Radial Wave Functions for the Cesium Atom*

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This paper presents the radial wave functions for 26 electronic orbitals of the cesium atom. For each orbital the electron is considered to move in a screened Coulomb potential which is taken to be approximately the Thomas-Fermi potential for a singly charged cesium ion. The states obtained here are improvements over those obtained by Russek, Sherman, and Flinchbaugh and extend the scope of that work as well.

I. INTRODUCTION

In a recent paper, Russek, Sherman, and Flinchbaugh,[1] henceforth referred to as I, have obtained exact radial eigenfunctions for an electron in a screened Coulomb potential where the screening function is given by a particular functional form which can be made to closely approximate a realistic screening function (e.g., the Thomas-Fermi ion) by the adjustment of two parameters. The solution for that set of values of the parameters which give optimal fit to the Thomas-Fermi screening function is therefore equivalent to the approximate solution of the radial eigenvalue equation. The present work is an extension of that paper in that the form of the screening function is generalized to one which contains five adjustable parameters. In particular the radial wave functions have been obtained for all the normally filled states (these number 12 different radial functions) and for most of the excited states that are likely to be encountered (14 different radial functions in this category). It should be stressed, however, that the radial functions which follow from the present method are not the most accurate ones currently available for the normally filled states. Herman and Skillman[2] tabulate the radial functions for the filled states of cesium obtained from a Hartree-Fock-type calculation in which the exchange terms are approximated by an averaged free electron gas exchange potential. The significance of the present radial functions for the filled states is thus limited to the ease with which calculations may be made using them. The main contribution is the calculation of the optically excited states, which are improvements over those presented in I. In this domain the Thomas-Fermi ion potential is undoubtedly better than that used by Herman and Skillman, where the self-energy term is removed in an arbitrary and very approximate way.

It was shown in I that

$$\chi_{nl}(\rho)=(d\zeta/d\rho)^{-\frac{1}{2}}\chi_{nl}{}^{H}[\zeta(\rho)] \tag{1}$$

is an exact solution to the radial equation for an electron in a screened Coulomb field if the screening function is of the form

$$\frac{Z}{\gamma}-f(\rho)=-\frac{\rho}{\zeta}\left(\frac{d\zeta}{d\rho}\right)^{2}+\frac{l(l+1)}{2\rho}\left[1-\frac{\rho^{2}}{\zeta^{2}}\left(\frac{d\zeta}{d\rho}\right)^{2}\right]$$
$$-\rho\left[\frac{E}{\gamma^{2}}+\frac{1}{2n^{2}}\left(\frac{d\zeta}{d\rho}\right)^{2}\right]-\frac{\rho}{2}\left(\frac{d\zeta}{d\rho}\right)^{\frac{1}{2}}\frac{d^{2}}{d\rho^{2}}\left(\frac{d\zeta}{d\rho}\right)^{-1/2}, \tag{2}$$

where the functional dependence of ζ on ρ is here unspecified except for a few general conditions. Here $\rho=\gamma r$, where γ is a constant to be determined later and r is expressed in Bohr radii, the $\chi_{nl}{}^{H}$ are the hydrogenic wave functions, $f(\rho)$ is the screening function, and E is the energy of the electron expressed in atomic units.

The functional form for ζ used in I contained two parameters which were adjusted to make the screening function match the Thomas-Fermi screening function at two points. Difficulty was encountered in matching the screening function at small values of radius for the p and d states. This difficulty was reflected in relatively poor agreement with experiment of the energies obtained for these states and in calculations for hyperfine structure where the principal contribution comes from the values of the wave function at small radial coordinates.

To improve on those results the present work employs a five-parameter function of the form

$$\zeta=\frac{1-\alpha-\delta}{\beta}\ln(1+\beta\rho)+\alpha\rho+\frac{\delta\rho}{1+\lambda\rho+\mu\rho^{2}}, \tag{3}$$

where α, β, δ, λ, and μ are the undetermined parameters. This reduces to the form used in I (when $\delta=\lambda=\mu=0$) but allows greater flexibility at small values of ρ. Results give a much better fit to the Thomas-Fermi screening function in most significant regions reducing the error by as much as a factor of five. The calculations of energy states also show much better agreement with spectroscopic data. The same technique is used to obtain inner as well as outer states and agreement with x-ray data seems to indicate that this procedure is reasonably valid here too. However, it should be noted that for such states as the $1s$ state one would normally apply a relativistic correction to the energy. This was not done and therefore the results for the lower lying states should not be taken too seriously.

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[1] A. Russek, C. H. Sherman, and D. E. Flinchbaugh, Phys. Rev. **126**, 573 (1962).

[2] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

TABLE I. Values of α, β, δ, λ, and μ, for 26 states of cesium.

State	α	β	δ	λ	μ	γ
10s	0.0306	0.0680	0.218	0.0160	0.000120	55.0
9s	0.0331	0.0670	0.225	0.0155	0.000100	55.0
8s	0.0369	0.0660	0.230	0.0150	0.0000900	55.0
7s	0.0433	0.0560	0.259	0.0145	0.0000890	55.0
6s	0.0583	0.0420	0.263	0.0141	0.0000840	55.0
5s	0.125	0.0400	0.168	0.0145	0.0000900	55.0
4s	0.299	0.0350	0.167	0.0212	0.0000900	55.0
3s	0.516	0.0300	0.185	0.0340	0.0000810	55.0
2s	0.708	0.0250	0.169	0.0500	0.0000800	55.0
1s	0.926	0.0080	0.060	0.0310	0.0000370	55.0
10p	0.0304	0.0750	0.280	0.0170	0.000150	51.8
9p	0.0324	0.0740	0.295	0.0160	0.000140	51.8
8p	0.0352	0.0710	0.305	0.0155	0.000125	52.1
7p	0.0398	0.0660	0.335	0.0150	0.0000900	52.4
6p	0.0480	0.0500	0.336	0.0150	0.0000600	52.9
5p	0.0700	0.0520	0.230	0.0143	0.0000900	52.6
4p	0.265	0.0350	0.205	0.0212	0.0000900	53.5
3p	0.465	0.0346	0.197	0.0357	0.0000900	53.5
2p	0.716	0.0210	0.175	0.0410	0.0000720	54.1
9d	0.0317	0.121	0.386	0.0162	0.000260	44.1
8d	0.0330	0.121	0.390	0.0150	0.000240	44.3
7d	0.0347	0.110	0.401	0.0150	0.000220	45.0
6d	0.0370	0.100	0.420	0.0140	0.000200	45.9
5d	0.0410	0.0700	0.440	0.0110	0.0000600	48.3
4d	0.195	0.0427	0.200	0.0150	0.0000900	50.3
3d	0.444	0.0370	0.190	0.0150	0.000270	52.1

II. RESULTS

Table I gives the values of the parameters in ζ and the values of γ for 26 states of cesium including those given in I.

As in I, the best results are obtained for the s states and the worst results for the d states. For outer states the deviations from the Thomas-Fermi screening function as given by Kobayashi[3] are kept within ten percent between 0 Bohr radii (B.r.) and 20 B.r., and within ten percent for the inner states between 0 and 5 B.r. A typical screening function curve for the 6p state of cesium along with curves given by Russek, Sherman, and Flinchbaugh and Kobayashi are given below in Fig. 1.

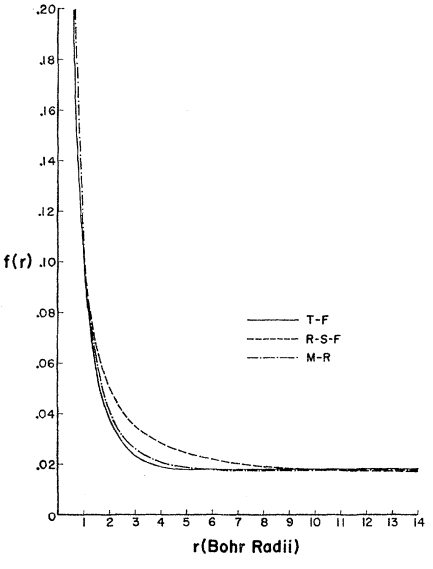

FIG. 1. Comparison of Thomas-Fermi, Russek-Sherman-Flinchbaugh, and Moses-Russek screening functions for the 6p state of cesium.

[3] S. Kobayashi, Mem. Fac. Liberal Arts Educ., Kagawa Univ. 2, 68 (1959).

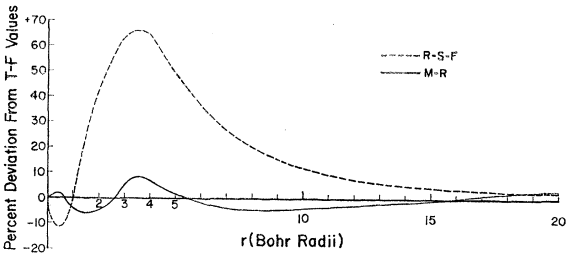

FIG. 2. Percent deviation of screening function from Thomas-Fermi screening function versus distance from nuclear center for Russek-Sherman-Flinchbaugh data and Moses-Russek data for 8p state of cesium.

In order to obtain a clear picture of the superior match of the new five-parameter ζ function over the two-parameter ζ function used in I, the percentage deviation from the Thomas-Fermi value for both is plotted in Fig. 2 for the 8p state of cesium. This curve typifies the improvement that can be seen in all states.

As shown in I, the electron energy is given, in atomic units, by

$$E=-\gamma^2\alpha^2/2n^2. \quad (4)$$

Values of energies for different states of cesium are

TABLE II. Calculated and experimental values of energies for each of 26 states of cesium.

State	Energy calculated from $E=(-\alpha^2\gamma^2)(2n^2)^{-1}$ (a.u.)	Experimental energy (a.u.)	Percent difference
10s	−0.0141	−0.0142	0.70
9s	−0.0204	−0.0205	0.49
8s	−0.0321	−0.0323	0.62
7s	−0.0578	−0.0585	1.20
6s	−0.143	−0.143	0.00
5s	−0.945	−0.956	1.15
4s	−8.45	−8.49	0.47
3s	−44.7	−44.9	0.45
2s	−189.0	−209.0	9.57
1s	−1300.0	−1320.0	1.52
10p	−0.0124	−0.0121	2.42
9p	−0.0175	−0.0171	2.29
8p	−0.0262	−0.0257	1.91
7p	−0.0443	−0.0433	2.26
6p	−0.0896	−0.0905	0.99
5p	−0.271	−0.110[a]	
4p	−6.29	−5.79	7.95
3p	−34.4	−37.6	8.51
2p	−188.0	−191.0	1.57
9d	−0.0120	−0.0117	2.50
8d	−0.0166	−0.0164	1.20
7d	−0.0249	−0.0244	2.01
6d	−0.0400	−0.0401	0.25
5d	−0.0785	−0.0771	1.78
4d	−2.99	−2.87	4.01
3d	−29.7	−27.0	9.09

[a] Not believed to be accurate.

TABLE III. Values of A_i and a_i used in the expansion (6) expressing r as a function of ζ.

State	A_1	A_2	A_3	A_4	A_5	a_1	a_2	a_3	a_4	a_5
10s	0.496	0.902	−0.840	0.750	−0.308	0.0025	0.0177	0.0924	0.220	0.384
9s	0.486	0.986	−0.865	0.573	−0.162	0.0023	0.0183	0.0780	0.175	0.247
8s	0.513	0.900	−0.925	0.575	−0.065	0.0027	0.0188	0.0942	0.176	0.719
7s	0.484	0.950	−0.930	0.780	−0.275	0.0023	0.0168	0.0804	0.174	0.316
6s	0.510	0.785	−0.620	0.362	−0.0371	0.0020	0.0132	0.0691	0.115	0.301
5s	0.241	0.437	0.540	−0.330	0.112	0.00080	0.00521	0.0154	0.0597	0.116
4s	0.128	0.343	0.678	−0.205	0.0560	0.00041	0.00320	0.0151	0.0705	0.172
3s	0.0512	0.147	0.310	0.255	0.237	0.00020	0.00132	0.00550	0.0147	0.0407
2s	0.0381	0.116	0.203	0.277	0.366	0.00020	0.00130	0.00540	0.0138	0.0558
1s	0.0370	0.113	0.178	0.310	0.362	0.00010	0.00130	0.00520	0.0135	0.0794
10p	0.462	0.902	−1.00	0.972	−0.336	0.0027	0.0201	0.130	0.235	0.371
9p	0.430	0.980	−0.945	0.644	−0.109	0.0026	0.0198	0.110	0.202	0.547
8p	0.425	1.00	−0.855	0.800	−0.370	0.0025	0.0197	0.0979	0.219	0.311
7p	0.400	1.05	−1.28	1.06	−0.230	0.0024	0.0184	0.104	0.177	0.369
6p	0.432	1.04	−1.38	1.63	−0.722	0.0021	0.0162	0.0854	0.169	0.263
5p	0.267	1.00	−0.365	0.140	−0.042	0.0010	0.0111	0.0611	0.187	0.359
4p	0.132	0.331	0.895	−0.502	0.144	0.00040	0.00330	0.0178	0.0438	0.0870
3p	0.0810	0.186	0.415	0.765	−0.447	0.00031	0.00231	0.00901	0.0447	0.0626
2p	0.0460	0.135	0.275	1.16	−0.616	0.00020	0.00162	0.00690	0.0405	0.0659
9d	0.350	1.25	−9.31	10.0	−1.29	0.0037	0.0360	0.298	0.358	1.28
8d	0.360	1.30	−4.34	8.50	−4.82	0.0041	0.0369	0.243	0.420	0.596
7d	0.347	1.41	−2.68	4.85	−2.93	0.0036	0.0356	0.175	0.371	0.528
6d	0.428	1.50	−2.65	2.48	−0.785	0.0045	0.0395	0.151	0.238	0.319
5d	0.319	1.52	−2.14	4.70	−3.40	0.0023	0.0228	0.0947	0.258	0.346
4d	0.172	0.382	0.650	−0.313	0.109	0.00060	0.00460	0.0175	0.0747	0.146
3d	0.0720	0.194	0.390	0.450	−0.106	0.00030	0.00220	0.00960	0.0365	0.0863

listed in Table II. Comparison with experimental data given by Bacher and Goudsmit[4] for upper states and x-ray absorption data[5] for lower states showed agreement to be good.

As pointed out in I, for the calculation of the expectation value of $g(r)$ one must evaluate integrals of the type

$$\langle g(r)\rangle = N_{nl}^2 \int_0^\infty g(r)\chi_{nl}^2(r)dr$$

$$= N_{nl}^2 \int_0^\infty g(r)[\chi_{nl}{}^H(\zeta)]^2\left[\frac{dr}{d\zeta}\right]^2 d\zeta \qquad (5)$$

for the nlth state. (Here N_{nl} is the normalization constant.) The integrand in Eq. (5) is partly a function of r and partly a function of ζ. To simplify the evaluation of these, r is expressed as an exponential series in ζ as follows:

$$r = (\zeta/\gamma)(1-1/\alpha)(\textstyle\sum_i A_i e^{-a_i\zeta}) + (\zeta/\gamma\alpha). \qquad (6)$$

The values of A_i and a_i were obtained from a semilogarithmic plot of $(\rho/\zeta - 1/\alpha)/(1-1/\alpha)$ versus ζ. Series were carried out to five terms. The values of the A_i and a_i are given in Table III. With the substitution of (6) into the $(dr/d\zeta)^2$ factor and a power series expansion of $g(r)$, the integrals can be evaluated as in I.

ACKNOWLEDGMENTS

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[4] R. F. Bacher and S. Goutsmit, *Atomic Energy States* (McGraw-Hill Book Company, Inc., New York, 1932).

[5] R. D. Hill, E. L. Church, and J. W. Mihelich, Rev. Sci. Instr. 23, 523 (1952).