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Accurate Analytical Self-Consistent Field Functions for Atoms.

VI. The Ground States of Mo^+ and Mo*

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Self-consistent field calculations by the expansion method were carried out for the ground states of Mo^+ and Mo. Compared with solutions of the Hartree-Fock equations by the numerical integration technique, the wave functions obtained are accurate to 2–3 decimal places, and the total energies to about 5 significant figures.

INTRODUCTION

ACCURATE calculations of atomic wave functions by means of the self-consistent field (SCF) expansion method[1–3] have recently been carried out for a number of practical cases.[4–8] This paper reports similar calculations for the $4d^5$, ^6S state of Mo^+ and the $4d^55s$, ^7S state of Mo (these are the ground states of these systems).

These open shell configurations require the evaluation of the appropriate vector coupling coefficients suitable for our SCF formalism[3]; formulas and tables of these

TABLE I. Optimized exponents ζ of the basis functions for Mo^+ and Mo.

Basis function \ Atom and state	Mo^+ $4d^5$, ^6S	Mo $4d^55s$, ^7S
$1s$	42.000	42.000
$3s$	46.657	50.183
$3s$	35.659	34.807
$3s$	26.613	24.367
$3s$	19.390	18.298
$3s$	13.662	14.090
$3s$	8.605	8.587
$3s$	7.585	6.759
$4s$	4.751	4.928
$4s$	3.133	3.265
$5s$		2.000
$5s$		1.119
$2p$	21.000	21.000
$4p$	27.307	27.405
$4p$	19.939	19.980
$4p$	13.336	13.096
$4p$	8.896	8.799
$4p$	4.492	4.468
$4p$	2.794	2.751
$3d$	14.000	14.000
$5d$	24.694	26.473
$5d$	14.256	14.023
$5d$	9.566	9.522
$5d$	6.567	7.370
$5d$	4.114	4.045
$5d$	2.230	2.123
$5d$	0.973	0.912

TABLE II. Eigenvectors of coefficients $C_{i\lambda p}$ for Mo^+.

Basis function	Eigenvectors			
	$1s$	$2s$	$3s$	$4s$
$1s$	0.98758	−0.31507	0.13262	−0.05169
$3s$	0.01187	0.00109	0.00332	0.00001
$3s$	0.00792	0.06576	−0.04912	0.01321
$3s$	−0.00045	0.44137	−0.14011	0.06908
$3s$	0.00000	0.54425	−0.51394	0.19074
$3s$	0.00012	0.02491	0.15555	−0.01722
$3s$	−0.00037	0.01841	1.03017	−0.61565
$3s$	0.00027	−0.01292	0.04848	0.02065
$4s$	−0.00001	0.00074	0.01912	0.79148
$4s$	0.00001	−0.00027	−0.00331	0.37660
		$2p$	$3p$	$4p$
$2p$		0.82661	−0.35774	0.12959
$4p$		0.04848	−0.01812	0.00590
$4p$		0.16398	−0.01932	0.00571
$4p$		0.01383	0.48088	−0.21178
$4p$		−0.00034	0.60268	−0.27199
$4p$		0.00004	0.02173	0.70346
$4p$		−0.00004	−0.00362	0.44730
			$3d$	$4d$
$3d$			0.38510	−0.10380
$5d$			0.01110	−0.00296
$5d$			0.30358	−0.07794
$5d$			0.38554	−0.07703
$5d$			0.07042	0.10823
$5d$			0.00702	0.51536
$5d$			−0.00130	0.53462
$5d$			0.00031	0.04295

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TABLE III. Eigenvectors of coefficients $C_{i\lambda p}$ for Mo.

Basis function	Eigenvectors				
	1*s*	2*s*	3*s*	4*s*	5*s*
1*s*	0.98754	−0.31502	0.13264	+0.05188	0.01327
3*s*	0.00800	−0.00194	0.00181	+0.00038	−0.00008
3*s*	0.01651	0.11790	−0.05957	−0.02145	−0.00439
3*s*	−0.01162	0.58494	−0.22926	−0.09814	−0.02954
3*s*	0.01209	0.34257	−0.46722	−0.18440	−0.03800
3*s*	−0.00723	0.04105	0.20749	+0.06206	0.00534
3*s*	0.00367	−0.00446	1.07280	+0.54237	0.15093
3*s*	−0.00235	0.00398	0.00524	+0.06896	0.01986
4*s*	0.00048	−0.00108	0.02372	−0.74878	−0.25518
4*s*	−0.00015	0.00031	−0.00535	−0.44972	−0.07175
5*s*	0.00003	−0.00008	0.00128	+0.00083	0.53425
5*s*	−0.00001	0.00002	−0.00041	+0.00217	0.59981
		2*p*	3*p*	4*p*	
2*p*		0.82660	−0.35757	0.12966	
4*p*		0.04709	−0.01993	0.00679	
4*p*		0.16550	−0.00997	0.00144	
4*p*		0.01416	0.50245	−0.22151	
4*p*		−0.00085	0.57520	−0.26000	
4*p*		0.00015	0.01937	0.72474	
4*p*		−0.00008	−0.00310	0.42833	
			3*d*	4*d*	
3*d*			0.38246	−0.10025	
5*d*			0.01229	−0.00417	
5*d*			0.33295	−0.07665	
5*d*			0.31938	−0.10328	
5*d*			0.10507	0.12304	
5*d*			0.01156	0.54941	
5*d*			−0.00206	0.51883	
5*d*			0.00047	0.06305	

TABLE IV. Calculated energies and comparison with experiment.[a]

Atom or ion	State	Calculated total energy	Energies relative to ground state		
			Calculated	Experimental	Calculated minus experimental
Mo$^+$	$4d^5$, ^6S	−3975.3308	0.2134	0.2609	−0.0475
Mo	$4d^55s$, ^7S	−3975.5442	0	0	0

[a] See Ref. 13.

TABLE V. Orbital energies ϵ.

	Mo$^+$ $4d^5$, ^6S	Mo $4d^55s$, ^7S
1*s*	−721.44964	−721.19997
2*s*	−103.09458	−102.84930
3*s*	−18.82853	−18.58302
4*s*	−3.00874	−2.76183
5*s*		−0.22201
2*p*	−94.68898	−94.44255
3*p*	−15.53172	−15.28502
4*p*	−1.97491	−1.72263
3*d*	−9.52999	−9.28263
4*d*	−0.60934	−0.35714

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

Atom or ion	State	E_p/E_k
Mo$^+$	$4d^5$, ^6S	−2.0000082
Mo	$4d^55s$, ^7S	−2.0000102

TABLE VII. Radial functions $P_{i\lambda}(r)$ for Mo$^+$.

r	1*s*	2*s*	3*s*	4*s*	2*p*	3*p*	4*p*	3*d*	4*d*
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.001	0.516	−0.164	0.069	−0.027	0.002	−0.001	0.000	0.000	−0.000
0.002	0.989	−0.315	0.133	−0.052	0.007	−0.003	0.001	0.000	−0.000
0.003	1.422	−0.453	0.191	−0.074	0.016	−0.007	0.003	0.000	−0.000
0.004	1.818	−0.578	0.243	−0.095	0.028	−0.012	0.004	0.000	−0.000
0.005	2.179	−0.692	0.291	−0.113	0.043	−0.019	0.007	0.000	−0.000
0.006	2.508	−0.794	0.334	−0.130	0.061	−0.026	0.010	0.000	−0.000
0.007	2.806	−0.885	0.372	−0.145	0.082	−0.035	0.013	0.001	−0.000
0.008	3.075	−0.967	0.406	−0.158	0.104	−0.045	0.016	0.001	−0.000
0.009	3.318	−1.039	0.436	−0.170	0.129	−0.056	0.020	0.001	−0.000
0.010	3.535	−1.101	0.462	−0.180	0.157	−0.068	0.024	0.001	−0.000
0.015	4.303	−1.295	0.541	−0.210	0.318	−0.137	0.050	0.005	−0.001
0.020	4.656	−1.325	0.549	−0.213	0.510	−0.219	0.079	0.010	−0.003
0.025	4.726	−1.233	0.505	−0.196	0.719	−0.308	0.111	0.019	−0.005
0.030	4.606	−1.055	0.423	−0.163	0.936	−0.399	0.144	0.030	−0.008
0.035	4.366	−0.816	0.315	−0.121	1.152	−0.488	0.176	0.045	−0.012
0.040	4.056	−0.540	0.191	−0.072	1.361	−0.572	0.206	0.062	−0.017
0.050	3.352	0.065	−0.076	0.033	1.743	−0.718	0.258	0.107	−0.029
0.060	2.663	0.666	−0.335	0.134	2.062	−0.827	0.296	0.164	−0.044
0.070	2.060	1.210	−0.560	0.221	2.309	−0.895	0.318	0.230	−0.062
0.080	1.562	1.670	−0.736	0.288	2.485	−0.922	0.325	0.304	−0.081
0.090	1.168	2.040	−0.860	0.334	2.595	−0.911	0.318	0.385	−0.102
0.100	0.863	2.310	−0.930	0.359	2.648	−0.865	0.298	0.469	−0.125
0.120	0.460	2.611	−0.928	0.349	2.614	−0.690	0.227	0.643	−0.170
0.140	0.240	2.655	−0.774	0.278	2.450	−0.439	0.129	0.815	−0.213
0.160	0.123	2.527	−0.519	0.167	2.213	−0.146	0.017	0.976	−0.252
0.180	0.063	2.300	−0.209	0.037	1.944	0.158	−0.097	1.121	−0.286
0.200	0.032	2.027	0.120	−0.098	1.672	0.453	−0.204	1.247	−0.312
0.250	0.006	1.345	0.874	−0.385	1.073	1.070	−0.409	1.467	−0.347
0.300	0.001	0.819	1.393	−0.543	0.647	1.462	−0.505	1.564	−0.339

Table VII. (*Continued*)

r	1s	2s	3s	4s	2p	3p	4p	3d	4d
0.350		0.474	1.656	−0.562	0.376	1.641	−0.496	1.564	−0.296
0.400		0.266	1.715	−0.473	0.213	1.660	−0.409	1.495	−0.228
0.450		0.147	1.638	−0.311	0.119	1.574	−0.269	1.383	−0.144
0.500		0.080	1.484	−0.110	0.066	1.428	−0.102	1.250	−0.052
0.600		0.024	1.100	0.310	0.021	1.077	0.248	0.971	0.139
0.700		0.007	0.747	0.663	0.007	0.754	0.552	0.720	0.315
0.800		0.002	0.480	0.906	0.002	0.503	0.779	0.518	0.464
0.900		0.001	0.297	1.041	0.001	0.325	0.924	0.363	0.582
1.000			0.180	1.088		0.205	0.997	0.251	0.669
1.200			0.064	1.010		0.079	0.991	0.116	0.766
1.400			0.024	0.831		0.031	0.874	0.054	0.786
1.600			0.009	0.638		0.013	0.722	0.025	0.758
1.800			0.004	0.471		0.005	0.573	0.012	0.707
2.000			0.001	0.338		0.002	0.445	0.006	0.646
3.000				0.054			0.103		0.359
4.000				0.007			0.019		0.164
8.000									0.013
12.000									0.002

Table VIII. Radial functions $P_{i\lambda}(r)$ for Mo.

r	1s	2s	3s	4s	5s	2p	3p	4p	3d	4d
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.001	0.515	−0.164	0.069	−0.027	0.007	0.002	−0.001	0.000	0.000	−0.000
0.002	0.989	−0.315	0.133	−0.052	0.013	0.007	−0.003	0.001	0.000	−0.000
0.003	1.422	−0.453	0.191	−0.075	0.019	0.016	−0.007	0.003	0.000	−0.000
0.004	1.818	−0.578	0.243	−0.095	0.024	0.028	−0.012	0.004	0.000	−0.000
0.005	2.179	−0.691	0.291	−0.114	0.029	0.043	−0.019	0.007	0.000	−0.000
0.006	2.508	−0.794	0.334	−0.131	0.033	0.061	−0.026	0.010	0.000	−0.000
0.007	2.806	−0.885	0.372	−0.146	0.037	0.082	−0.035	0.013	0.001	−0.000
0.008	3.075	−0.967	0.406	−0.159	0.041	0.104	−0.045	0.016	0.001	−0.000
0.009	3.318	−1.039	0.436	−0.171	0.044	0.129	−0.056	0.020	0.001	−0.000
0.010	3.535	−1.101	0.462	−0.181	0.046	0.157	−0.068	0.025	0.001	−0.000
0.015	4.303	−1.295	0.541	−0.211	0.054	0.318	−0.137	0.050	0.005	−0.001
0.020	4.656	−1.325	0.549	−0.214	0.055	0.510	−0.219	0.079	0.010	−0.003
0.025	4.726	−1.234	0.505	−0.196	0.050	0.719	−0.308	0.111	0.018	−0.005
0.030	4.606	−1.055	0.423	−0.164	0.042	0.936	−0.399	0.144	0.030	−0.008
0.035	4.366	−0.817	0.315	−0.121	0.031	1.152	−0.488	0.176	0.044	−0.012
0.040	4.056	−0.540	0.191	−0.072	0.018	1.361	−0.572	0.206	0.062	−0.016
0.050	3.352	0.065	−0.076	0.033	−0.009	1.743	−0.718	0.258	0.107	−0.028
0.060	2.663	0.666	−0.335	0.135	−0.035	2.062	−0.827	0.296	0.164	−0.043
0.070	2.059	1.210	−0.560	0.222	−0.057	2.309	−0.895	0.319	0.230	−0.060
0.080	1.562	1.670	−0.736	0.290	−0.074	2.485	−0.922	0.326	0.305	−0.080
0.090	1.168	2.036	−0.860	0.336	−0.086	2.595	−0.911	0.318	0.385	−0.100
0.100	0.863	2.310	−0.930	0.360	−0.092	2.648	−0.865	0.298	0.469	−0.122
0.120	0.460	2.611	−0.928	0.350	−0.089	2.614	−0.690	0.227	0.644	−0.166
0.140	0.240	2.655	−0.774	0.279	−0.070	2.450	−0.439	0.129	0.816	−0.209
0.160	0.123	2.528	−0.519	0.168	−0.042	2.213	−0.146	0.017	0.977	−0.247
0.180	0.063	2.301	−0.209	0.037	−0.008	1.944	0.158	−0.097	1.121	−0.279
0.200	0.032	2.027	0.121	−0.098	0.027	1.672	0.453	−0.204	1.246	−0.305
0.250	0.006	1.344	0.874	−0.387	0.100	1.073	1.070	−0.410	1.466	−0.338
0.300	0.001	0.819	1.393	−0.545	0.139	0.647	1.462	−0.505	1.564	−0.331
0.350		0.474	1.656	−0.564	0.141	0.376	1.641	−0.497	1.564	−0.290
0.400		0.267	1.715	−0.474	0.114	0.213	1.660	−0.409	1.496	−0.224
0.450		0.147	1.639	−0.312	0.068	0.119	1.574	−0.270	1.384	−0.142
0.500		0.080	1.484	−0.110	0.013	0.066	1.428	−0.102	1.250	−0.051
0.600		0.024	1.100	0.312	−0.097	0.021	1.077	0.248	0.970	0.136
0.700		0.007	0.746	0.666	−0.182	0.007	0.754	0.553	0.719	0.309
0.800		0.002	0.479	0.910	−0.229	0.002	0.503	0.780	0.518	0.454
0.900		0.001	0.297	1.045	−0.240	0.001	0.325	0.925	0.364	0.568
1.000			0.180	1.091	−0.220		0.205	0.998	0.252	0.653
1.200			0.064	1.011	−0.122		0.079	0.991	0.116	0.748
1.400			0.023	0.829	0.009		0.031	0.873	0.053	0.771
1.600			0.009	0.635	0.141		0.013	0.720	0.025	0.747
1.800			0.003	0.467	0.259		0.005	0.572	0.013	0.699
2.000			0.001	0.334	0.357		0.002	0.444	0.007	0.641
3.000				0.049	0.561			0.105		0.374
4.000				0.004	0.505			0.020		0.189
8.000					0.114					0.021
12.000					0.010					0.004

coefficients for a large class of states have recently been derived.[9]

RESULTS AND DISCUSSION

Some of the important results are presented in Tables I–VIII. Since the basis sets were chosen so as to identically satisfy the cusp conditions,[6] we did not include the cusp values in the tables.

We believe that the total energies computed represent the Hartree-Fock values to about five significant figures, and that the radial functions $P_{i\lambda}(r)$ represent the Hartree-Fock functions to 2–3 decimal places. Better accuracy could be obtained by extensive exponent optimizations, which would require a large amount of computer time.

A numerical SCF calculation *without* exchange on Mo^+ was published by Ridley.[10] The numerical orbitals for Mo^+ of this work disagree with those by Ridley (after normalization) mostly in the second decimal place; in the critical area of the outer loop of the 4*d* orbital they disagree even in the first decimal place. A similar disagreement exists for Cu^+, where calculations with[7,11] and without[12] exchange are available.

Since total experimental energies are not available, we can only meaningfully compare the difference of the computed energies of Mo^+ and Mo with the experimental ionization potential[13] of Mo. This is shown in Table IV.

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Electron-Energy Distribution Function and Electron Average Energy in Ar-CO_2 and Ar-H_2 Mixtures[*]

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Electron-energy distribution functions and electron average energies are calculated for low-energy electrons in Ar-CO_2 and in Ar-H_2 mixtures in the presence of a static electric field. It is shown that one part of carbon dioxide or of molecular hydrogen in 10 000 parts of argon is sufficient to alter appreciably the electron-energy distribution function and the electron average energy from the values they would have in pure argon.

I. INTRODUCTION

THAT small amounts of molecular gases, when added to argon, alter appreciably the value that the electron drift velocity exhibits in pure argon has been verified both experimentally[1] and theoretically.[2,3] There is, however, very little mention in the literature of the change in the electron distribution function and the electron average energy induced by the addition of molecular impurities to argon. A technique for solving the Boltzmann equation for the phase-space distribution function for electrons immersed in certain binary gas mixtures in the presence of a static electric field has been presented in a previous article.[2] In the present study, use is made of this theory to calculate the electron-energy distribution function and electron average energy as a function of the molecular-impurity concentration in argon. Carbon dioxide and molecular hydrogen have been chosen as the molecular impurities. The Ar-CO_2 mixture has been chosen because of the good agreement between experimental and theoretical electron drift velocity data for this mixture.[2] The agreement between theory and experiment lends validity to the experimental cross-section and molecular energy-absorption data used in the theoretical analysis. The Ar-H_2 mixture has been chosen for study because electron drift velocity measurements in this mixture have been used to determine the momentum transfer and inelastic cross sections for hydrogen and argon.[4]

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