TABLE III. Values of the integrals R_2 for positive ions, neutral atoms, and negative ions with d^n configurations (in cm^{-1}).

Configuration	State	Positive Ion System	 R_2	Neutral Atom System	 R_2	Negative Ion System	 R_2
$3d^2$	${}^3_2F$	Sc$^+$	0.69	Ti	1.35	Sc$^-$	0.56
$3d^3$	${}^4_3F$	Ti$^+$	1.05	V	1.81	Ti$^-$	0.95
$3d^4$	${}^5_4D$	V$^+$	1.45	Cr	2.32	V$^-$	1.36
$3d^5$	${}^6_5S$	Cr$^+$	1.92	Mn	2.91	Cr$^-$	1.84
$3d^6$	${}^5_4D$	Mn$^+$	2.37	Fe	3.47	Mn$^-$	2.29
$3d^7$	${}^4_3F$	Fe$^+$	2.91	Co	4.12	Fe$^-$	2.83
$3d^8$	${}^3_2F$	Co$^+$	3.53	Ni	4.86	Co$^-$	3.44
$3d^9$	${}^2_1D$	Ni$^+$	4.21	Cu	5.68	Ni$^-$	4.13
$3d^{10}$	${}^1_0S$	Cu$^+$	4.99	Zn	6.59	Cu$^-$	4.90

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[*] This work has been supported in part by the National Research Council of Canada.

[1] The dipole-dipole electron-spin coupling constants for the same systems considered here, and some isoelectronic series, have been evaluated by J. Thorhallsson and S. Fraga (unpublished results).

[2] See, e.g., G. Malli and S. Fraga, Theoret. Chim. Acta (Berlin) 6, 278 (1966).

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PHYSICAL REVIEW VOLUME 178, NUMBER 1 5 FEBRUARY 1969

Accurate Analytical Self-Consistent-Field Wave Functions for Ag$^+$

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(Received 12 August 1968)

Self-consistent-field calculations by the analytical expansion method were carried out for the ground state of Ag$^+$ ($Z=47$), $4d^{10}$, ^1S. All the expansion basis sets were selected so as to satisfy precisely the cusp condition. The deviations from the tail nodal extinction for the radial functions $P_{i\lambda}(r)$ do not exceed 0.000 08. The results represent the most accurate analytical wave functions for Ag$^+$ available.

INTRODUCTION

Accurate analytical self-consistent-field (SCF) wave functions for the silver ion are needed for certain applications in solid-state physics.[1,2] Also, the knowledge of such wave functions will shift the frontier[3] of accurate analytical calculations further into the periodic system of atoms. (Furthermore, the actual accuracy achieved in this work for the tail nodal extinction has been unprecendented for such a heavy atomic system).

We carried out the SCF calculations for the ground state of $Ag^+, 4d^{10}, {}^1S$, by means of the analytical expansion method.[4] The computation was done with a program[4] for the IBM line of large-memory computers.[5] All of the orbital exponents $\zeta_{\lambda p}$ of the basis functions (except those restricted by the cusp condition) were subjected to repeated and exhaustive optimizations.

RESULTS AND DISCUSSION

The terminology, the atomic units,[6] and the notation[4] used are the usual ones.[7]

The most important results are given in Tables I and II. The numerical tabulations of the orbital wave functions, etc., are given in Tables III–V[8]; these tables are deposited at the Library of Congress[8]; in these tables the radial part of the orbital $\varphi_{i\lambda\alpha}(r, \theta, \varphi)$ multiplied by r is denoted by $P_{i\lambda}(r)$. [The numerical Tables III and IV[8] of $P_{i\lambda}(r)$ present a direct demonstration of the satisfaction of the tail nodal extinction.]

TABLE I. The total energy E (a.u.), the virial theorem and the orbital energies ϵ (a.u.) for Ag^+, $4d^{10}$, ${}^1S$.

Quantity		Value
E		$-5197.478\,3$
E_p/E_k		$-2.000\,005\,2$
ϵ	1s	-914.121
	2s	-135.161
	3s	-26.200
	4s	-4.285
	2p	-125.465
	3p	-22.229
	4p	-2.964
	3d	-14.962
	4d	-0.824

We assume that the radial wave functions $P_{i\lambda}(r)$ represent the Hartree-Fock values to about two to three decimal places. The Hartree-Fock total energy is represented to about five significant figures. The registered deviations from the tail nodal extinction for the radial functions $P_{i\lambda}(r)$ never exceed 0.000 08 (Tables III and IV[8]). (To achieve such high accuracy for a system with 46 electrons required additional laborious optimizations on certain well chosen and coupled exponents $\zeta_{\lambda p}$.) Since the cusp condition[9] is precisely satisfied for all the orbitals by a special choice of the

TABLE II. The orbtial exponents $\zeta_{\lambda p}$ of the basis functions and the eigenvectors of coefficients $C_{i\lambda p}$ for Ag^+, $4d^{10}$, ${}^1S$.

Basis function	Exponents	Eigenvectors			
		1s	2s	3s	4s
1s	47.000 00	0.988 74	−0.318 28	0.137 97	−0.057 43
3s	52.776 82	0.009 65	0.000 49	0.001 21	0.004 71
3s	40.614 96	0.008 73	0.058 79	−0.034 66	−0.010 39
3s	30.234 48	−0.001 25	0.430 73	−0.171 66	0.138 25
3s	22.157 46	0.000 70	0.553 31	−0.462 89	0.075 30
3s	16.060 27	−0.000 33	0.034 28	−0.022 36	0.236 20
3s	10.837 37	0.000 07	0.010 93	0.866 20	−0.838 49
3s	8.863 55	−0.000 04	−0.005 67	0.348 51	0.064 31
4s	5.436 19	0.000 01	0.000 37	0.010 11	0.899 87
4s	3.543 49	−0.000 00	−0.000 16	−0.001 03	0.247 00
		2p	3p	4p	
2p	23.500 00	0.842 23	−0.377 76	0.148 83	
4p	28.812 65	0.068 80	−0.034 64	0.010 05	
4p	21.425 75	0.132 18	0.053 64	−0.018 04	
4p	13.849 32	0.004 97	0.629 08	−0.330 81	
4p	9.723 49	−0.000 21	0.413 10	−0.181 19	
4p	5.312 43	−0.000 06	0.007 48	0.813 95	
4p	3.264 36	−0.000 03	0.000 20	0.348 15	
		3d	4d		
3d	15.666 67	0.432 05	−0.138 36		
5d	26.702 05	0.015 26	−0.006 41		
5d	15.717 64	0.323 98	−0.089 99		
5d	10.877 49	0.330 50	−0.089 20		
5d	7.367 87	0.038 92	0.292 59		
5d	4.456 64	0.001 68	0.559 24		
5d	2.509 96	−0.000 33	0.353 05		
5d	1.101 40	0.000 08	0.018 92		

basis set,[9] the cusp values are not included in the tables. The virial theorem[10] is satisfied to almost six significant figures (Table I).

A preliminary and orientational numerical SCF calculation *without* exchange on Ag$^+$ was published by Black.[11] The numerically represented orbitals $P_{i\lambda}(r)$ of this work (Tables III and IV[8]) disagree considerably with those by Black (after normalization). A large disagreement is, of course, typical, when comparing calculations with and without exchange.[3,12]

A numerical SCF calculation *with* exchange on Ag$^+$ was published by Worsley.[13] The numerically represented orbitals $P_{i\lambda}(r)$ of this work (Tables III and IV[8]) usually agree with those by Worsley to at least two decimal places.[14]

Earlier an approximate analytical calculation for Ag$^+$ was carried out, with minimum basis sets for the s and p symmetries, and with four basis functions for the d symmetry (exponents optimized).[15] We found that at least for the 3d and 4d orbitals the numerically represented functions $P_{i\lambda}(r)$ agree with the more accurate ones of this work to almost two decimal places. For the s and p symmetries the shortcomings (due to their minimum set description) are, of course, much more pronounced, in comparison with an accurate description used in this work.

ACKNOWLEDGMENTS

The assistance of the Texas Christian University Research Foundation and of the Wright-Patterson Air Force Base is appreciated.

The authors acknowledge the use of the computer program constructed mainly at the Laboratory of Molecular Structure and Spectra, The University of Chicago, under the direction of Professor C. C. J. Roothaan.

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