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Accurate Analytical Self-Consistent-Field Functions for Atoms. VIII. The Ground States of K^+, K, and Ca

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Self-consistent-field calculations by the expansion method were carried out for the ground states of K^+, K, and Ca. The merit of this calculation is in its accuracy. Compared with solutions of the Hartree-Fock equations by the numerical-integration technique, the wave functions are considered accurate to three decimal places. The deviations from the nodal condition for the radial functions do not exceed 0.00006. The cusp condition is exactly satisfied.

INTRODUCTION

THE self-consistent-field (SCF) expansion method[1–3] has been applied in a series[4–9] of accurate calculations of atomic wave functions. This paper reports accurate calculations for the $3s^23p^6$, ^1S state of K^+, the $4s^1$, ^2S state of K, and the $4s^2$, ^1S state of Ca.

RESULTS AND DISCUSSION

The results are presented in Tables I–V.[10] The cusp values are not presented since the cusp conditions[6] were kept identically satisfied.

We assume that the radial functions $P_{i\lambda}(r)$ represent the Hartree-Fock values to three decimal places.

A numerical SCF calculation with exchange on K^+ was carried out by Hartree and Hartree.[11] Their numerical orbitals agree with ours practically to three decimal places.

A numerical SCF tabulation without exchange and without a full self-consistency for the $4s$ orbital of K was published by Gibbons and Bartlett.[12] Their numerical tabulation disagrees with ours in the second decimal place, particularly in the outermost nodal region of the $4s$ orbital.

A numerical SCF calculation with exchange on the $4s$ orbital of Ca was carried out by Hartree and Hartree.[13] Their calculation represents the solution of the Hartree-Fock equation without allowance for the perturbation of the core by the two $4s$ electrons. Our $4s$ orbital agrees with theirs to two decimal places; the difference is always smaller than 0.003.

The comparison of the total energies with other calculations[14–17] is given in Table III. The "numerical"

Table I. Optimized exponents ζ of the basis functions for K^+, K, and Ca.

Atom and state / Basis function	K^+ $3s^23p^6$, ^1S	K $3p^64s$, ^2S	Ca $3p^64s^2$, ^1S
$1s$	19.0000	19.0000	20.0000
$3s$	20.8678	20.8678	22.0757
$3s$	14.3322	14.4292	15.1048
$3s$	9.4704	9.3273	9.9852
$3s$	6.7489	6.4998	7.2167
$3s$	3.7102	3.5585	3.7902
$3s$	2.5312	2.3276	2.5921
$3s$	1.9378		
$4s$		1.0600	1.4168
$4s$		0.6427	0.8587
$2p$	9.5000	9.5000	10.0000
$4p$	16.4887	16.4012	17.3718
$4p$	9.9617	9.9612	10.4808
$4p$	7.1782	7.2089	7.5803
$4p$	4.5314	4.5414	4.7717
$4p$	2.8419	2.8380	2.9791
$4p$	1.9132	1.8571	1.8414

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[10] The numerical tabulations of the radial wave functions $P_{i\lambda}(r)$ are presented to five decimal places in Tables VI–VIII. These tables are deposited as Document No. 8593 with the American Documentation Institute, Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, 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.

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TABLE II. Eigenvectors of coefficients $C_{i\lambda p}$ for K^+, K, and Ca.

Atom and state Basis function	K^+ $3s^23p^6$ ^1S	K $3p^64s$ ^2S	Ca $3p^64s^2$ ^1S
	1*s*	1*s*	1*s*
1*s*	0.97567	0.97567	0.97661
3*s*	0.02829	0.02821	0.02649
3*s*	0.00989	0.00981	0.01082
3*s*	−0.00056	−0.00035	−0.00156
3*s*	0.00024	0.00019	0.00079
3*s*	−0.00002	−0.00006	−0.00026
3*s*	−0.00008	−0.00001	0.00009
3*s*	0.00003		
4*s*		0.00000	−0.00002
4*s*		0.00000	0.00001
	2*s*	2*s*	2*s*
1*s*	−0.28014	−0.28011	−0.28337
3*s*	−0.00388	−0.00564	−0.00393
3*s*	0.19047	0.19350	0.19524
3*s*	0.60998	0.65701	0.61705
3*s*	0.28478	0.23889	0.26999
3*s*	−0.00029	−0.00238	0.00490
3*s*	0.00365	0.00244	−0.00020
3*s*	−0.00104		
4*s*		−0.00031	0.00015
4*s*		0.00015	−0.00006
	3*s*	3*s*	3*s*
1*s*	0.09231	0.09234	0.09776
3*s*	0.00105	0.00114	0.00047
3*s*	−0.06756	−0.06608	−0.06932
3*s*	−0.22222	−0.25236	−0.24719
3*s*	−0.21218	−0.18181	−0.20077
3*s*	0.53551	0.65814	0.69274
3*s*	0.55604	0.50746	0.46905
3*s*	0.07605		
4*s*		0.00025	−0.00214
4*s*		0.00053	0.00095
		4*s*	4*s*
1*s*		−0.01773	−0.02334
3*s*		−0.00108	−0.00027
3*s*		0.01618	0.01745
3*s*		0.03940	0.05696
3*s*		0.05417	0.05770
3*s*		−0.18274	−0.21100
3*s*		−0.05231	−0.10064
3*s*			
4*s*		0.62615	0.53663
4*s*		0.45075	0.56311
	2*p*	2*p*	2*p*
2*p*	0.66464	0.66462	0.67864
4*p*	0.01348	0.01384	0.01300
4*p*	0.24205	0.24004	0.24112
4*p*	0.17459	0.17529	0.15826
4*p*	0.00335	0.00468	0.00258
4*p*	0.00136	0.00085	0.00087
4*p*	−0.00041	−0.00025	−0.00027
	3*p*	3*p*	3*p*
2*p*	−0.20310	−0.20257	−0.22114
4*p*	−0.00334	−0.00346	−0.00299
4*p*	−0.06499	−0.06417	−0.07118
4*p*	−0.01192	−0.01336	0.00489
4*p*	0.41067	0.40813	0.46767
4*p*	0.53118	0.54150	0.55774
4*p*	0.17027	0.16623	0.07060

TABLE III. Calculated total energies E and comparison with other calculations.

Atom or ion	State	Calculated total energy		
		This work	Other calculations	
			Analytical	Numerical
K^+	$3s^23p^6$, ^1S	−599.01753	−599.01711[a,b]	...
K	$3p^64s$, ^2S	−599.16467	−599.16447[c]	−596.5710[d]
Ca	$3p^64s^2$, ^1S	−676.75811	−676.75801[c]	−674.0165[d]

[a] See Ref. 14. (We consider the value −559.01711 printed in Ref. 14 as a misprint.)

[b] Bagus (Ref. 15) obtained the value −599.01752 with a completely different basis set (without the cusp condition restriction).

[c] See Ref. 16.

[d] These are estimates based on numerical SCF results (see Ref. 17).

TABLE IV. Orbital energies ϵ.

	K^+ $3s^23p^6$, ^1S	K $3p^64s$, ^2S	Ca $3p^64s^2$, ^1S
1*s*	−133.75238	−133.53342	−149.36368
2*s*	−14.70817	−14.49034	−16.82272
3*s*	−1.96384	−1.74912	−2.24531
4s		−0.14738	−0.19552
2*p*	−11.73828	−11.51968	−13.62925
3*p*	−1.17056	−0.95479	−1.34065

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

Atom or ion	State	E_p/E_k
K^+	$3s^23p^6$, ^1S	−2.0000252
K	$3p^64s$, ^2S	−2.0000285
Ca	$3p^64s^2$, ^1S	−2.0000329

SCF energies in this table are actually based upon the Hartree-Fock numerical SCF calculations using the Slater's approximation.[17]

The total experimental energies for K^+, K, and Ca are not available. To obtain a comparison with experiment[18] we calculated in a usual way[19] the correlation energy difference between K^+ and K; this value is −0.01238 atomic units.

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[19] See Ref. 8, Table IV.