

Cesium Oscillator Strengths*†

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Cesium oscillator strengths are calculated using one-electron wave functions. These functions are numerical solutions of the Schrödinger equation with a central, symmetric potential and with the spin-orbit term. The potential is chosen so that the binding energies of the lowest ten levels agree with spectroscopic values to 3%; the next 30 levels agree to better than 1%. The validity of the wave functions is demonstrated by comparison of experimental and calculated values of: (i) ratios and magnitudes of principal series oscillator strengths, (ii) fine structure splitting of the doublets, and (iii) hyperfine splitting of the ground state. Oscillator strengths are presented for over one hundred transitions in the visible and infrared. Experimental support for many of these oscillator strengths is given by line intensity measurements.

I. INTRODUCTION

SPECTROSCOPIC examination of the light emitted by a plasma coupled with knowledge of oscillator strengths for the transitions involved can yield valuable information about temperatures and densities of the plasma. Because cesium is often used in plasma experiments and because of the lack of experimental values, the oscillator strengths for cesium have been calculated for transitions in the optical and infrared region.

The necessary matrix elements are calculated from wave functions that are solutions of the one-electron Schrödinger equation with a central symmetric potential. The spin-orbit interaction is included to obtain the doublet structure. The potential accounts for the nucleus and closed shell electrons and has been chosen so that the binding energies of the lowest 40 levels agree well with experiment. The accuracy of the wave functions themselves is considered by comparison of pertinent calculated quantities with experiment, where possible. These quantities include values and ratios of principal series oscillator strengths, spin-orbit splitting of the doublets, and ground-state hyperfine splitting. A more qualitative check of the oscillator strengths is provided by a measurement of the intensity of lines. All calculations are numerical.

Section II shows the equations and notation used, Sec. III presents the potential and discusses how it was obtained, and Sec. IV deals with the accuracy of the wave functions and presents the oscillator strengths.

II. EQUATIONS

The doublet levels of cesium are well determined by the one-electron, nonrelativistic Schrödinger equation with the spin-orbit term. The radial part of this equation in atomic units is

$$[d^2F(x)/dx^2 - V(x) + l(l+1)/x^2 + H']F(x) = \lambda F(x), \quad (1)$$

with

$$H' = \frac{\alpha_0^2}{2e^2} \frac{1}{x} \frac{dV(x)}{dx} \mathbf{L} \cdot \mathbf{S}.$$

The position x is the radius in units of the first Bohr radius ($a_0 = 0.529 \text{ \AA}$) and λ is the binding energy in units of the ground-state energy of infinite mass hydrogen (-13.605 eV). In the expression for the spin-orbit interaction, H' , the coefficient α_0 is the fine-structure constant ($\approx 1/137$). The potential $V(x)$ is spherically symmetric and describes the nucleus and the closed electron shells of cesium. It is usual to write the potential as

$$V(x) = -Z(x)e^2/x.$$

Expressed this way, $Z(x)$ shows the departure of the potential from the hydrogen potential ($Z=1$). The wave function for a state is written

$$u_{nljm} = \sum_{m_l+m_s=m} \alpha_{m_s}^{ljm} Y_{lm_l}(\theta, \varphi) \frac{F_{nlj}(x)}{x} \xi_{m_s}, \quad (2)$$

where the α_{m_s} are constants and Y_{lm_l} are spherical harmonics. The ξ_{m_s} are two eigenstates of the Pauli spin matrices with eigenvalues $\pm 1/2$. The wave functions for all states of a given level (values of nlj) have the same radial part. If the spin-orbit term in Eq. (1) is negligibly small, then $F(x)$ is independent of j and all states of a given doublet (values of nl) have the same radial part. This, however, is not true for cesium.

The oscillator strength for a transition from an initial level A (numbers nlj) to a lower level A' (numbers $n'l'j'$) with energy difference $h\nu$ is defined as¹

$$f(A, A') = \frac{8\pi^2 m \nu}{3h e^2} \left(\frac{1}{2j'+1} \right) S(A, A'), \quad (3)$$

with

$$S(A, A') = \sum_{m, m'} |\langle u_{n'l'j'm'} | e r | u_{nljm} \rangle|^2. \quad (4)$$

In terms of the f number, the intensity of energy emitted

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¹ E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1957).

in the transition (erg/sec) is

$$I(A, A') = \frac{8\pi^2 e^2 \hbar \nu^3}{mc^3} \left(\frac{2j'+1}{2j+1} \right) N(A) f(A, A'), \quad (5)$$

where $N(A)$ is the number of atoms in the initial level.

When Eq. (2) is substituted into Eq. (4), the summation can be performed. The result can be written

$$S(A, A') = e^2 \sigma^2 (nlj, n'l'j') K(lj, l'j'). \quad (6)$$

The quantity σ^2 involves only the integral over the radial part of the wave function,

$$\sigma^2(A, A') = a_0^2 \int F_{A'}^\dagger(x) F_A(x) x dx,$$

while the summation and integration over the spin and angular parts is included in K . This last is a symmetric quantity, i.e.,

$$K(lj, l'j') = K(l'j', lj).$$

Values of K of interest here are²

$$\begin{aligned} K(S_{1/2}, P_{1/2}) &= 2/3, & K(P_{1/2}, D_{3/2}) &= 4/3, \\ K(S_{1/2}, P_{3/2}) &= 4/3, & K(D_{5/2}, F_{7/2}) &= 3.4286, \\ K(P_{3/2}, D_{5/2}) &= 2.40, & K(D_{5/2}, F_{5/2}) &= 0.17143, \\ K(P_{3/2}, D_{3/2}) &= 0.2667, & K(D_{3/2}, F_{5/2}) &= 2.40. \end{aligned}$$

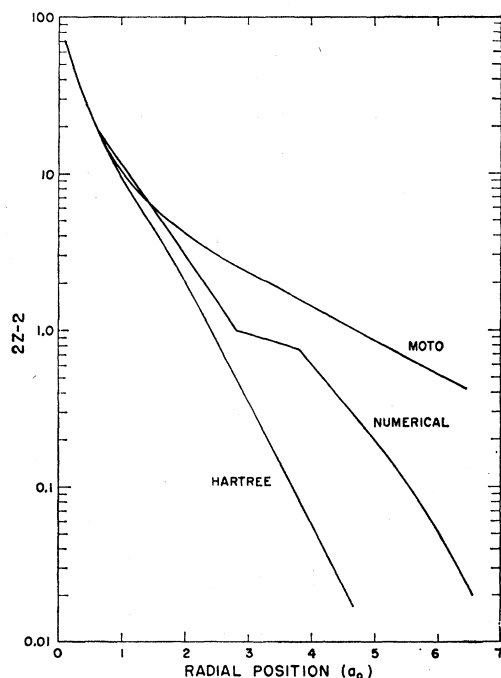


FIG. 1. The potential used here as compared with previous potentials. The quantity $Z(x)$ is an "effective charge" at the radial position x . For $x \geq 7.0$ all potentials have $2Z(x) - 2 = 0$. They agree precisely for $x \leq 0.5$ and become 108.0 at $x=0$.

² H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957), p. 273.

III. DETERMINATION OF $V(x)$

A potential must be chosen such that the binding energies obtained as solutions of Eq. (1) agree well with spectroscopic values.³ The associated eigenfunctions are then taken as the wave functions for the atoms.

For a given potential the wave functions and binding energies are obtained by numerical integration of Eq. (1) using standard and well-known techniques.⁴ These entail starting an inward integration from a very large radius and an outward integration from the origin and varying λ until the logarithmic derivatives of the two parts match at an intermediate point. A power-series solution is used for the starting values at the origin and the inward integration is begun at a sufficiently large radius that the wave function is decaying exponentially. Care must be taken to use the relativistic form of the spin-orbit interaction⁵ when developing the power series near the origin. The spin-orbit expression associated with Eq. (1) is nonrelativistic and is not valid at small radii. It becomes valid for cesium at $x \geq 0.002$.

The Hartree self-consistent field potential⁶ for Cs^+ was used as a first trial for the potential. The binding energies so obtained for the lower levels were small by approximately 30%, except those for $l=3$. These were accurate to better than 1%. These levels are very nearly hydrogenic, implying that their wave functions do not penetrate the cesium ion core. The accurate calculation of their energies implies that the Hartree potential is about the right size [$Z(x)=1$ at the proper radius].

Another potential has been obtained for cesium by Moto.⁷ He found a potential that gives reasonable values for the binding energies when the Schrödinger equation is solved in the WKB approximation. When this potential is used and the equation solved numerically, the binding energies are found to be high by about 50%. Moto's and Hartree's potential are the same at small radii, indicating that the inner core electrons are insensitive to the state of the valence electron.

A more satisfactory potential would be one that falls between the Hartree and Moto potentials. It would agree with them at small radii ($x \leq 0.50$) and become hydrogenic ($Z=1$) at the same radius as Hartree's ($x=7.0$). A plot of $\log(2Z-2)$ vs x is shown in Fig. 1. Both the Hartree and Moto potentials become almost linear at $x > 2.0$. The first attempts at an improved potential were ones that also dropped linearly in this

³ C. E. Moore, *Atomic Energy Levels as Derived from the Analyses of Optical Spectra*, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D.C., 1949).

⁴ D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).

⁵ See reference 2.

⁶ D. R. Hartree, *Proc. Roy. Soc. 143*, 506 (1934).

⁷ T. Moto, *Proc. Phys.-Math. Soc. Japan 12*, 93 (1930).

TABLE I. Comparison of calculated and experimental binding energies of cesium.

Level	λ (eV)		Error (%)	Level	λ (eV)		Error (%)
	Calculated	Spectroscopic			Calculated	Spectroscopic	
6S _{1/2}	0.28430	0.28636	-0.72	5D _{3/2}	0.15861	0.15415	+2.89
7S _{1/2}	0.11617	0.11736	-1.01	5D _{5/2}	0.15633	0.15326	+2.00
8S _{1/2}	0.06412	0.064640	-0.80				
9S _{1/2}	0.04072	0.040993	-0.67	6D _{3/2}	0.08094	0.080398	+0.67
10S _{1/2}	0.02853	0.028323	+0.73	6D _{5/2}	0.08031	0.080006	+0.38
11S _{1/2}	0.020636	0.020758	-0.59				
12S _{1/2}	0.015773	0.015871	-0.62	7D _{3/2}	0.04896	0.048860	+0.20
				7D _{5/2}	0.04868	0.048669	+0.03
6P _{1/2}	0.18675	0.18444	+1.25				
6P _{3/2}	0.17811	0.17938	-0.71	8D _{3/2}	0.03281	0.032782	+0.08
				8D _{5/2}	0.03267	0.032676	-0.02
7P _{1/2}	0.08904	0.087904	+1.29				
7P _{3/2}	0.08638	0.086253	+0.15	9D _{3/2}	0.02350	0.023494	+0.03
				9D _{5/2}	0.02341	0.023438	-0.12
8P _{1/2}	0.05250	0.051948	+1.06				
8P _{3/2}	0.051315	0.051194	+0.23	10D _{3/2}	0.01766	0.017672	-0.07
				10D _{5/2}	0.01761	0.017629	-0.11
9P _{1/2}	0.034680	0.034368	+0.91				
9P _{3/2}	0.034052	0.033961	+0.27	11D _{3/2}	0.01376	0.013768	-0.06
				11D _{5/2}	0.01372	0.013739	-0.14
10P _{1/2}	0.024610	0.024432	+0.73				
10P _{3/2}	0.024237	0.024187	+0.21	12D _{3/2}	0.011024	0.011030	-0.05
				12D _{5/2}	0.010996	0.011008	-0.11
11P _{1/2}	0.018380	0.018263	+0.65				
11P _{3/2}	0.018135	0.018104	+0.17	4F	0.062817	0.063225	-0.65
				5F	0.040270	0.040439	-0.42
12P _{1/2}	0.014250	0.014168	+0.58	6F	0.028066	0.028055	+0.04
12P _{3/2}	0.014089	0.014059	+0.21				

region but at various rates between the limits of Hartree and Moto.

For each trial potential the ground state (6s) and lowest $l=1$ (6p) and $l=2$ (5d) states were calculated. No single potential with $\log(2Z-2)$ falling linearly gave acceptable values for the binding energy of all three states. But it became clear that the charge distributions ($F^\dagger F x^2$) for the 6s and 6p state always peaked at $x > 4.50$, and for the 5d state it peaked at $x < 3.50$. A potential giving good binding energies for the 6s and 6p states was poor for the 5d state and vice versa. A relatively abrupt change in the potential at $x \approx 4.00$ might give all three with sufficient accuracy. In this way the potential marked "numerical" in Fig. 1 was determined. This potential gives accurate binding energies for the 40 lowest levels as indicated in Table I. Table II gives the values of $2Z(x)$ for the potential.

All calculations were done on an IBM 704 computer. The machine was programmed to try combinations of one, two, and then three exponential decay rates for $Z(x)-1$. The 6s, 6p, and 5d levels were calculated first and then higher levels if the first set agreed with experiment to within preset limits. The computer made simple interpolations to obtain the next potential. The final potential was determined by an evaluation of the computer results. The computer itself did not obtain a wholly satisfactory potential.

The irregular change in the potential is a reflection of the different penetrations of the various orbits. In particular, the lowest $l=2$ level penetrates considerably

TABLE II. Cesium potential. The position x is in units of Bohr radii.

x	$2Z(x)$	x	$2Z(x)$	x	$2Z(x)$
0.000	110.00	0.20	51.29	1.3	9.60
0.002	108.71	0.22	48.41	1.4	8.70
0.004	107.44	0.24	45.79	1.5	7.80
0.006	106.20	0.26	43.44	1.6	7.10
0.008	105.00	0.28	41.31	1.8	5.87
0.010	103.83	0.30	39.39	2.0	4.96
0.015	101.09	0.32	37.64	2.2	4.27
0.020	98.56	0.34	36.03	2.4	3.73
0.025	96.21	0.36	34.55	2.6	3.30
0.030	94.00	0.38	33.17	2.8	3.00
0.035	91.89	0.40	31.87	3.0	2.94
0.040	89.87	0.45	28.89	3.2	2.89
0.05	86.05	0.50	26.21	3.4	2.85
0.06	82.51	0.55	23.79	3.6	2.80
0.07	79.22	0.60	21.60	3.8	2.76
0.08	76.17	0.65	20.20	4.0	2.60
0.09	73.35	0.70	19.30	4.5	2.34
0.10	70.73	0.75	18.00	5.0	2.18
0.11	68.29	0.80	17.10	5.5	2.10
0.12	65.99	0.90	15.20	6.0	2.05
0.14	61.78	1.0	13.70	6.5	2.02
0.16	57.96	1.1	12.10	7.0	2.00
0.18	54.47	1.2	10.75	>7.0	2.00

This is consistent with its principal quantum number of 5 while the ground state has $n=6$.

IV. RESULTS AND ACCURACY

An accurate calculation of the binding energy of a state does not imply a similar accuracy in the wave function. In fact, the wave function error may be

considerable. A test on the wave functions is a comparison of calculated and experimental oscillator strengths. Table III shows such a comparison for the principal series of cesium, the only series for which experimental values⁸⁻¹¹ are available. The agreement is not unreasonable when the wide differences in the experimental results are considered.

Equations (3) and (4) show that the oscillator strength is dependent primarily on the wave functions at large radii. The wave functions are expected intuitively to be good at such radii because the potential has become hydrogenic. The difference in the oscillator strengths of transitions from the two levels of a doublet to the same final level is a test of the wave functions at small radii, because it is there that the spin-orbit interaction is large. Table III shows such ratios for the principal series and compares with experiment. A ratio of two comes about from the K 's, i.e.,

$$K(1\frac{3}{2}, 0\frac{1}{2})/K(1\frac{1}{2}, 0\frac{1}{2}) = 2,$$

while anything over 2 is due to differences in σ^2 . The continued increase of the calculated ratios has been

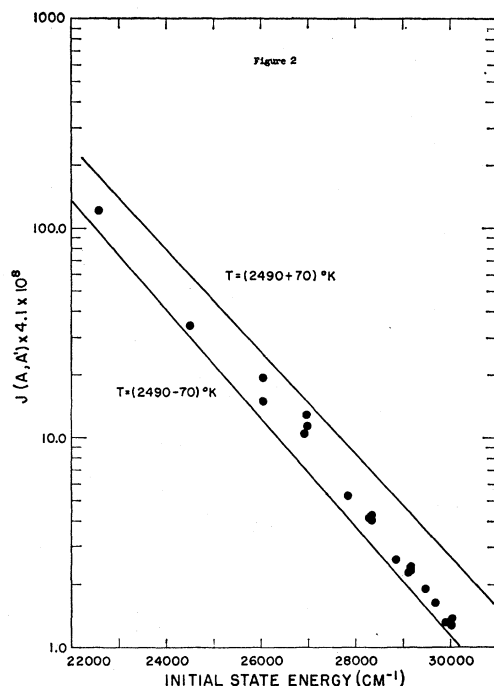


FIG. 2. Values of $J(A, A')$ for transitions in the sharp, diffuse, and fundamental series. The $J(A, A')$ are determined from measured values of the intensity (erg/sec per cm^3 of plasma for 4π steradians) and calculated values of the oscillator strength. The solid lines enclose the region determined by the radiative recombination temperature $T = 2490 \pm 70^\circ\text{K}$. The cathode temperature of the cell was $2470 \pm 40^\circ\text{K}$.

⁸ S. A. Korff and G. Breit, *Revs. Modern Phys.* **4**, 471 (1932).

⁹ G. Kvater and T. Meister, *Leningrad. Univ. Vestnik* No. 9, 137 (1952).

¹⁰ S. Sambursky, *Z. Physik* **49**, 731 (1938).

¹¹ H. White, *Introduction to Atomic Spectra* (McGraw-Hill Book Company, Inc., 1934), 1st ed., p. 119.

observed qualitatively by Kratz.¹² The reasonable values calculated for this ratio imply that the p -state wave functions behave properly at low radii.

The ground-state wave functions at small radii can be tested by a calculation of the hyperfine splitting of the state. It is assumed that all the splitting comes from the valence electron. The equations are¹³

$$\begin{aligned}\delta E &= \frac{1}{2}a(2I+1), \\ a &= \frac{4}{3}M_0(M_I/I)|R(0)|^2/(2\rho^2-\rho), \\ \rho &= (1-\alpha^2)^{1/2}, \\ \alpha &= Ze^2/\hbar c,\end{aligned}$$

where I is the nuclear spin, M_I is the magnetic moment of the nucleus, M_0 is the Bohr magneton, $R(0)$ is the radial part of the wave function at the nucleus, and δE is the hyperfine splitting. For cesium¹⁴

$$\begin{aligned}I &= 7/2, \\ M_I &= 1.303 \times 10^{-23} \text{ erg/G}, \\ M_0 &= 0.927 \times 10^{-20} \text{ erg/G}, \\ Z &= 55, \\ \rho &= 0.916, \\ R(0) &= 1.65 \times 10^{-11},\end{aligned}$$

giving

$$\begin{aligned}a &= 1.61 \times 10^{-17} \text{ erg}, \\ \delta E &= 6.44 \times 10^{-17} \text{ erg}.\end{aligned}$$

This splitting is 6.6% higher than the experimental value¹⁴ of 6.04×10^{-17} . If all the other quantities are correct, it indicates an error in the absolute value of the wave function at the origin of only 2.6%.

An approximate check on the accuracy of oscillator strengths for any series can be obtained by a measurement of the intensity of the lines. For a plasma in thermodynamic equilibrium at temperature T , the number of atoms in energy state E_A is

$$N(A) = (2j+1) \exp(-E_A/kT).$$

Equation (5) then gives

$$\log J(A, A') = \text{const} + (-E_A/kT),$$

with

$$J(A, A') = \frac{I(A, A')(c/\nu)^3}{(2j'+1)f(A, A')}.$$

Agnew¹⁵ has made measurements of $I(A, A')$ from a hot-cathode, low-voltage cesium discharge. From radiative recombination measurements, he places the electron temperature at $2490 \pm 70^\circ\text{K}$. Figure 2 shows values of $J(A, A')$ using the calculated oscillator strengths vs E_A . Lines of the sharp, diffuse, and fundamental series

¹² H. Kratz, *Phys. Rev.* **75**, 1844 (1949).

¹³ G. Breit, *Phys. Rev.* **35**, 1447 (1930).

¹⁴ N. Ramsey, *Nuclear Moments* (John Wiley & Sons, Inc., New York, 1953).

¹⁵ L. Agnew (to be published).

TABLE III. Comparison of calculated principal series oscillator strength f with experiment. The ratio for the doublet is R .

Initial state	Calculated		Korff and Breit ^a		Kvater and Meister ^b		Sambursky ^c
	f	R^d	f	R	f	R	
$6P_{3/2}$	0.814	2.06	0.66	2.06	0.796	2.03	2.0
$6P_{1/2}$	0.394		0.32		0.392		
$7P_{3/2}$	1.74×10^{-2}	6.12	1.15×10^{-2}	3.3-4.3	1.29×10^{-2}	4.29	5.0
$7P_{1/2}$	2.84×10^{-3}		2.69×10^{-3}		3.00×10^{-3}		
$8P_{3/2}$	3.49×10^{-3}	11.10	3.83×10^{-3}	4.7	2.74×10^{-3}	8.0	10.0
$8P_{1/2}$	3.17×10^{-4}				3.42×10^{-4}		
$9P_{3/2}$	1.25×10^{-3}	17.24	2.3×10^{-5}	...	7.66×10^{-4}	8.1	15.0
$9P_{1/2}$	7.25×10^{-5}				9.43×10^{-5}		
$10P_{3/2}$	6.2×10^{-4}	21.45	1.79×10^{-5}	...	4.17×10^{-4}	8.1	25.0
$10P_{1/2}$	2.89×10^{-5}				5.14×10^{-5}		
$11P_{3/2}$	3.56×10^{-4}	28.7	1.41×10^{-5}	...	2.27×10^{-4}	8.0	15.8
$11P_{1/2}$	1.24×10^{-5}				2.85×10^{-5}		
$12P_{3/2}$	2.08×10^{-4}	33.5	1.02×10^{-5}	...	1.58×10^{-4}	...	5.7
$12P_{1/2}$	6.2×10^{-6}						

^a Reference (8).^b Reference (9).^c References (10) and (11).^d The continual increase of the ratio, R , has been observed by Kratz (reference 12).

TABLE IV. Cesium oscillator strengths.

Transition (A,B)	$f(A,B)$	Transition (A,B)	$f(A,B)$	Transition (A,B)	$f(A,B)$
$7S_{1/2}, 6P_{3/2}$	0.208	$11S_{1/2}, 7P_{3/2}$	0.00455	$11P_{3/2}, 5D_{5/2}$	0.01842
$7S_{1/2}, 6P_{1/2}$	0.171	$11S_{1/2}, 7P_{1/2}$	0.00501	$5D_{3/2}, 6P_{1/2}$	0.2509
$8S_{1/2}, 6P_{3/2}$	0.0204	$12S_{1/2}, 7P_{3/2}$	0.00259	$6D_{5/2}, 6P_{3/2}$	0.3322
$8S_{1/2}, 6P_{1/2}$	0.0202	$12S_{1/2}, 7P_{1/2}$	0.00287	$6D_{3/2}, 6P_{3/2}$	0.0397
$9S_{1/2}, 6P_{3/2}$	0.00687	$13S_{1/2}, 7P_{3/2}$	0.001643	$6D_{3/2}, 6P_{1/2}$	0.2980
$9S_{1/2}, 6P_{1/2}$	0.00702	$13S_{1/2}, 7P_{1/2}$	0.001829	$7D_{5/2}, 6P_{3/2}$	0.0951
$10S_{1/2}, 6P_{3/2}$	0.00299	$14S_{1/2}, 7P_{3/2}$	0.001128	$7D_{3/2}, 6P_{3/2}$	0.0110
$10S_{1/2}, 6P_{1/2}$	0.00326	$14S_{1/2}, 7P_{1/2}$	0.001257	$7D_{3/2}, 6P_{1/2}$	0.0927
$11S_{1/2}, 6P_{3/2}$	0.00186			$8D_{5/2}, 6P_{3/2}$	0.0418
$11S_{1/2}, 6P_{1/2}$	0.00193	$7P_{3/2}, 7S_{1/2}$	1.115	$8D_{3/2}, 6P_{3/2}$	0.0048
$12S_{1/2}, 6P_{3/2}$	0.00117	$7P_{1/2}, 7S_{1/2}$	0.556	$8D_{3/2}, 6P_{1/2}$	0.0419
$12S_{1/2}, 6P_{1/2}$	0.00122	$8P_{3/2}, 7S_{1/2}$	0.02558	$9D_{5/2}, 6P_{3/2}$	0.0223
$13S_{1/2}, 6P_{3/2}$	0.00078	$8P_{1/2}, 7S_{1/2}$	0.00516	$9D_{3/2}, 6P_{3/2}$	0.0025
$13S_{1/2}, 6P_{1/2}$	0.00082	$9P_{3/2}, 7S_{1/2}$	0.00502	$9D_{3/2}, 6P_{1/2}$	0.0228
$14S_{1/2}, 6P_{3/2}$	0.00056	$9P_{1/2}, 7S_{1/2}$	0.00062	$10D_{5/2}, 6P_{3/2}$	0.0135
$14S_{1/2}, 6P_{1/2}$	0.00059	$10P_{3/2}, 7S_{1/2}$	0.00187	$10D_{3/2}, 6P_{3/2}$	0.0015
		$10P_{1/2}, 7S_{1/2}$	0.00017	$10D_{3/2}, 6P_{1/2}$	0.0139
$8S_{1/2}, 7P_{3/2}$	0.333	$11P_{3/2}, 7S_{1/2}$	0.000911	$11D_{5/2}, 6P_{3/2}$	0.0088
$8S_{1/2}, 7P_{1/2}$	0.297	$11P_{1/2}, 7S_{1/2}$	0.000062	$11D_{3/2}, 6P_{3/2}$	0.0010
$9S_{1/2}, 7P_{3/2}$	0.0256	$12P_{3/2}, 7S_{1/2}$	0.000486	$11D_{3/2}, 6P_{1/2}$	0.0092
$9S_{1/2}, 7P_{1/2}$	0.0305	$12P_{1/2}, 7S_{1/2}$	0.000027		
$10S_{1/2}, 7P_{3/2}$	0.00842			$6D_{5/2}, 7P_{3/2}$	0.309
$10S_{1/2}, 7P_{1/2}$	0.00964	$5D_{5/2}, 6P_{3/2}$	0.2042	$6D_{3/2}, 7P_{3/2}$	0.032
$7D_{5/2}, 7P_{3/2}$	0.282	$5D_{3/2}, 6P_{3/2}$	0.0211	$6D_{3/2}, 7P_{1/2}$	0.327
$7D_{3/2}, 7P_{3/2}$	0.034	$7P_{1/2}, 5D_{3/2}$	0.6516	$4F, 5D_{5/2}$	0.3244
$7D_{3/2}, 7P_{1/2}$	0.237	$7P_{3/2}, 5D_{3/2}$	0.208	$4F, 5D_{3/2}$	0.3022
$8D_{5/2}, 7P_{3/2}$	0.089	$7P_{3/2}, 5D_{5/2}$	1.533	$5F, 5D_{5/2}$	0.1272
$8D_{3/2}, 7P_{3/2}$	0.0105	$8P_{1/2}, 5D_{3/2}$	0.0915	$5F, 5D_{3/2}$	0.1215
$8D_{3/2}, 7P_{1/2}$	0.0822	$8P_{3/2}, 5D_{3/2}$	0.0299	$6F, 5D_{5/2}$	0.0650
$9D_{5/2}, 7P_{3/2}$	0.0410	$8P_{3/2}, 5D_{5/2}$	0.2185	$6F, 5D_{3/2}$	0.0627
$9D_{3/2}, 7P_{3/2}$	0.0047	$9P_{1/2}, 5D_{3/2}$	0.0309	$7F, 5D_{5/2}$	0.0383
$9D_{3/2}, 7P_{1/2}$	0.0391	$9P_{3/2}, 5D_{3/2}$	0.0100	$7F, 5D_{3/2}$	0.0373
$10D_{5/2}, 7P_{3/2}$	0.0228	$9P_{3/2}, 5D_{5/2}$	0.0733	$8F, 5D_{5/2}$	0.0241
$10D_{3/2}, 7P_{3/2}$	0.0026	$10P_{1/2}, 5D_{3/2}$	0.0143	$8F, 5D_{3/2}$	0.0235
$10D_{3/2}, 7P_{1/2}$	0.0221	$10P_{3/2}, 5D_{3/2}$	0.0045	$9F, 5D_{5/2}$	0.0164
$11D_{5/2}, 7P_{3/2}$	0.0142	$10P_{3/2}, 5D_{5/2}$	0.0335	$9F, 5D_{3/2}$	0.0160
$11D_{3/2}, 7P_{3/2}$	0.0016	$11P_{1/2}, 5D_{3/2}$	0.00798	$10F, 5D_{5/2}$	0.0115
$11D_{3/2}, 7P_{1/2}$	0.0139	$11P_{3/2}, 5D_{3/2}$	0.00248	$10F, 5D_{3/2}$	0.0114

TABLE V. Comparison with the Coulomb approximation of Bates and Damgaard.^a

Transition	Calculated oscillator strengths	
	Present work	Coulomb approximation
$6P_{1/2}, 6S_{1/2}$	0.394	0.348
$6P_{3/2}, 6S_{1/2}$	0.814	0.750
$7P_{1/2}, 6S_{1/2}$	0.00284	0.00671
$7P_{3/2}, 6S_{1/2}$	0.0174	0.0174
$8P_{1/2}, 6S_{1/2}$	0.000317	0.00134
$8P_{3/2}, 6S_{1/2}$	0.00349	0.0046
$6D_{5/2}, 6P_{3/2}$	0.332	0.298
$6D_{3/2}, 6P_{3/2}$	0.0397	0.0351
$6D_{3/2}, 6P_{1/2}$	0.298	0.284
$7D_{5/2}, 6P_{3/2}$	0.0951	0.0880
$7D_{3/2}, 6P_{3/2}$	0.0110	0.0102
$7D_{3/2}, 6P_{1/2}$	0.0927	0.109
$8D_{5/2}, 6P_{3/2}$	0.0418	0.0405
$8D_{3/2}, 6P_{3/2}$	0.0048	0.0045
$8D_{3/2}, 6P_{1/2}$	0.0419	0.0419

^a See reference 17.

are included. Ideally, the values would fall on a straight line of slope $(kT)^{-1}$. The deviation from any straight line is due to errors in $f(A, A')$ and experimental uncertainties in the measurement of $I(A, A')$. The values do, however, all fall within the region specified by the radiative recombination temperature, indicated by the solid lines on the plot. This implies that the calculated oscillator strengths are accurate to better than 50%. Table IV presents the calculated oscillator strengths.

The quadratic Stark shift of the $7P$ levels has been measured¹⁶ and provides a further check of the $7P$

wave functions. In an electric field of 100 kV/cm the shifts are 1.17 cm^{-1} and 1.49 cm^{-1} for the $7P_{1/2}$ and $7P_{3/2}$ levels. The corresponding values calculated from the wave functions obtained here are 1.18 and 1.51. This good agreement is further evidence of the validity of the wave functions at larger radii.

A common procedure for calculating oscillator strengths is the Coulomb approximation of Bates and Damgaard.¹⁷ It is expected that this method would give quite accurate values for an alkali metal and it is worthwhile to compare the results of such a calculation with values obtained here. Table V shows such a comparison for the lower transitions of the principal and diffuse series. The Coulomb approximation agrees well in the diffuse series but differs considerably for the $nP_{1/2} \rightarrow 6S_{1/2}$ transitions. This is because the Coulomb wave functions do not include the effects of the spin-orbit interaction correctly, and these effects are most significant for the P levels.

Finally, since the wave functions used here are eigenfunctions of an Hermitian operator, they are orthogonal and the usual sum rules apply.

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¹⁶ Y. T. Tao, *Z. Physik* **77**, 307 (1932).¹⁷ D. R. Bates and A. Damgaard, *Phil. Trans. Roy. Soc. London* **A242**, 101 (1949).