2$, ^1S	-2.0001377
Al	$3s^23p$, ^2P	-2.0001188
	$3s^23d$, ^2D	-2.0001375
	$3s^24s$, ^2S	-2.0001351
	$3s^24p$, ^2P	-2.0000817
	$3s^24f$, ^2F	-2.0001363
	$3s3p^2$, ^4P	-2.0001314
	$3s3p^2$, ^2D	-2.0001323
	$3s3p^2$, ^2P	-2.0001212
	$3s3p^2$, ^2S	-2.0001282
	$3p^3$, ^4S	-2.0000611
Cu$^+$	$3d^{10}$, ^1S	-2.0000744
Cu	$3d^{10}4s$, ^2S	-2.0000667
	$3d^{10}4p$, ^2P	-2.0000763
	$3d^94s^2$, ^2D	-2.0000719

Numerical Hartree-Fock procedure for Cu$^+$ was carried out by Piper.[17] His orbitals agree to about three decimal places with the orbitals of this work.

Analytic Hartree-Fock functions for the excited state $3d^94s^2$, ^2D of Cu were calculated by Watson.[18] The author used approximation by Nesbet[13] for treating open shells.

Finally, our computed energies are compared with experimental energies in Table VI. Since total experimental energies are not available, we have compared energy differences between excited states and ground states. Since we neglected spin-orbit interaction in the calculations, we averaged the experimental energies as obtained from Moore's tables[19] over the multiplet components.

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