

## 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.<sup>1</sup> 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.<sup>2-4</sup>

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

### 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  $\lambda$  and  $\alpha$  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

$$\varphi_{i\lambda\alpha} = \sum_p \chi_{p\lambda\alpha} C_{i\lambda p}, \quad (1)$$

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

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

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

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

$n_{\lambda p}$  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<sup>5</sup>

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

TABLE I. Comparison with other calculations.

Quantity \ Source of calculation	Other authors	This work
Al, $3s^2 3p, {}^2P$ ; $E[\text{au}]$	-241.8692 <sup>a</sup>	-241.8762
Cu <sup>+</sup> , $3d^{10}, {}^1S$ ; $E[\text{au}]$	-1638.7049 <sup>b</sup>	-1638.7215
Cu, $3d^9 4s^2, {}^2D$ ; $E[\text{au}]$	-1638.9310 <sup>c</sup>	-1638.9438
Al;	$R^2_{4s, 3p}$	5.17 <sup>d</sup>
Al;	$R^2_{3p, 3d}$	10.85 <sup>d</sup>

<sup>a</sup> See Ref. 12.

<sup>b</sup> See Ref. 16.

<sup>c</sup> See Ref. 18.

<sup>d</sup> See Ref. 15.

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TABLE II. Optimized exponents  $\zeta$  of the basis functions for Al<sup>+</sup>, Al and its excited states.

Atom and state Basis function	Al <sup>+</sup>	Al	Al	Al	Al	Al	Al	Al	Al	Al	Al
	3s <sup>2</sup> , <sup>1</sup> S	3s <sup>2</sup> 3p, <sup>2</sup> P	3s <sup>2</sup> 3d, <sup>2</sup> D	3s <sup>2</sup> 4s, <sup>2</sup> S	3s <sup>2</sup> 4p, <sup>2</sup> P	3s <sup>2</sup> 4f, <sup>2</sup> F	3s3p <sup>2</sup> , <sup>4</sup> P	3s3p <sup>2</sup> , <sup>2</sup> D	3s3p <sup>2</sup> , <sup>2</sup> P	3s3p <sup>2</sup> , <sup>2</sup> S	3p <sup>3</sup> , <sup>4</sup> S
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	1.75275	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 <sup>a</sup>	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					

<sup>a</sup> 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  $\varphi_{i\alpha}$  in terms of known basis functions, they would generally not satisfy the cusp condition. Nevertheless, for a special choice<sup>7</sup> of basis functions the cusp condition can be identically satisfied, namely, if

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

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  $\varphi_{i\alpha}$  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  $\zeta$  of the basis functions for Cu<sup>+</sup>, Cu, and its excited states.

Atom and state Basis function	Cu <sup>+</sup>	Cu	Cu	Cu
	3d <sup>10</sup> , <sup>1</sup> S	3d <sup>10</sup> 4s, <sup>2</sup> S	3d <sup>10</sup> 4p, <sup>2</sup> P	3d <sup>9</sup> 4s <sup>2</sup> , <sup>2</sup> D
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  $C_{\lambda\mu}$  for  $Al^+$ ,  $Al$ , and its excited states.

Atom and Basis state function	$Al^+$ $3s^2 1S$	$Al$ $3s^2 3p, 2P$	$Al$ $3s^2 3d, 2D$	$Al$ $3s^2 4s, 2S$	$Al$ $3s^2 4p, 2P$	$Al$ $3s^2 4f, 2F$	$Al$ $3s^2 5s, 1P$	$Al$ $3s^2 5p, 2D$	$Al$ $3s^2 5p, 2P$	$Al$ $3s^2 5p, 2S$	$Al$ $3p^2 4S$
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	0.03196	0.03196	0.03196	0.03186	0.03186	0.03188	0.03186	0.03183
3s	0.01650	0.01658	0.01650	0.01651	0.01650	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	0.0004	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	-0.00002	-0.00003	-0.00001
3s	0.00002	0.00001	0.00002	0.00006*	0.00002	0.00002	0.00001	0.00001	0.00001	0.00001	0.00001
4s			-0.00003	-0.00003							
4s			0.00001	0.00001							
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	-0.01036	-0.01007	-0.01038	-0.01037	-0.01317	-0.01315	-0.01311	-0.01314	-0.01086
3s	0.08624	0.08597	0.08624	0.08533	0.08629	0.08626	0.09932	0.09926	0.09917	0.09925	0.09014
3s	0.49005	0.48970	0.49172	0.49172	0.48979	0.49002	0.52205	0.52236	0.52290	0.52250	0.50908
3s	0.51903	0.51986	0.51844	0.51844	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	0.00011
3s	0.00083	0.00043	0.00069	0.00158*	0.00085	0.00087	0.00002	0.00000	-0.00010	-0.00001	0.00001
4s			-0.00062	-0.00062							
4s			0.00012	0.00012							
1s	0.06254	0.05799	0.06234	0.06241	0.06219	0.06254	0.05901	0.06100	0.06649	0.06153	0.06153
3s	0.00340	0.00361	0.00376	0.00391	0.00336	0.00365	0.00408	0.00459	0.00655	0.00513	0.00655
3s	-0.02517	-0.02459	-0.02613	-0.02654	-0.02497	-0.02589	-0.02734	-0.02935	-0.03634	-0.03095	-0.03095
3s	-0.11284	-0.11661	-0.12616	-0.12564	-0.12775	-0.12715	-0.12967	-0.13168	-0.13490	-0.13032	-0.13032
3s	-0.17457	-0.16482	-0.17707	-0.17826	-0.17338	-0.17629	-0.16438	-0.16438	-0.19548	-0.16975	-0.16975
3s	0.58538	0.56879	0.58215	0.58034	0.58209	0.60115	0.61266	0.64007	0.68597	0.64470	0.64470
3s	0.48636	0.52051	0.49330	0.49968	0.49260	0.47633	0.46461	0.44612	0.41452	0.44385	0.44385
3s	0.00078	0.00095	0.00094	-0.00730*	-0.00260	-0.00435	0.00041	0.00110	-0.01173	0.00116	0.00116
4s			0.00521	0.00521							
4s			-0.00048	-0.00048							
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	-0.01722	-0.00561	-0.00556	-0.00674	0.00558	-0.01949	-0.02105	-0.02090	-0.02046	-0.02175
4p	0.00418	0.00418	0.00418	0.00418	0.00418	0.00418	0.00435	0.00599	0.00682	0.00656	0.00780
4p	-0.00031	-0.00031	-0.00031	-0.00031	-0.00031	-0.00031	-0.00022	-0.00057	-0.00075	-0.00075	-0.00135
2p			0.00464	0.00464							
3p			0.00464	0.00464							
2p	-0.09649	-0.09649	0.00464	0.00464	0.00464	0.00018	-0.10567	-0.09907	-0.08440	-0.09651	-0.10481
4p	-0.00038	-0.00038	0.03428	0.03428	0.00054	0.00973	0.00045	0.00029	0.00014	0.00019	0.00057
4p	-0.04149	-0.04149	0.17653	0.17653	0.01303	0.21953	-0.04336	-0.04246	-0.03748	-0.04269	-0.03902
4p	-0.03076	-0.03076	0.59782	0.59782	0.03535	0.02719	-0.03720	-0.02960	-0.02124	-0.02536	-0.04306
4p	0.39807	0.39807	0.36928	0.36928	0.04877	0.06157	0.43003	0.44019	0.43596	0.44573	0.25043
4p	0.06282	0.06282	0.00052	0.00052	0.02200	0.02200	0.05066	0.05247	0.06123	0.06128	0.39933
4p	0.62389	0.62389	0.18874	0.18874	0.12829	0.12829	0.59788	0.59911	0.66773	0.58426	0.44559
4p	0.03384	0.03384	0.14620	0.14620	0.103517	0.103517	0.02108	0.03079	0.04101	0.04452	0.01173
4p			0.91553	0.91553	0.01017	0.01017					
4s			0.02922	0.02922							

\* Corresponds to basis function 4s.



TABLE VI. Comparison of calculated energies with experimental energies.<sup>a</sup>

Atom or ion	State	Calculated total energy	Energies relative to ground state		
			Calculated	Experimental	Calculated minus experimental
Al <sup>+</sup>	3s <sup>2</sup> , 1S	-241.67379	0.20244	0.21972	-0.01728
Al	3s <sup>2</sup> 3p, 2P	-241.87623	0	0	0
	3s <sup>2</sup> 3d, 2D	-241.73174	0.14449	0.14753	-0.00304
	3s <sup>2</sup> 4s, 2S	-241.77080	0.10543	0.11524	-0.00981
	3s <sup>2</sup> 4p, 2P	-241.73947	0.13676	0.14991	-0.01315
	3s <sup>2</sup> 4f, 2F	-241.70504	0.17119	0.18801	-0.01682
	3s3p <sup>2</sup> , 4P	-241.79037	0.08586	0.13223	-0.04637
	3s3p <sup>2</sup> , 2D	-241.69111	0.18512	...	...
	3s3p <sup>2</sup> , 2P	-241.60543	0.27080	0.25802 <sup>b</sup>	0.01278 <sup>b</sup>
	3s3p <sup>2</sup> , 2S	-241.64455	0.23168	0.23555 <sup>b</sup>	-0.00387 <sup>b</sup>
	3p <sup>3</sup> , 4S	-241.52175	0.35448	...	...
	Cu <sup>+</sup>	3d <sup>10</sup> , 1S	-1638.7215	0.2347	0.2839
Cu	3d <sup>10</sup> 4s, 2S	-1638.9562	0	0	0
	3d <sup>10</sup> 4p, 2P	-1638.8445	0.1117	0.1397	-0.0280
	3d <sup>9</sup> 4s <sup>2</sup> , 2D	-1638.9438	0.0124	0.0557	-0.0433

<sup>a</sup> See Ref. 19.<sup>b</sup> 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<sup>2</sup>4p 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 hydrogenlike. 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.<sup>1</sup> According to Cohen, Crowe, and DuMond,<sup>9</sup> 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.<sup>10</sup> The eigenvalues, sometimes called orbital energies, are denoted by  $\epsilon$ . The radial

TABLE VII. Orbital energies  $\epsilon$ .

	Al <sup>+</sup> 3s <sup>2</sup> , 1S	Al 3s <sup>2</sup> 3p, 2P	Al 3s <sup>2</sup> 3d, 2D	Al 3s <sup>2</sup> 4s, 2S	Al 3s <sup>2</sup> 4p, 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 <sup>2</sup> 4f, 2F	Al 3s3p <sup>2</sup> , 4P	Al 3s3p <sup>2</sup> , 2D	Al 3s3p <sup>2</sup> , 2P	Al 3s3p <sup>2</sup> , 2S	Al 3p <sup>3</sup> , 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 <sup>+</sup> 3d <sup>10</sup> , 1S	Cu 3d <sup>10</sup> 4s, 2S	Cu 3d <sup>10</sup> 4p, 2P	Cu 3d <sup>9</sup> 4s <sup>2</sup> , 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		

<sup>9</sup> E. R. Cohen, K. M. Crowe, J. W. M. DuMond, *Fundamental Constants of Physics* (Interscience Publishers, Inc., New York, 1957).<sup>10</sup> 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<sup>10</sup> 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  $\text{Al}^+$  was calculated by Biermann and Harting<sup>11</sup> 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.<sup>12</sup> These authors used approximations based upon the methods of Nesbet<sup>13</sup> for treating open shells.

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

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

also yielded considerable discrepancies (see Table I).

Analytic Hartree-Fock functions for the ground state of  $\text{Cu}^+$  were computed by Watson.<sup>16</sup> 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

<sup>11</sup> L. Biermann and H. Harting, *Z. Astrophys.* **22**, 81 (1943).

<sup>12</sup> R. E. Watson and A. J. Freeman, *Phys. Rev.* **123**, 521 (1961).

<sup>13</sup> R. K. Nesbet, *Proc. Roy. Soc. (London)* **A230**, 312 (1955); and subsequent articles.

<sup>14</sup> L. Biermann, *Nachr. Akad. Wiss. Göttingen, Math. Physik. Kl. IIa*, **H.2**, 116 (1946).

<sup>15</sup> L. Biermann and K. Lübeck, *Z. Astrophys.* **25**, 325 (1948).

<sup>16</sup> For review and further reference see R. E. Watson, *Phys. Rev.* **118**, 1036 (1960).

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

Atom or ion	State	$E_p/E_k$
$\text{Al}^+$	$3s^2, ^1S$	-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
$\text{Cu}^+$	$3d^{10}, ^1S$	-2.0000744
Cu	$3d^{10}4s, ^2S$	-2.0000667
	$3d^{10}4p, ^2P$	-2.0000763
	$3d^{10}4s^2, ^2D$	-2.0000719

decimal places, except for the  $3d$  orbitals, which agreed to about two decimal places.

Numerical Hartree-Fock procedure for  $\text{Cu}^+$  was carried out by Piper.<sup>17</sup> 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.<sup>18</sup> The author used approximation by Nesbet<sup>13</sup> 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<sup>19</sup> over the multiplet components.

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<sup>17</sup> W. W. Piper, *Phys. Rev.* **123**, 1281 (1961).

<sup>18</sup> R. E. Watson, *Phys. Rev.* **119**, 1934 (1960).

<sup>19</sup> C. E. Moore, *U. S. Nat. Bur. Std. Circular No. 467* (U. S. Government Printing Office, Washington, D. C., 1949).