

ULTRAVIOLET WAVELENGTHS AND OSCILLATOR STRENGTHS FOR $3d$ - nf TRANSITIONS IN THE HELIUM ISOELECTRONIC SEQUENCE

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ABSTRACT

Accurate variational wave functions and energies have been obtained for the 4^1F , 5^1F , 6^1F , 4^3F , 5^3F , and 6^3F states of the helium isoelectronic sequence through $Z = 16$. The trial functions are eighteen-term configuration-interaction expansions in members of a denumerably complete basis set (Sturmian functions). These have been used with previously calculated 3^1D and 3^3D wave functions to obtain wavelengths and oscillator strengths for $3d$ - nf transitions. For He I and Li II, the only species in which these transitions have been observed, the calculated energies agree with observations to within 0.000002 atomic unit. The discrepancy between calculated and observed wavelengths is in the worst case one part in 4700 and is generally much smaller. For higher members of the sequence, the predicted wavelengths range from 2077 Å for Be III to 48 Å for S XV. Oscillator strengths were calculated by means of the dipole length, velocity, and acceleration formulae, and agreement among the three values is in most cases to within 2 percent.

I. INTRODUCTION

Recent observations of soft X-ray spectra of solar flares have revealed the presence of emission lines from the helium isoelectronic sequence as far as Ca XIX in one case (Meekins *et al.* 1968) and as far as Fe XXV in another (Neupert *et al.* 1967). Furthermore, recent ionization-equilibrium calculations have shown that at solar-corona temperatures, the two-electron ions of the lighter elements should be the dominant species (Cox and Tucker 1969). However, except for helium itself and singly ionized lithium, there is very little information, either experimental or theoretical, available on the spectra of two-electron atoms. Wiese, Smith, and Glennon (1966) list 128 lines and oscillator strengths for He I and fifty-two lines and oscillator strengths for Li II. Green, Johnson, and Kolchin (1966) have calculated oscillator strengths for 203 lines in He I. But beyond Li II there exist no data for levels above $n = 3$ and $l = 2$. This paper reports the results of variational calculations of energies and wave functions for the three lowest ^1F and ^3F states of the helium isoelectronic sequence through S XV, and oscillator strengths for transitions to these states from the 3^1D and 3^3D states.

II. WAVE FUNCTIONS AND ENERGIES

The trial functions used in the variational calculation of eigenvalues and eigenfunctions of the two-electron Schrödinger equation are configuration-interaction expansions

$$\psi = \sum_i c_i \psi_i \quad (1)$$

in which each configuration is the linear combination of Slater determinants

$$\begin{aligned} \psi = \sum_{m_1} C(l_1 l_2 L; m_1, -m_1) [& | \phi_{n_1 l_1 m_1}(k_1 r_1) \alpha \phi_{n_2 l_2 m_2}(k_2 r_2) \beta | \\ & \pm | \phi_{n_2 l_2 m_2}(k_2 r_1) \alpha \phi_{n_1 l_1 m_1}(k_1 r_2) \beta |] , \end{aligned} \quad (2)$$

where $C(l_1 l_2 L; m_1, -m_1)$ is a Clebsch-Gordan coefficient with $M_L = 0$ and the plus and minus signs indicate singlet and triplet states, respectively. The single-particle functions are members of the denumerably complete set of functions

$$\phi_{nlm}(\xi, \theta, \phi) = \frac{[\Gamma(n-l)]^{1/2}}{[\Gamma(n+l+1)]^{3/2}} \xi^l e^{-\xi/2} L_{n-l-1}^{2l+1}(\xi) Y_l^m(\theta, \phi) \quad (3)$$

of the scaled variable $\xi = 2kr$. These functions differ from hydrogenic functions in that the principal quantum number n does not appear in the argument of the radial part. Their properties have been discussed by many authors, for example, Pauling and Wilson (1935) and, more recently, Rotenberg (1962). They have several advantages over other possible basis sets. Being single-particle functions, they are considerably simpler to use than Hylleraas-type functions, which contain the interelectron coordinate r_{12} explicitly. Of particular importance is the fact that, although these functions are somewhat more complicated than Slater-type orbitals, quite good results can be obtained for excited states of two-electron atoms with only the two nonlinear parameters k_1 and k_2 of equation (2) (Brown 1968), in contrast to the large number of nonlinear parameters which are necessary with Slater-type orbitals (Weiss 1961; Green, Kolchin, and Johnson 1965).

In order to apply the variational principle, the expansion (1) is substituted into the Schrödinger equation

$$\mathfrak{H}\psi = E\psi, \quad (4)$$

in which the Hamiltonian, in atomic units, is

$$\mathfrak{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - Z\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}}. \quad (5)$$

Variation of the linear parameters c_i of equation (1) leads to the matrix eigenvalue problem

$$\sum_j [H_{ij} - ES_{ij}]c_j = 0, \quad (6)$$

where

$$H_{ij} = \langle \psi_i | \mathfrak{H} | \psi_j \rangle \quad \text{and} \quad S_{ij} = \langle \psi_i | \psi_j \rangle. \quad (7)$$

In the present work the matrix eigenvalue equation (6) was solved by the inverse-iteration scheme described by

$$[H - \epsilon S]c_{n+1} = Sc_n, \quad (8)$$

where ϵ is a constant. It is found that this method gives rapid convergence to the eigenvector corresponding to the eigenvalue closest to ϵ , independent of the choice of initial vector c_0 . All that is required, then, as a starting point for the computation of the wave function for an excited state is a rough estimate of the energy. After the eigenvector c has been determined, the Rayleigh quotient

$$E = c^\dagger H c / c^\dagger S c \quad (9)$$

gives an upper bound to the energy of the state in question. The nonlinear parameters k_1 and k_2 were varied in a systematic manner which has been described elsewhere (Brown 1968).

The number and type of configuration to be included in the expansion (1) were determined by trial and error for $Z = 2$, and this set was then used for the rest of the isoelectronic sequence. The final set of eighteen configurations is shown in Table 1, along with typical sets of expansion coefficients obtained. Those shown are for O VII, but there is little difference throughout the isoelectronic sequence. There was no tendency for the

TABLE 1
CONFIGURATIONS USED IN CALCULATING THE n^1F AND n^3F WAVE FUNCTIONS
AND TYPICAL EXPANSION COEFFICIENTS OBTAINED*

Configuration	4^1F	4^3F	5^1F	5^3F	6^1F	6^3F
1s 4f	.20509246	.20548811	.04875829	.04875575	-.00137457	-.00137320
1s 5f	-.07576178	-.07554047	.18553954	.18554751	-.02830338	-.02829827
1s 6f	.02099941	.02084595	-.07039459	-.07038390	-.19183494	-.19184153
1s 7f	-.00501444	-.00495026	.01687642	.01688039	.03628620	.03627355
1s 8f	.00108210	.00106866	-.00324583	-.00323981	-.00412438	-.00412959
1s 9f	-.00021103	-.00020151	.00052939	.00053560	.00036273	.00035651
2s 4f	.00063551	.00081815	.00002156	.00002112	-.00000050	-.00000035
2s 5f	-.00023522	-.00030357	.00008224	.00008146	-.00001224	-.00001195
2s 6f	.00006445	.00008014	-.00003058	-.00003153	-.00008424	-.00008389
2s 7f	-.00001711	-.00002339	.00000841	.00000765	.00001709	.00001738
3s 4f	.00000167	.00000386	-.00000001	.00000040	.00000002	-.00000011
3s 5f	-.00000088	-.00000012	-.00000002	.00000046	.00000003	-.00000013
2p 3d	-.00017162	-.00016504	-.00012173	-.00011840	.00006710	.00006569
2p 4d	-.00002181	-.00001369	-.00009291	-.00008847	.00008139	.00007942
2p 5d	-.00001581	-.00000969	-.00002202	-.00001854	.00005189	.00005028
3p 3d	.00004225	.00003752	.00002213	.00002015	-.00000893	-.00000815
2p 5g	.00011776	.00011768	.00002944	.00002940	-.00000139	-.00000138
2p 6g	.00005388	.00005385	.00005176	.00005171	-.00000372	-.00000370

* Coefficients shown are for O VII.

TABLE 2
CALCULATED AND OBSERVED n^1F AND n^3F TOTAL ENERGIES (ATOMIC UNITS)
AND $3d$ - nf WAVELENGTHS (Å) FOR He I AND Li II

	He I _{calc}	He I _{obs} *	Li II _{calc}	Li II _{obs} *
-E(4^1F)	2.03125428	2.031255	4.62501336	4.625008
-E(5^1F)	2.02000164	2.020004	4.58000505	4.579997
-E(6^1F)	2.01388950	2.013889	4.55555741	4.555560
-E(4^3F)	2.03125432	2.031255	4.62501383	4.625013
-E(5^3F)	2.02000168	2.020004	4.58000554	4.579979
-E(6^3F)	2.01388952	2.013889	4.55555778	4.555560
$\lambda(3^1D - 4^1F)$	18707.	18703.	4679.9	4679.7
$\lambda(3^1D - 5^1F)$	12796.	12794.	3200.5	3200.3
$\lambda(3^1D - 6^1F)$	10921.	10920.	2731.5	2731.5
$\lambda(3^3D - 4^3F)$	18696.	18692.	4673.3	4673.2
$\lambda(3^3D - 5^3F)$	12790.	12789.	3197.4	3196.7
$\lambda(3^3D - 6^3F)$	10917.	10916.	2729.2	2729.2

* Wiese, Smith and Glennon 1966.

various types of configurations to change in relative importance as a function of Z , as has been noted, for example, by Zare (1966, 1967) in configuration-interaction calculations on the Mg sequence. This difference in behavior is probably due to the fact that the phrase "configuration interaction" can have two quite different meanings. In the present work, the configurations do not represent actual excited states of the atom, but are simply members of a convenient basis set. In fact, one of the reasons for using Sturmian functions is that the nodes of the radial part do not move out from the origin with increasing principal quantum number, but remain concentrated in the region of space in which the function to be represented is expected to have its most interesting features (Slater 1960). On the other hand, in the work of Zare (1966, 1967) the configurations do represent physical states of the atom.

In Table 2 are shown the total energies obtained for the 4^1F , 5^1F , 6^1F , 4^3F , 5^3F , and 6^3F states of He I and Li II and the respective experimental values. For some of the Li II levels, the theoretical energies appear to be lower than the experimental, which is probably due to the fact that the experimental values are uncertain by 0.00001 atomic unit (Moore 1949). Also shown in Table 2 are vacuum wavelengths for $3d-nf$ transitions calculated with $3d$ energies obtained previously (Brown 1968). Since these are the only two species for which there are available experimental values, the energies for the other members of the isoelectronic sequence are shown separately in Table 3.

III. OSCILLATOR STRENGTHS

Absorption oscillator strengths were calculated by means of the dipole length, velocity, and acceleration formulae (Chandrasekhar 1945)

$$f_l = \frac{2}{3}(E_j - E_i) |\langle \psi_i | \mathbf{r}_1 + \mathbf{r}_2 | \psi_j \rangle|^2, \quad (10a)$$

$$v = \frac{2}{3}(E_j - E_i)^{-1} |\langle \psi_i | \nabla_1 + \nabla_2 | \psi_j \rangle|^2, \quad (10b)$$

$$f_a = \frac{2}{3}(E_j - E_i)^{-3} |\langle \psi_i | \frac{Z\mathbf{r}_1}{r_1^3} + \frac{Z\mathbf{r}_2}{r_2^3} | \psi_j \rangle|^2, \quad (10c)$$

in which degeneracies in the initial state and final state have been averaged over and summed over, respectively. If the wave functions in the transition integrals in the above equations were the exact solution of the Schrödinger equation for the two states, then the three equations (10a), (10b), and (10c) would give the same result. However, equation (1) is an approximate solution. The three forms of the oscillator strength will then give different results, and agreement among the three is often taken as a measure of the accuracy of the wave functions used. By the nature of the variational procedure, any complete set of functions, if enough terms were included in the expansion, could be made to give an answer as close as desired to the experimental energy. Thus the energy alone is not a very good criterion. It is almost always found that the length and velocity formulae give better agreement with observed values than does the acceleration formula. When there are no observed values available, it is usually found that the acceleration formula gives results which disagree with the other two (Weiss 1963; Schiff and Pekeris 1964; Green *et al.* 1966).

In Table 4 the oscillator strengths obtained in the present work are compared with the Coulomb-approximation calculations of Wiese *et al.* (1966) for Li II. The results for He I are quite similar. It can be seen that, at least for the transitions considered here, the Coulomb approximation is capable of much greater accuracy than is usually claimed for it.

Tables 5 and 6 list the predicted vacuum wavelengths and oscillator strengths for the rest of the isoelectronic sequence through $Z = 16$. In most cases the agreement among the three f -values is to within 2 percent. Furthermore, the acceleration value does not

TABLE 3
CALCULATED TOTAL ENERGIES (ATOMIC UNITS) FOR THE n^1F AND n^3F LEVELS

Ion	4^1F	5^1F	6^1F	4^3F	5^3F	6^3F
Be III	-8.28127084	-8.18000784	-8.12500278	-8.28127248	-8.18000941	-8.12500395
B IV	-13.00002660	-12.82000970	-12.72222555	-13.00003003	-12.82001288	-12.72222791
C V	-18.78128068	-18.50001090	-18.34722579	-18.78128645	-18.50001607	-18.34722961
N VI	-25.62503364	-25.22001158	-25.00000360	-25.62504206	-25.22001902	-25.00000903
O VII	-33.53128565	-32.98001192	-32.68055898	-33.53129702	-32.98002183	-32.68056621
F VIII	-42.50003718	-41.78001195	-41.38889211	-42.50005166	-41.78002448	-41.38890119
Ne IX	-52.53128812	-51.62001184	-51.12500288	-52.53130593	-51.62002710	-51.12501392
Na X	-63.62503867	-62.50001151	-61.88889131	-63.62505992	-62.50002959	-61.88890437
Mg XI	-75.78128897	-74.42001107	-73.68055751	-75.78131370	-74.42003204	-73.68057257
Al XII	-89.00003907	-87.38001059	-86.50000152	-89.00006735	-87.38003451	-86.50001868
Si XIII	-103.28128896	-101.38001000	-100.34722322	-103.28132092	-101.38003691	-100.34724252
P XIV	-118.62503869	-116.42000934	-115.22222264	-118.62507437	-116.42003928	-115.22224410
S XI	-135.03128828	-132.50000862	-131.12499984	-135.03132773	-132.50004164	-131.12502346

appear to be consistently any less believable than the other two. For the $3d-5f$ transitions it is the length value which seems to be slightly out of step, and for the $3d-6f$ transitions it is the velocity value. It has been pointed out by Chandrasekhar (1945) that the three f -value formulae (10a), (10b), and (10c) emphasize the behavior of the wave functions in different regions of space. It thus seems reasonable to expect that the type of wave function used in the present work represents a better approximation to the solution of the Schrödinger equation over a wider range of distances from the nucleus than do other possible forms of trial functions.

TABLE 4
COMPARISON OF OSCILLATOR-STRENGTH
CALCULATIONS FOR Li II

Transition	Coulomb Approximation*	Present Work
$3^1D-4^1F..$.. .	1.02	...
$f_{len}.....$.. .	..	1.005
$f_{vel}.....$.. .	...	1.015
$f_{acc}.....$.. .	...	0.976
$3^1D-5^1F..$.. .	0.158	...
$f_{len}.....$.. .	...	0.1604
$f_{vel}.....$.. .	...	0.1578
$f_{acc}.....$.. .	...	0.1591
$3^1D-6^1F..$.. .	0.0528	...
$f_{len}.....$.. .	...	0.05498
$f_{vel}.....$.. .	...	0.05445
$f_{acc}.....$.. .	...	0.05237
$3^3D-4^3F.....$.. .	1.01	...
$f_{len}.....$.. .	..	1.005
$f_{vel}.....$.. .	...	1.014
$f_{acc}.....$.. .	...	0.967
$3^3D-5^3F.....$.. .	0.158	...
$f_{len}.....$.. .	...	0.1603
$f_{vel}.....$.. .	...	0.1579
$f_{acc}.....$.. .	...	0.1596
$3^3D-6^3F.....$.. .	0.0530	...
$f_{len}.....$.. .	..	0.05503
$f_{vel}.....$.. .	...	0.05456
$f_{acc}.....$.. .	...	0.05266

* Wiese, Smith, and Glennon 1966.

All of the calculations reported here are nonrelativistic. It is clear from Table 2 that, for low Z , relativistic corrections are unimportant. For higher values of Z , for which such corrections become important, accurate nonrelativistic wave functions are needed as a starting point in the calculation of these corrections. Such a study is now in progress, and preliminary results indicate (Woosley 1968) that, in the present work, the largest error due to neglect of these effects is approximately 0.2 Å.

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TABLE 5
CALCULATED WAVELENGTHS AND ABSORPTION OSCILLATOR STRENGTHS
FOR THE SINGLET TRANSITIONS

Ion	3 ¹ D - 4 ¹ F				3 ¹ D - 5 ¹ F				3 ¹ D - 6 ¹ F			
	λ (Å)	f _{l_{en}}	f _{ve1}	f _{acc}	λ (Å)	f _{l_{en}}	f _{ve1}	f _{acc}	λ (Å)	f _{l_{en}}	f _{ve1}	f _{acc}
Be III	2081.3	1.011	1.015	.992	1423.1	.1600	.1570	.1566	1214.5	.05397	.05392	.05244
B IV	1172.2	1.014	1.016	1.000	800.70	.1588	.1566	.1558	683.39	.05366	.05385	.05274
C V	797.74	1.016	1.018	1.006	512.54	.1584	.1565	.1557	437.37	.05356	.05380	.05294
N VI	520.72	1.016	1.017	1.007	355.96	.1584	.1565	.1555	303.75	.05345	.05374	.05307
O VII	382.60	1.016	1.017	1.008	261.54	.1579	.1563	.1558	223.18	.05353	.05379	.05325
F VIII	292.95	1.017	1.018	1.010	200.24	.1576	.1564	.1561	170.87	.05351	.05378	.05324
Ne IX	231.47	1.017	1.018	1.011	158.22	.1585	.1565	.1558	135.02	.05344	.05375	.05336
Na X	187.49	1.017	1.018	1.012	128.16	.1575	.1560	.1555	109.36	.05347	.05377	.05345
Mg XI	154.95	1.017	1.018	1.012	105.92	.1580	.1565	.1560	90.38	.05348	.05377	.05340
Al XII	130.21	1.017	1.018	1.013	89.00	.1579	.1565	.1561	75.95	.05351	.05379	.05346
Si XIII	110.95	1.017	1.018	1.013	75.84	.1578	.1565	.1561	74.61	.05349	.05378	.05350
P XIV	95.66	1.017	1.018	1.013	65.39	.1577	.1565	.1561	55.80	.05350	.05379	.05354
S XV	83.33	1.017	1.018	1.013	56.96	.1576	.1565	.1562	48.61	.05351	.05379	.05357

TABLE 6
CALCULATED WAVELENGTHS AND ABSORPTION OSCILLATOR STRENGTHS
FOR THE TRIPLET TRANSITIONS

Ion	3 ³ D - 4 ³ F					3 ³ D - 5 ³ F				3 ³ D - 6 ³ F			
	λ (Å)	f _{10n}	f _{ve1}	f _{acc}		λ (Å)	f _{10n}	f _{ve1}	f _{acc}	λ (Å)	f _{10n}	f _{ve1}	f _{acc}
Be III	2077.8	1.008	1.013	.983		1421.4	.1604	.1574	.1557	1213.2	.05424	.05419	.05268
B IV	1169.1	1.013	1.016	.995		799.75	.1588	.1569	.1558	682.60	.05385	.05403	.05296
C V	748.47	1.014	1.015	.998		511.94	.1586	.1567	.1557	436.94	.05366	.05395	.05316
N VI	519.88	1.014	1.015	1.001		355.57	.1592	.1568	.1555	303.46	.05367	.05394	.05324
O VII	382.02	1.015	1.016	1.004		261.26	.1582	.1567	.1559	222.98	.05370	.05396	.05341
F VIII	292.52	1.015	1.016	1.005		200.05	.1579	.1567	.1560	170.73	.05370	.05395	.05340
Ne IX	231.16	1.016	1.016	1.006		158.07	.1576	.1567	.1561	134.91	.05369	.05394	.05350
Na X	187.25	1.016	1.016	1.008		128.05	.1576	.1567	.1562	109.28	.05368	.05393	.05359
Mg XI	154.77	1.015	1.016	1.009		105.83	.1585	.1567	.1560	90.32	.05359	.05389	.05352
Al XII	130.06	1.016	1.016	1.009		88.93	.1581	.1567	.1561	75.90	.05360	.05389	.05357
Si XIII	110.82	1.016	1.016	1.010		75.78	.1579	.1567	.1561	64.67	.05361	.05389	.05360
P XIV	95.56	1.016	1.016	1.011		65.34	.1578	.1567	.1561	55.76	.05361	.05390	.05364
S XV	83.25	1.016	1.017	1.011		56.92	.1578	.1567	.1562	48.58	.05362	.05390	.05367

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