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Photoabsorption by Cesium*

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Oscillator strengths and the photoionization cross section for the ground state of cesium are computed using a semiempirical model potential involving two adjustable parameters and based only on the lowest few spectroscopic term values. The spin-orbit interaction is included in the model potential, and the effects of core polarization are explicitly taken into account in both the model potential and the dipole transition matrix element. The doublet-line-strength ratios for discrete transitions are in good agreement with Agnew's measured values, and no support is given other indications that the line strength for $6s\,1/2$-$np\,1/2$ is vanishingly small somewhere in the region $n = 10$–15. Good agreement with two recent measurements of the spin-orbit effect in photoionization is also obtained. The oscillator strengths and photoionization cross section are significantly lower than the measured values of Agnew, and Marr and Creek, respectively, but the total atomic polarizability is in excellent agreement with a recent measurement.

I. INTRODUCTION

Photoabsorption by the heavy alkali metals is strongly influenced by the spin-orbit effect. Fermi pointed out that it is the cause of the anomalously high doublet-line-strength ratios for the discrete principal-series transitions,[1] and Seaton showed that it also explains the nonzero minima observed in the photoionization cross sections.[2] More recently, Fano suggested that the effect could be used to produce beams of highly polarized electrons by photoionization, using circularly polarized light.[3(a)]

Electric dipole transitions in the heavy alkali metals are also influenced by core polarization, i.e., the dipole moment induced in the core by the valence electron.[4] This has been shown to reduce the oscillator strengths for the resonance transitions by a small, but non-negligible amount,[5(a)] and to have an increasingly large effect on higher discrete transitions and the photoionization cross section.[5(b)–7]

Both of these effects are most pronounced in cesium. The earliest observations of the anomalous doublet-line-strength ratios and nonzero minimum in the photoionization cross section are probably those of Sambursky,[8] and Mohler and Boeckner,[9] respectively. The Fano effect mentioned above has been studied experimentally very recently.[10,11]

Several theoretical studies have contributed to increased understanding of these effects. Stone[12] developed a numerical, semiempirical model potential which included the spin-orbit interaction explicitly. The resulting potential therefore incorporated the core-polarization contribution to the valence-electron Hamiltonian impicitly as well, but the effect of core polarization in the dipole matrix element was not included. The doublet-line-strength ratios obtained for the principal series were in good qualitative agreement with experiment, increasing continuously along the series.

Hameed *et al.*[5(a)] used Hartree–Fock wave functions (neglecting the spin-orbit interaction and core polarization in the valence-electron Hamiltonian) to study the effect of core polarization in the dipole matrix element for the resonance transition in the alkali metals. Agreement with experiment was significantly improved, particularly for cesium.

Beigman *et al.*[6] used a semiempirical model potential incorporating core polarization explicitly and allowing for fine structure. A consistent core-polarization correction was incorporated in the dipole matrix element. By allowing the dipole polarizability of the core to be one of two free parameters, and fitting to the experimental values of the second principal-series oscillator strengths as well as spectroscopic term values, good quantitative agreement with other measured quantities was obtained.

Weisheit[7] also used a semiempirical model potential, which was based on the Hartree–Fock core potential with corrections for core polarization and the spin-orbit interaction. In addition to two adjustable parameters accounting for short-range effects (exchange, etc.), the quadrupole polarizability of the core and the effective nuclear charge Z_{eff} in a spin-orbit potential of the form Z_{eff}/r^3 were treated as free parameters in fitting to spectroscopic term values. The correction for core polarization in the dipole matrix element was determined by an additional fit to precise experimental data for photoionization.

Calculations have recently been performed by Chang and Kelly using relativistic Hartree–Fock equations, thereby taking the spin-orbit interaction automatically into account.[13] The results clearly demonstrate that more is required than a careful treatment of the spin-orbit interaction, i.e., electron correlations such as the core polarization effect must be included.

These studies, in particular Refs. 6 and 7, demonstrate convincingly that the experimental photoabsorption observations can be explained with a reasonable theoretical treatment of core-polarization effects and the spin-orbit interaction. These calculations rely, however, on normalization to some of the experimental photoabsorption data. It is not certain, therefore, that such semiempirical models can provide reliable results in other cases for which such data are not available or are of poor quality.

The present work, also based on a semiempirical model potential, is an attempt to deal with this question. It is an improvement on previous calculations in several respects: (i) The core dipole (including dynamical effects) and quadrupole contributions to the valence-electron Hamiltonian are included and constrained to have asymptotic forms consistent with the best available data; (ii) the standard form of the spin-orbit potential is used, including an additional relativistic correction; (iii) no experimental data other than spectroscopic term values of the few lowest states are used in the calculations; and (iv) the core-polarization correction to the dipole matrix element, including a new second-order term, is accomplished in a manner consistent with that in the model potential.

II. MODEL POTENTIAL

The wave equation for the radial part of the outer electron wave function is taken to be

$$\left(\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}+V(r)+V_{\mathrm{so}}(r)+\epsilon_{nlj}\right)P_{nlj}(r)=0\ , \tag{1}$$

where $V(r)$ is composed of two terms,

$$V(r)=V(\lambda,r)+V_p(r)\ ; \tag{2}$$

$V_{\mathrm{so}}(r)$ is the spin-orbit potential and ϵ_{nlj} is the energy (in rydbergs) of the outer electron (bound or free).

The potential $V(\lambda, r)$ is the scaled Thomas–Fermi statistical model potential[14] with limiting forms

$$V(\lambda,r)_{r\widetilde{\rightarrow}0}\,2Z/r\ ,\quad V(\lambda,r)_{r\widetilde{\rightarrow}\infty}\,2/r\ , \tag{3}$$

where Z is the nuclear charge and λ is a scaling parameter, of order unity, which enters at intermediate values of r. The polarization potential $V_p(r)$ represents the effect of induced core moments on the outer electron, and is taken to be

$$V_p(r)=\frac{\alpha_d}{r^4}\left(1-e^{-(r/r_c)^6}\right)+\frac{\alpha_q-3\beta a_0}{r^6}\left(1-e^{-(r/r_c)^{10}}\right)\ , \tag{4}$$

where α_d and α_q are the dipole and quadrupole core polarizabilities, respectively, and the term in β (a_0 is the Bohr radius) is a dynamical correction to the α_d term to allow for the fact that the core dipole does not respond instantaneously to the motion of the outer electron.

Since $V_p(r)$ is expected to be a significant contribution to $V(r)$ only well outside the core, (4) is written as the product of the limiting forms[15] for large r and cutoff functions chosen to be unity at $r=\infty$ and to have the appropriate dependence on r for small r. Other forms of these functions could be adopted; for example, the form $(r^2+r_c^2)^{-2}$ is often used in the dipole term. This would be inappropriate in the present context, however, as it would introduce an additional r^{-6} term for large r. The parameter r_c is a cutoff radius, of the order of the core radius, to be determined along with the scale parameter λ in $V(\lambda, r)$ by fitting to observed term values. These are the only free parameters in the present calculation.

The spin-orbit potential is

$$V_{\mathrm{so}}(r)=\tfrac{1}{2}\alpha^2\frac{1}{r}\frac{dV}{dr}\left[1+\tfrac{1}{4}\alpha^2V(r)\right]^{-2}\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}\ , \tag{5}$$

where α is the fine-structure constant. The derivative in (5) is obtained by numerical differentiation of (2).

The term in brackets in (5) is an additional relativistic correction[16] which gives the proper behavior to the spin-orbit potential near the origin. This correction is safely neglected in perturbation calculations of the fine-structure splittings because the behavior of the unperturbed wave functions near the origin, $O(r^{l+1})$, prevents divergent integrals. In (1), however, the uncorrected potential is $\sim 2Z/r$ at $r \sim 0.005a_0$, and the correction becomes significant for cesium ($\sim 10\%$) at $r \sim 0.015a_0$, thereby strongly affecting the power-series development of $P_{nlj}(r)$ near the origin required for numerical integration of (1). In this respect the present treatment of the spin-orbit interaction differs from that of either Beigman *et al.*[6] or Weisheit.[7] The former did not include the spin-orbit potential explicitly but rather did the equivalent of using λ_j in $V(\lambda, r)$. The latter used an *ad hoc* potential of the form Z_{eff}/r^3, with Z_{eff} chosen to give the best agreement with observed doublet splittings for the principal series.

The polarizabilities used in (4) are from calculations by Heinrichs,[17] $\alpha_d = 19.03a_0^3$, and by Sternheimer,[18] $\alpha_q = 118.26a_0^5$. The dynamical constant β is not known for cesium, so the upper limit $\beta = \alpha_d/\Delta E_c = 19.18a_0^4$ was adopted,[15] where ΔE_c is the excitation energy (in rydbergs) of the lowest core state which contributes to α_d. No quadrupole or dynamical contribution was included in the potential of Beigman *et al.*[6] Weisheit[7] adopted the value $581.6a_0^5$ for the coefficient of the $1/r^6$ potential, compared with the value $60.71a_0^5$ in the present work.

With the potential as defined by (2)–(5), the wave equation (1) was solved with various values of λ and r_c until good agreement was obtained with spectroscopic values of ϵ_{6pj}, $j=\frac{1}{2}$ and $\frac{3}{2}$. This technique allowed a precise and unique determination of the two free parameters with reference to a single multiplet.

The potential so obtained did not give completely satisfactory term values for the s states. We therefore proceeded to hold λ fixed and varied r_c until the correct term value for the 6s state was obtained. This approach does not introduce any lack of orthogonality providing the parameters are fixed for a given value of l, and is consistent with the effect of "core relaxation" obtained in Hartree–Fock calculations. There is, in fact, no *a priori* reason why the effective radius of the core, represented by r_c, should not be a function of the angular momentum of the outer electron.[15] The alternate procedure of holding r_c fixed and varying λ for the 6s state was also carried out. This gave considerably larger errors for the term values of higher s states, often by orders of magnitude.

The results of the first procedure (λ_c fixed, r_c varied) were therefore adopted, both because of the better agreement with the measured s-state term values and because this is more consistent with the present treatment of the non-spherically-symmetric components of the core–valence-electron interaction, i.e., the multipole interactions, as perturbations to $V(\lambda, r)$. The potential parameters λ and $r_c^{(l)}$ adopted are given in Table I, along with calculated and experimental term values for the lowest few states.

The results for the s states were checked by comparison of calculated and experimental values for the hyperfine splitting. The formula used is[21]

$$\Delta\nu=\tfrac{8}{3}\pi\,\mu_B\,\mu\,\frac{2I+1}{I}\,|\psi(0)|^2F_r(1-\delta)(1-\epsilon)\ , \qquad (6)$$

where the three terms on the right-hand side are a correction to the regular Fermi expression to account for relativistic effects, and electrostatic and magnetic volume corrections. μ_B and μ are, respectively, the Bohr magneton and nuclear magnetic moment, I is the nuclear spin, and $\psi(0)$ is the wave function at the origin. The values of μ and the correction factors F_r, δ, and ϵ were taken from Ref. 21. Improved calculations of some of these corrections have been made.[22] The results are compared with experiment in Table II.

TABLE I. Calculated (a) (free parameters in the model potential are $\lambda=1.07927$, $r_c^{(0)}=3.333$, $r_c^{(1)}=4.132$) and spectroscopic (b) (experimental data are from Refs. 19 and 20, with the series limit of Ref. 19 used in all cases), term values for cesium, in rydbergs.

lj/n	6	7	8	9	
0 $\frac{1}{2}$	−0.286205	−0.117312	−0.064610	−0.040972	(a)
	−0.286198	−0.117289	−0.064603	−0.040969	(b)
1 $\frac{1}{2}$	−0.184335	−0.087792	−0.051886	−0.034331	(a)
	−0.184334	−0.087854	−0.051918	−0.034347	(b)
1 $\frac{3}{2}$	−0.179286	−0.086186	−0.051159	−0.033939	(a)
	−0.179285	−0.086204	−0.051165	−0.033940	(b)

TABLE II. Values of cesium wave functions at the origin expressed as $|R(0)|^2=4\pi|\psi(0)|^2$ a.u.; and calculated and experimental values of the hyperfine splittings, in MHz.

State	$\lvert R(0)\rvert^2$	$\Delta\nu_{\text{calc}}$[a]	$\Delta\nu_{\text{expt}}$
6s	39.39	9799	9193
7s	9.320	2319	
8s	3.729	927.7	870 ± 12[b]
9s	1.869	465.0	405 ± 25[c]

[a] Using formula (6).

[b] Rf spectroscopic measurement, Ref. 23.

[c] Decoupling measurement, Ref. 24.

The present results are 1–6% higher than obtained using the simple semiempirical formula[21] for $|\psi(0)|^2$. This latter formula is known to give results consistently larger than experiment for the alkalis.[24] Since the present results indicate fairly good agreement with the semiempirical formula for $|\psi(0)|^2$, the discrepancies are most probably due to uncertainty in the corrections F_r, δ, or ϵ,[25] in all calculations of which dependence on electron binding energy or degree of ionization have been neglected. Use of the improved values[22] for δ and ϵ increases the calculated values by about 2%.

In Sec. III we shall be concerned with photoabsorption into the $l=1$ continuum. The accuracy of the solutions of (1) for these final states was assessed by comparing the calculated phase shifts for e^--Cs^+ scattering at zero energy for $l=1$, with values obtained from extrapolating the observed quantum defects of the npj states to the series limit. The calculated and experimental values (modulo π) were found to agree to better than 1% for both $j=\frac{1}{2}$ and $j=\frac{3}{2}$.

III. DIPOLE MATRIX ELEMENT

The theory of the core-polarization correction to the dipole matrix element has been discussed many times,[4–7] and will not be rederived in full detail here. It is important to realize, however, that there is an essential difference between the approach implicit in the use of the wave equation (1), and that of Hameed *et al.*[5(a)] In this latter work Hartree–Fock wave functions were used for the valence electron, i.e., the perturbation $V_p(r)$ was neglected. The core-polarization correction to the matrix element was then obtained by a perturbation expansion over a basis set which is the product of unperturbed core- and valence-electron wave functions. The potential $V_p(r)$ in (1), however, was obtained from an initial perturbation expansion for the core wave function for a fixed valence electron, in the spirit of the Born–Oppenheimer approximation.[15] The appropriate total atomic wave function is then just the product of this expansion with the valence wave function obtained from (1).

The total atomic wave function can be written

$$\Psi(\vec{R}, \vec{r}) = N(r)[\phi(\vec{R}) + \chi(\vec{R}, \vec{r})]\psi(\vec{r}) , \tag{7}$$

where $\psi(\vec{r})$ is the normalized valence wave function obtained from (1), $\phi(\vec{R})$ is the unperturbed core wave function, $\chi(\vec{R}, \vec{r})$ is the perturbation due to the outer electron, and $N(r)$ is the normalization function of the core wave function defined by[15]

$$N(r) \equiv [1 + \int \chi(\vec{R}, \vec{r})\chi(\vec{R}, \vec{r}) d\vec{R}\,]^{-1/2} , \tag{8}$$

which has the limiting form

$$N(r) \underset{r\to\infty}{\approx} 1 - \beta/2r^4 . \tag{9}$$

The dipole matrix element for valence-electron transitions is

$$\vec{M}_{if} = \langle \Psi_f | \vec{r} + \vec{D} | \Psi_i \rangle , \tag{10}$$

where $\vec{D} = \sum_k \vec{R}_k$, and $\vec{R}_k$ is the position vector of the kth core electron. Using (7) and (8) this becomes

$$\vec{M}_{if} = \langle \psi_f | N_f N_i [(1 + \int \chi_f \chi_i d\vec{R})\vec{r} + \langle \phi_f | \vec{D} | \chi_i \rangle + \langle \chi_f | \vec{D} | \phi_i \rangle] | \psi_i \rangle . \tag{11}$$

We note that if $\chi_f = \chi_i$ then $N_f = N_i$, and the first term in brackets reduces to $\vec{r}$, as it should. But since an l-dependent potential is used in the present work, this implies $\chi_f \neq \chi_i$ and such a reduction would be only an approximation. For large r the last two terms in brackets are $-\hat{r}\alpha_d/2r^2$, so we can write (11) as

$$\vec{M}_{if} = \langle \psi_f | N_f N_i \{(1 + \int \chi_f \chi_i d\vec{R}) - \tfrac{1}{2}(\alpha_d/r^3)[f(r, r_c^{(i)}) + f(r, r_c^{(f)})]\} \vec{r} | \psi_i \rangle , \tag{12}$$

where $f(r, r_c)$ is the cutoff function for χ which has the appropriate r dependence for both large and small r, and is consistent with that used in $V_p(r)$. Treating the normalization functions in a similar fashion we obtain finally

$$\vec{M}_{if} = \langle \psi_f | \left(1 + \frac{\beta}{r^4} g(r, r_c^{(f)})\right)^{-1/2} \left(1 + \frac{\beta}{r^4} g(r, r_c^{(i)})\right)^{-1/2} \times \left(1 + \frac{\beta}{r^4} g(r, \overline{r}_c) - \frac{1}{2}\frac{\alpha_d}{r^3}[f(r, r_c^{(i)}) + f(r, r_c^{(f)})]\right) \vec{r} | \psi_i \rangle , \tag{13}$$

where $g(r, r_c)$ is a cutoff function for $N(r)$ and $\overline{r}_c$ is a weighted average of $r_c^{(f)}$ and $r_c^{(i)}$.

If we were to now make the approximation $r_c^{(i)} = r_c^{(f)} = \overline{r}_c$ and neglect the terms in β, we would obtain the form

$$\vec{M}_{if} = \langle \psi_f | [1 - (\alpha_d/r^3) f(r, \overline{r}_c)] \vec{r} | \psi_i \rangle . \tag{14}$$

This form was used by Hameed *et al*,[5(a)] by Beigman *et al.*[6] with $\overline{r}_c$ chosen *ab initio* and α_d chosen with reference to experimental values for $6s$-$7pj$ oscillator strengths, and by Weisheit[7] with α_d as in the present work and $\overline{r}_c$ chosen with reference to experimental photoionization data. The form (13) is used in the present work, with $r_c^{(i)}$ and $r_c^{(f)}$ taken from Table I, $\overline{r}_c$ defined by $\overline{r}_c \equiv [r_c^{(i)} r_c^{(f)}]^{1/2}$, and the functions $f(r, r_c)$ and $g(r, r_c)$ taken to be

$$f(r, r_c) = 1 - e^{-(r/r_c)^3} , \qquad g(r, r_c) = 1 - e^{-(r/r_c)^6} , \tag{15}$$

which are consistent with the forms used in (4) and have the appropriate limiting forms for both large and small r.

For transitions from the ground state to the state npj (kpj, where $k^2 = \epsilon$, in the continuum) we define $M_{2j} = |\vec{M}_{6s,npj}|$, in terms of which the spin-orbit perturbation parameter of Fano is[3(a)]

$$X = (2M_3 + M_1)/(M_3 - M_1) \tag{16}$$

and the doublet-line-strength (or absorption-oscillator-strength) ratio and total photoionization cross section can be expressed as

$$\rho \equiv f_{3/2}/f_{1/2} \simeq S_{3/2}/S_{1/2} = 2(X+1)^2/(X-2)^2 \tag{17}$$

and

$$\sigma(\nu)/h\nu \propto M_1^2 + 2M_3^2 \propto (M_3 - M_1)^2 (X^2 + 2) . \tag{18}$$

The second relationship in (17) is only approximate because of the finite energy difference of the upper states.

Although perturbation theory is not used in the present evaluation of M_{2j}, it is useful to consider the spin-orbit effect as a perturbation ΔM on the unperturbed matrix element M_0, i.e.,

$$M_3 = M_0 + \tfrac{1}{3}\Delta M , \quad M_1 = M_0 - \tfrac{2}{3}\Delta M \tag{19}$$

and

$$X = 3M_0/\Delta M , \tag{20}$$

which clearly illustrates the physical implication of X. The ratio ρ is seen to have a pole for $M_1 = 0$ and is zero for $M_3 = 0$, and since ΔM is expected to be a slowly varying function of energy,[2] the total cross section has a minimum near $X = 0$, the magnitude of which is determined primarily by that of ΔM.

Other measurable quantities can be expressed in terms of X, e.g., the degree of spin orientation of ejected photoelectrons for ionization of unpolarized atoms by circularly polarized light,[3]

$$P = (2X+1)/(X^2+2) + \Delta(\delta) ; \tag{21}$$

TABLE III. Absorption oscillator strengths $f_{3/2}$ for transitions $6s - np\frac{3}{2}$ in cesium and the ratios $\rho = f_{3/2}/f_{1/2}$. The superscripts are the appropriate powers of 10 by which the entry is multiplied.

	$f_{3/2}$			ρ		
n	a	b	c	a	b	d
6	7.074^{-1}	7.404^{-1}	7.14 ± 0.15	2.077	2.093	2.03 ± 0.02
7	1.039^{-2}	1.050^{-2}	1.33^{-2}	4.308	5.160	4.15 ± 0.28
8	1.643^{-3}	1.639^{-3}	2.94^{-3}	7.605	10.54	7.63 ± 0.76
9	5.150^{-4}	5.120^{-4}	9.10^{-4}	12.74	21.08	11.0 ± 1.8
10	2.241^{-4}	2.231^{-4}	4.17^{-4}	20.33	41.95	21.5 ± 4.1
11	1.179^{-4}	1.171^{-4}	2.23^{-4}	30.99	84.00	28 ± 7
12	6.999^{-5}	6.886^{-5}	1.26^{-4}	45.28	172.6	32 ± 10
13	4.543^{-5}	4.485^{-5}	7.9^{-5}	63.76	407.7	37 ± 13
14	3.098^{-5}	3.067^{-5}	5.8^{-5}	87.57	1168	50 ± 25
15	2.225^{-5}	2.209^{-5}	4.3^{-5}	115.9	4288	
16	1.656^{-5}	1.609^{-5}	3.3^{-5}	149.4	9914	
17	1.273^{-5}	1.263^{-5}	2.7^{-5}	188.3	3093	

[a] Present results.

[b] Calculation of Ref. 7.

[c] From the lifetime measurement of Ref. 26 for $n = 6$; measurements of Ref. 27 for $n > 6$.

[d] Measurements of Ref. 28 for $n = 6$, and Ref. 27 for $n > 6$.

or the ion counting-rate asymmetry for ionization of spin-polarized atoms by alternately left- and right-circularly polarized light,[10]

$$Q(2X - 1)/(X^2 + 2) \; ; \tag{22}$$

or the degree of spin polarization of ejected photoelectrons for ionization of spin-polarized atoms by light polarized linearly perpendicular to and parallel to the spin quantization axis

$$R_\perp = X^2/(X^2 + 2) - \Delta(\delta) \, , \tag{23}$$

$$R_\parallel = (X^2 - 2)/(X^2 + 2) - \Delta(\delta) \, . \tag{24}$$

The function $\Delta(\delta)$ is[3(b)]

$$\Delta(\delta) = \tfrac{8}{9} \{ [(X - 2)(X + 1)]/(X^2 + 2) \} \sin^2(\tfrac{1}{2}\delta) \, , \tag{25}$$

where $\delta = \delta_{1/2} - \delta_{3/2}$ for δ_j the phase shift of state kpj in the continuum. This small correction is required by the phase normalization of the photoelectron wave functions, i.e., $M_{6s,kpj} = |\vec{M}| e^{i\delta_j}$.

IV. RESULTS AND DISCUSSION

Oscillator strengths for absorption from the ground state obtained using (13) and solutions of (1) are given in Table III. The results of recent measurements and calculation are also given for comparison.

For $n > 6$ the results for $f_{3/2}$ are in excellent agreement with those of Weisheit,[7] but the results for ρ, hence $f_{1/2}$, are considerably different. In particular, the present results do not give a pole, or maximum in ρ, anywhere in the discrete spectrum. The explanation for this is most probably the different treatment of the spin-orbit interaction in the present work, in particular, the relativistic correction. It is clear from (19) that for transitions to states with large n, the large ratios observed and calculated are due to the fact that the spin-orbit correction to the matrix element for $f_{1/2}$ is nearly as large as the unperturbed matrix element itself, and hence M_1 is very small. It also follows that in this case $f_{1/2}$ is much more sensitive to the treatment of P_{nlj} near the origin. To illustrate this, term values and oscillator strengths for $n = 14-17$ were recomputed without the relativistic correction in (5). The term values obtained did not differ from those obtained with the relativistic correction by more than 0.03%, and $f_{3/2}$ increased by at most 8%. But $f_{1/2}$ was much more strongly affected, yielding $\rho \sim 400-5000$ for $n = 14-17$. A maximum in ρ was indicated in the neighborhood of $n = 18-19$, compared with $n = 16-17$ in the calculation of Weisheit.

For the resonance transition $n = 6$, the present results for both $f_{1/2}$ and $f_{3/2}$ are smaller than those obtained by Weisheit[7] by about 5%. Since the effect of the spin-orbit interaction is almost negligible for these transitions (the energy difference alone giving $\rho = 2.099$), the difference probably reflects the different forms of the core-polarization correction used, (13) and (14). If this correction is neglected entirely in (13), the present results are increased by 16%.

Oscillator strengths calculated by Beigman *et al.*[6] are in excellent agreement with the present results for the resonance transition, but larger by 30–70% for $n = 7-15$. The present results for ρ for these latter transitions are also considerably larger, the values of Beigman *et al.* being typically 18 for $n = 12$ and 40 at the series limit. This reflects their effective normalization to the measurements of Kvater and Meister[28] for $n = 7$.

Comparisons were also made, for $n = 6-9$, with the calculations of Stone[12] and Warner,[29] who did not include the core-polarization correction to the dipole operator, by dropping all such terms in (13). The results were in excellent agreement with those of Stone for both $f_{3/2}$ and ρ for $n = 6$, and in good agreement for $f_{3/2}$ for $n > 6$. The poor agreement for $f_{1/2}$ for $n > 6$ is probably due to the sensitivity of the results to the calculated term values, as pointed out by Warner. Agreement with the calculations of Warner was generally poor, probably due to the relatively simple model potential employed in that work, which did not include the effect of core polarization. It may also be noted that the present results for the resonance transition are in excellent agreement, perhaps fortuitously, with the Coulomb-approximation calculations of Heavens.[30] For higher transitions the agreement is, of course, poor because of the importance of the core-polarization and spin-orbit effects.

Considering experimental results, other lifetime measurements[31,32] for the $6p\,\frac{3}{2}$-state lead to values of $f_{3/2}$ differing from the experimental value given in Table III by as much as 17%, even if results of methods requiring cesium vapor pressure data are ignored. Lifetime measurements for the $7p$ and $8p$ states have also been performed,[31,32] but the probability of transition to other states is large by comparison with that for decay to the ground state, and hence these data do not provide very sensitive checks on the principal-series oscillator strengths.

The range of measured oscillator strengths for higher transitions is even greater than that for the resonance transition. The results of Agnew[27] and Kvater and Meister[28] are in reasonable agreement for $f_{3/2}$ for $n = 7-12$, but differ substantially for $n > 12$. Considerable differences for $f_{1/2}$ are noted for $n > 8$. The results of Agnew are given in Table III, and are seen to range from 130–200% of the present results. There is no obvious reason for this discrepancy, but it is remarked by Agnew that the measured values increased with decreasing argon pressure in the vapor cell, and the zero-argon-density results are quoted.

There is clearly a need for an exhaustive critical analysis of the experimental oscillator-strength data, but this is beyond the scope of the present work. Measured values of the oscillator-strength ratios ρ, which should be less sensitive to experimental uncertainty, are in much better agreement with each other and with theoretical results for at least the first few transitions. An exhaustive tabulation of experimental results for $n = 7,\ 8$ has been given by Baum *et al.*[10] The average value of ρ for the $7p$ state (15 measurements from 1914 to 1966) is 3.97 and for the $8p$ state (11 measurements over the same period) is 6.70. If only measurements since 1930 are considered, three for the $7p$ state and four for the $8p$ state, the averages are 4.18 and 8.08, respectively.

The difference between the present calculated values of ρ and those of Agnew[29] is not as significant as it appears, since small errors in ΔM can lead to large errors in $f_{1/2}$, hence in ρ, in the region where $f_{1/2}$ is small. If we assume, for example, that the measured values of ρ are exact, and that errors in the calculation reside primarily in ΔM, not M_0, then an estimate for the uncertainty in the tabulated values of $f_{3/2}$ can be obtained as follows. Since $f_{3/2} \propto |M_3|^2$, with (19) and (20) we obtain

$$d(\ln f_{3/2}) = -[2/(X+1)]d\,(\ln X)\ . \tag{26}$$

We use (17) to compare values of X obtained in the present calculation with those obtained from the measured values of ρ. This leads to values of X differing by at most 10% for $n = 7-14$, and to the conclusion, using (26), that the tabulated values of $f_{3/2}$ are perhaps too large (using the worst case, $n = 13$) by 5%. This also implies, of course, that the calculated values of $f_{1/2}$ may be too small by as much as a factor of 2. This illustrates the reason for not tabulating the calculated values of $f_{1/2}$; i.e., it may be more reliable, particularly when ρ is large, to obtain $f_{1/2}$ from calculated values of $f_{3/2}$ and measured values of ρ.

The present values for ρ are consistently ~80% of the values measured by Sambursky[8] for $n = 7-10$, and in excellent agreement with those measured by Fulop and Stroke[33] for the same principal quantum numbers; whereas for $n > 10$ both experiments yielded a maximum in ρ, with the ratios then decreasing to 5 and 18, respectively, at $n = 12$ (Fig. 1). These two experiments were performed in emission whereas that of Agnew was performed in absorption.

The sensitivity of the calculated values of ρ to the adjustable parameters in the model potential was investigated by varying the values of λ, $r_c^{(0)}$, and $r_c^{(1)}$ sufficiently (± 0.0003, ± 0.01, and ± 0.01, respectively) to increase the rms error in the calculated term values for $n = 6$ by more than an order of magnitude. In the worst cases, changes in ρ ranged from negligible for $n = 6$ through $\pm 5\%$ for $n = 12$ to $\pm 15\%$ for $n = 17$, and changes in other tabulated quantities never exceeded a few percent.

Baum *et al.*[10] also attempted to obtain informa-

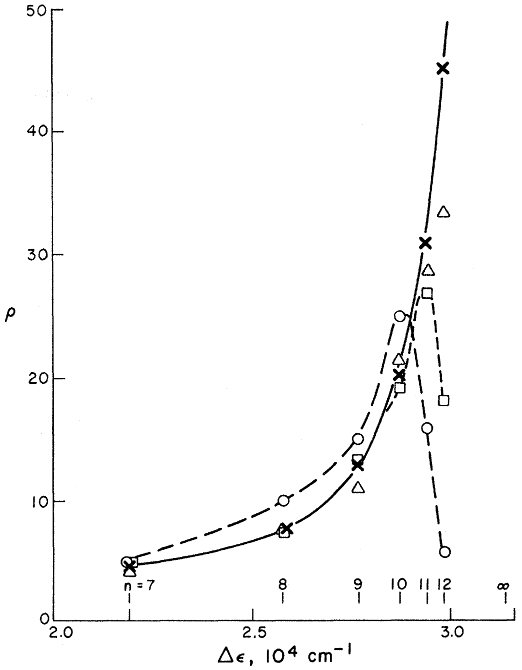

FIG. 1. Principal-series absorption oscillator-strength ratio ρ. Experimental results of Sambursky (Ref. 8) (○), Agnew (Ref. 27) (△), Fulop and Stroke (Ref. 33) (□); and present results (×). Connecting lines were added freehand for the sake of clarity only.

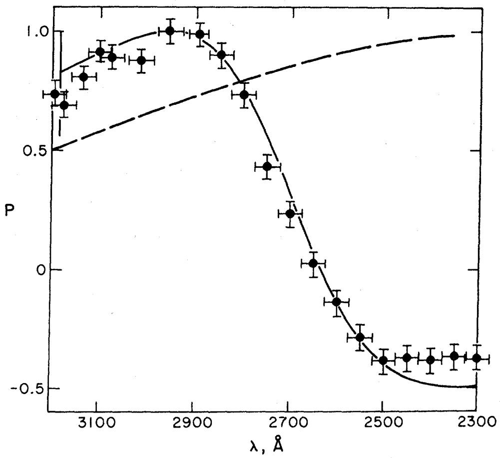

FIG. 2. Polarization parameter P, the degree of spin orientation of ejected photoelectrons for ionization of unpolarized cesium atoms by circularly polarized light. Experimental data of Ref. 11, calculation of Ref. 13 (dashed line), and present calculation (solid line).

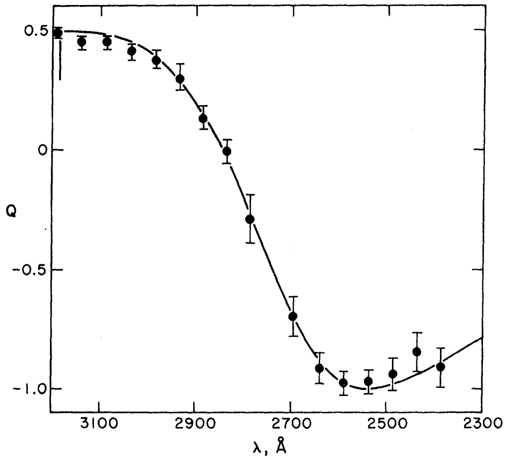

FIG. 3. Polarization parameter Q, the ion counting-rate asymmetry for ionization of spin-polarized cesium atoms by alternately left- and right-circularly polarized light. Experimental data of Ref. 10 and present calculation (solid line).

tion on the line-strength ratios by extrapolating the results of measurements in the continuum into the discrete spectrum. Their conclusion was that a pole, or maximum, in ρ exists in the region $n=10-15$, a result supported by two measurements[8,33] and the calculation of Weisheit.[7] Similar continuum measurements by Heinzmann *et al.*[11] indicate that no such pole exists anywhere in the discrete spectrum.

Turning to results obtained in the continuum, the calculated quantities P and Q given by (21) and (22) are compared with experimental results[10,11] in Figs. 2 and 3. In the experiment of Baum *et al.*[10] the quantity actually measured was $P_{at}Q$, where P_{at} is the unknown degree of spin polarization of the target atoms. The values of P_{at} and a parametrized function $X(\epsilon)$ were then extracted from these data by regression analysis. It was found that $X<2$ at threshold, and hence that extrapolation into the discrete spectrum indicated the existence of a pole in ρ, as previously mentioned.

This conclusion is suspect for the following reason. Consider (22) rewritten as

$$X=[1\pm(1-2Q^2-Q)^{1/2}]/Q\ . \tag{27}$$

Clearly X has a branch point at $Q=0.5$, where $dQ/dX=0$. Hence in the neighborhood of $Q=0.5$, the values of X extracted by regression analysis are expected to be extremely sensitive to very small unknown systematic errors in the measured values of $P_{at}Q$, or to the particular analytic form chosen for the trial function $X(\epsilon)$. It also follows that a very slight maximum in $P_{at}Q$ above threshold leads unambiguously to the conclusion that $X>2$ at threshold, and therefore that a pole in ρ does not exist. The experimental uncertainty in the measured values of $P_{at}Q$, although quite small, does not seem to preclude a maximum in $P_{at}Q$, and therefore the possibility of a second branch in the function $X(\epsilon)$ being consistent with the experimental results cannot be ignored. This may be illustrated by considering that the experimental values of Q in Fig. 3 were obtained from the data for

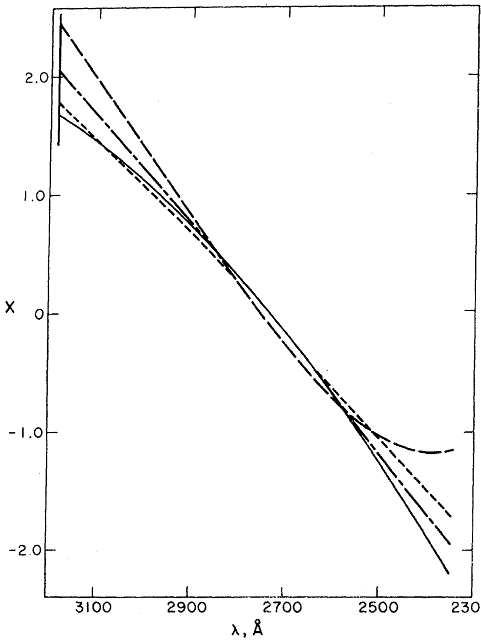

FIG. 4. Fano spin-orbit perturbation parameter X for cesium. Results derived from measurements of $P_{at}Q$ in Ref. 10 (solid line); from measurements of P in Ref. 11 (long dashes); calculation of Ref. 7 (short dashes); and present calculation (long-short dashes).

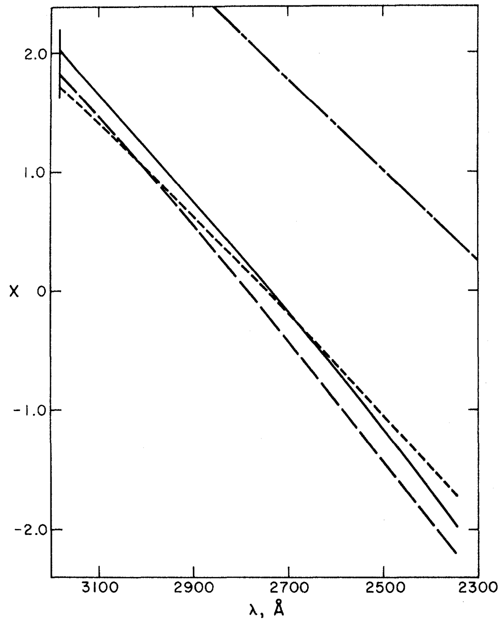

FIG. 5. As Fig. 4. Results of the present calculation (solid line); neglecting the second-order corrections to the dipole matrix element (long dashes); neglecting the relativistic correction to the spin-orbit potential (short dashes); and calculation of Ref. 13 (long-short dashes).

$P_{at}Q$ using $P_{at} = 0.142$. If the value 0.138 is used instead, the present curve is everywhere within the limits of experimental uncertainty. It might also be noted that the present curve of X is more easily represented by a series in increasing positive powers of wavelength rather than in increasing positive powers of photon energy, which latter form was adopted for the trial function $X(\epsilon)$ in Ref. 10.

A curve of X was also extracted from the measurements of P by Heinzmann *et al.*[11] The small correction $\Delta(\delta)$ in (21) was neglected, but since with the present results for δ, $\Delta(\delta)$ never exceeds 0.003 from threshold to 1300 Å this approximation seems justified. The two curves of X obtained from experiment and theory are shown in Fig. 4. It should be noted that the remarks made concerning the difficulty of extracting X from Q near $Q = 0.5$ apply also to extracting X from P near $P = -0.5$, the region where the curve of Heinzmann *et al.* diverges from the others.

Resolution of the discrepancy between the two measured curves of X could perhaps be achieved by measurements of $R_\perp$ or $R_\parallel$ near threshold, particularly $R_\parallel$. The value $X = 2$ yields $R_\perp = \frac{2}{3}$ and $R_\parallel = \frac{1}{3}$, whereas the X curves of Baum *et al.*[10] and Heinzmann *et al.*[11] predict $R_\perp \sim 59\%$ and 75%, and $R_\parallel \sim 17\%$ and 50%, respectively, at threshold.

The zero points of all curves of X agree particularly well. In the calculation of Weisheit,[7] it was the experimental values for this zero point that determined the choice of $\bar{r}_c$ in (14). By dropping the relativistic correction in (5) before solving (1) for the continuum wave functions, this latter curve was reproduced very well (Fig. 5). Since this approximation affects primarily ΔM, the zero point of X is very little changed. Also shown is the result obtained by neglecting terms in β in (13). In this case the effect is to shift the zero point of M_0 slightly, with little effect on ΔM. Neglecting the core-polarization corrections in (13) entirely yielded a curve of X shifted even further to shorter wavelengths than the result of Chang and Kelly.[13]

The present results for the total photoionization cross section are compared with other results in Fig. 6. To facilitate any further use, the present results are given in Table IV. Values of f_j for $n > 17$ could be obtained by interpolating the oscillator density using Tables III and IV.

The measured cross sections of Mohler and Boeckner[9] and Braddick and Ditchburn[36] are in good agreement at threshold with that of Marr and Creek,[34] shown in Fig. 5, and have minima of 0.036 and 0.080 Mb at 2650 and 2800 Å, respectively. Considering the experimental difficulties of separating atomic and molecular absorption, which can be of roughly equal magnitude in vapor cell measurements, the disagreement between the

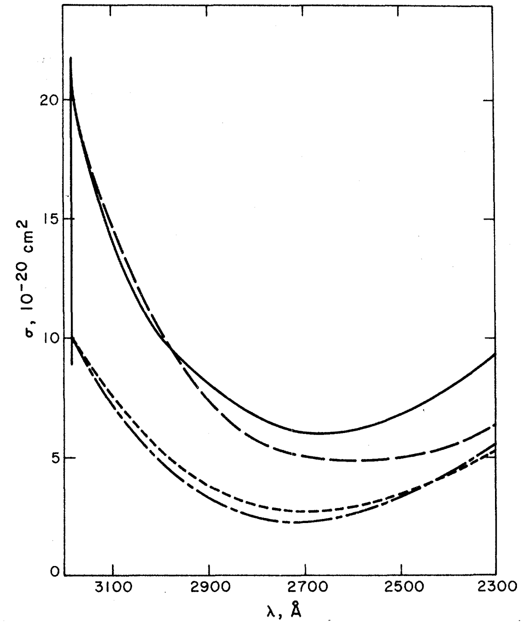

FIG. 6. Total photoionization cross section for the ground state of cesium. Experimental results of Ref. 34 (solid line); relative measurement of Ref. 11 normalized (Ref. 35) to that of Ref. 34 at 3160 Å (long dashes); calculation of Ref. 7 (short dashes); and present calculation (long-short dashes).

TABLE IV. Results for photoabsorption by the ground state of cesium into the p continuum. The quantities σ, $X, P, Q, R_\perp$, and $R_\parallel$ are defined in the text.

λ (Å)	σ (10^{-20} cm^2)	X	P (×10)	Q (×10)	$R_\perp$ (×10)	$R_\parallel$ (×10)
3183	10.000	2.065	8.190	4.997	6.806	3.613
3175	9.721	2.030	8.268	4.999	6.732	3.464
3125	8.100	1.808	8.759	4.965	6.206	2.410
3075	6.706	1.584	9.238	4.808	5.570	1.135
3025	5.528	1.358	9.658	4.465	4.807	−0.394
2975	4.553	1.131	9.936	3.847	3.911	−2.190
2925	3.770	0.901	9.949	2.850	2.901	−4.214
2875	3.166	0.668	9.531	1.376	1.845	−6.329
2825	2.730	0.434	8.513	−0.604	0.882	−8.257
2775	2.451	0.197	6.814	−2.973	0.213	−9.597
2750	2.366	0.078	5.736	−4.212	0.052	−9.918
2725	2.317	−0.042	4.550	−5.420	0.030	−9.961
2675	2.317	−0.284	2.055	−7.540	0.406	−9.205
2625	2.440	−0.529	−0.267	−9.028	1.240	−7.532
2575	2.675	−0.777	−2.132	−9.809	2.323	−5.359
2525	3.013	−1.027	−3.451	−9.998	3.454	−3.092
2475	3.441	−1.281	−4.285	−9.783	4.501	−0.992
2425	3.950	−1.538	−4.746	−9.337	5.409	−0.827
2375	4.530	−1.798	−4.948	−8.783	6.166	2.344
2325	5.171	−2.062	−4.982	−8.196	6.786	3.587

calculated and experimental cross sections is not surprising.

The difference between the present result at the minimum (0.023 Mb at 2700 Å) and that of Weisheit[7] can be taken as typical of the difference between the two calculations for ΔM. This difference is 16%, and is consistent with the difference between the two calculations of X in the continuum and ρ in the discrete spectrum. The calculation of Beigmann *et al.*[6] yielded values for the cross section at threshold of 0.014 Mb, and a minimum of 0.0018 Mb at 2480 Å. The value of ΔM was calculated by Seaton[2] using perturbation theory, yielding a value for the cross section of 0.030 Mb at the assumed minimum[36] of 2800 Å. Using the present value of 2700 Å for the position of the minimum, the perturbation-theoretic value of the cross-section minimum is reduced to 0.027 Mb.

By analysis similar to that leading to (26) we can also obtain from (18)

$$d[\ln\sigma(\nu)] = -[4/(X^2+2)]\,d(\ln X) \ . \tag{28}$$

Since $X \sim 2$ at threshold, with an uncertainty $\sim 20\%$ if the result of Heinzmann *et al.*[11] is taken as exact, (28) yields an uncertainty in the value of the calculated cross section at threshold $\sim 15\%$. This rests on the assumption that all of the uncertainty in $\sigma(\nu)$ is due to that in ΔM, which is not strictly valid, but reasonable in view of the facts that reasonable results are obtained for $f_{3/2}$ for $n = 6$ ($M_0 \gg \Delta M$) and for the zero point of $X(M_0 = 0)$, which are almost totally dependent on M_0.

Finally, we can compare the atomic polarizability of cesium obtained in the present work with other determinations. The total atomic polarizability can be written

$$\alpha_t = \alpha_v + \alpha_c - \alpha_{vc} \ , \tag{29}$$

where α_v is the polarizability of the valence electron alone, i.e., neglecting any interaction between the electric field and the core, α_c is the polarizability of the ionic core (referred to previously as α_d), and α_{vc} represents the effect of the dipole moment induced in the core by the valence electron.

With the present definition of the matrix element $\vec{M}_{if}$ (10), the first and the last terms in (29) are given by the usual expression

$$\alpha_v - \alpha_{vc} = \frac{4}{9}\sum{}' \frac{2\,|\vec{M}_{6s,np3/2}|^2}{\epsilon_{np3/2} - \epsilon_{6s}} + \frac{|\vec{M}_{6s,np1/2}|^2}{\epsilon_{np1/2} - \epsilon_{6s}} \ , \tag{30}$$

where the summation includes all dipole-allowed transitions of the valence electron to discrete and continuum states. It follows that evaluation of (30), neglecting all core-polarization corrections in (13), yields α_v alone, and hence α_{vc} by comparison of the two results. Inclusion of all excited states of the core in (30) would simply require addition of α_c to the left-hand side.

Before discussion of the results, a correspondence between the present definition of α_v and α_{vc} and the quantities computed by Sternheimer[37] may be established. We first make the simplifying approximation

$$\alpha_v - \alpha_{vc} \simeq \frac{4}{3}\sum{}' \frac{|\vec{M}_{6s,np}|^2}{\epsilon_{np} - \epsilon_{6s}} \ , \tag{31}$$

where now fine-structure effects are neglected, and ϵ_{np} is the center of gravity of the doublet. Using the approximate form (14) of $\vec{M}_{if}$ and expanding (31) we obtain

$$\alpha_v - \alpha_{vc} \simeq \tfrac{4}{3}\langle P_{6s}|r|P'\rangle - \alpha_c \tfrac{4}{3}\langle P_{6s}|(1/r^2)f(r,\bar{r}_c)|P'\rangle \ , \tag{32}$$

where

$$P'(r) \equiv \sum{}' \frac{|P_{np}\rangle\langle P_{np}|r[1-(\alpha_c/r^3)f(r,\bar{r}_c)]|P_{6s}\rangle}{\epsilon_{np} - \epsilon_{6s}} \ . \tag{33}$$

Now using the approximate form of (1), neglecting fine structure, it easily follows that $P'(r)$ is an approximate solution of the equation

$$\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + V(r) + \epsilon_{6s}\right) P'(r) = -r\left(1 - \frac{\alpha_c}{r^3} f(r,\bar{r}_c)\right) P_{6s}(r) \ . \tag{34}$$

This equation is formally equivalent to that of Sternheimer defining the perturbation function $u'_{1b}(r)$, differing only in the forms of $V(r)$ and the core-polarization correction function $f(r, \bar{r}_c)$. Thus the first term and coefficient of $-\alpha_c$ in (32) are formally equivalent to the polarizability $\alpha_{v,b}$ and coefficient $\xi_{v,b}(r_1)$, respectively, of that work. If the core-polarization correction in the

TABLE V. Calculated values of the valence-electron polarizability α_v and the core–valence-electron polarizability correction $\alpha_{\rm vc}$; and calculated and experimental values of the total atomic polarizability α_t, in units of 10^{-24} cm^3.

α_v	$\alpha_{\rm vc}$	α_c[a]	α_t[b]	
65.72	9.24	2.82	59.30	Eq. (30)
71.31	13.26	3.14	61.19	Ref. 37
			59.6 ± 1.8	Ref. 38

[a] Values used in the calculations.

[b] For a complete bibliography of other experimental and theoretical values, see Ref. 39.

matrix element of (33) is neglected, the corresponding results of Sternheimer are $\alpha_{v,a}$ and $\xi_{v,a}(r_1)$. We can therefore obtain results corresponding to the present definitions of α_v and $\alpha_{\rm vc}$ from the tabulated quantities of Sternheimer using the relations

$$\alpha_v = \alpha_{v,a}\,, \quad \alpha_{\rm vc} = \alpha_{v,a} - \alpha_{v,b} + \xi_{v,b}(r_1)\alpha_c\ . \qquad (35)$$

The results of the two calculations are given in Table V, along with the values of α_c used in the two works and recent experimental determination of α_t. It follows from the foregoing discussion that the excellent agreement between the calculated values of α_t is somewhat fortuitous. The difference between the two values of α_v, which are independent of any core-polarization correction in the matrix elements, is considerably greater, and is almost certainly due to the different forms of $V(r)$, hence also $P_{6s}(r)$. Comparison of the calculated values of the ground-state hyperfine splitting supports this conclusion, that of Sternheimer being 7944 MHz. The resonance transition contributes 99% of α_v, and therefore neglect of fine-structure effects in (32)–(34) should introduce an error of not more than 0.2%. The uncertainty in the present result for α_t is predominantly that in the direct contribution from α_c, as $\alpha_v - \alpha_{\rm vc}$ should be relatively insensitive to small changes in α_c due to the semiempirical nature of the present calculation.

It should also be pointed out that the excellent agreement referred to by Mowat[40] between measured and calculated[41] values of the Stark shift in the ground-state hyperfine structure of Cs^{133} is fortuitous. As the Stark shift is proportional to the atomic polarizability, Mowat finds confirmation in the fact that the atomic polarizability calculated by Feichtner *et al.*[41] is in excellent agreement with that of Sternheimer. The two values compared, however, were calculations of $\alpha_{v,a}$ and $\alpha_{v,b}$, respectively, which Sternheimer finds differ by ~ 10%. In additiion, Feichtner *et al.* emphasize that the calculated polarizability (65.07 Å^3) is almost certainly too large and suggest instead the use of an experimental value of α_t (53.8 Å^3), which gives a Stark shift only 81% of the experimental result.

The polarizability most appropriate in such a calculation is not, in fact, any of $\alpha_{v,a}$, $\alpha_{v,b}$, or α_t, but $\alpha_v - \alpha_{\rm vc}$. The direct ionic polarizability α_c does not appear since any shift induced by this effect will be equal for the two hyperfine states, and therefore not affect the difference. Mowat also finds relatively poor agreement between measured and calculated ratios of Stark shifts for the other alkali metals to that of Cs^{133}. If the polarizabilities $\alpha_v - \alpha_{\rm vc}$ of Sternheimer are used rather than α_t, the discrepancies are halved, to at most 9%.

As a further check on the sensitivity of the results to the choice of free parameters in the model potential, the alternative procedure discussed in Sec. II, and rejected on empirical grounds, was carried to completion for purposes of comparison. Differences with the results given in Tables III–V ranged from negligible for the oscillator strength of the resonance transition and polarizability, to a 33% and 25% increase in the values of σ and X, respectively, at threshold, and a shift in the position of the zero in X to shorter wavelengths by ~ 100 Å. This further illustrates a point alluded to in the foregoing discussion, that semiempirical model potentials which accurately reproduce one or two spectroscopic term values can yield quite different results for other quantities.

V. CONCLUSIONS

It has been shown that reasonable results can be obtained for photoabsorption in cesium, which is strongly influenced by the spin-orbit interaction and core polarization, using a semiempirical model potential and spectroscopic term values for the lowest few states, and without any effective normalization to experimental photoabsorption data. Relativistic effects in the spin-orbit interaction are found to be extremely important, and less so second-order terms in the core-polarization correction to the dipole matrix element. This justifies reasonable confidence that the method can be used in other cases for which these effects may be important and for which accurate spectroscopic data are not available. Some differences with experimental results are observed, and further experimental work seems warranted.

The model potential and wave functions discussed in this paper will be used in a future close-coupling calculation of electron scattering by cesium.

Note added in proof. The coefficient of the r^{-6} term in (4) should be $\alpha_q - 6\beta a_0$, which is very sensitive to small errors in the adopted values of α_q and β. The present results were obtained, in effect, with the correct form of $V_p(r)$ and the effective value $\alpha_q = 175.8 a_0^5$.

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