Semiclassical parameterization of the $l \geq 3$ energy levels in Cs I

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A simple semiclassical model is used to describe the $l \geq 3$ term energies in Cs I. The passive electrons are treated as a thin hollow shell of charge that can be polarized and penetrated by an active electron in a quantized Kepler orbit. The data are parameterized by weighted nonlinear least-squares adjustment of effective values for the dipole and quadrupole polarizabilities, the core radius, and the penetrated charge. The formulation represents the data well, permits predictive extrapolations, and provides intuitive insights into penetration effects. It is shown that apparent differences in the effective quadrupole polarizabilities inferred from the f and g series are removed when penetration effects are included.

1. INTRODUCTION

Term values for high-n and -l states in many-electron atoms differ only slightly from the values for a hydrogenic ion with the same net core charge. The observed differences are often attributed to a polarization of the core electrons and can be parameterized in terms of two empirical quantities phenomenologically associated with the dipole and quadrupole polarizabilities. The effective dipole polarizabilities deduced from this parameterization agree well with estimates obtained by other methods, but the effective quadrupole polarizabilities not only disagree with theoretical estimates (including corrections for nonadiabatic effects) but also yield different values when inferred from separate Rydberg series within the same ion. It has long been suspected that the source of these discrepancies may be associated with core penetration or exchange effects (relativistic effects and configuration interaction are also possibilities). Sansonneti *et al.*[1] recently made precision measurements of the f–g transitions in neutral cesium by using high-resolution Fourier spectroscopy and, in combination with earlier measurements,[2] have formulated their results in terms of the core polarization model. In order to account for the differences between the effective quadrupole polarizabilities inferred from the f and g series, they have made corrections for penetration, exchange, and relativistic effects by using a procedure involving Hartree–Fock calculations. An alternative approach was recently suggested[3] in which penetration effects are treated semiclassically by considering quantized Kepler orbits traversing hollow shells of charge. This simple model provides a means of extending the semiclassical polarization parameterization to include an effective core radius and an effective quantity of penetrated charge. We report here the application of the semiclassical approach[3] to parameterize the energy level measurements for Cs I.[1,2]

2. SEMICLASSICAL MODEL

The term energy of an active electron orbiting a passive core of net charge ζ, effective dipole polarizability of $\alpha_d{}'$ and effective quadrupole polarizability $\alpha_q{}'$ is given by[3]

$$T = R \left[\langle \zeta r^{-1} \rangle + \alpha^2 (\langle \zeta^2 r^{-2} \rangle - \tfrac{3}{4} \langle \zeta r^{-1} \rangle^2) \right.$$
$$\left. - \alpha^2 \langle (l \cdot s) \zeta r^{-3} \rangle + \langle \alpha_d{}' r^{-4} \rangle + \langle \alpha_q{}' r^{-6} \rangle \right], \quad (1)$$

where R and a_o are the reduced mass-corrected Rydberg energy and Bohr radius, respectively, α is the fine-structure constant, and l and s are the orbital and spin angular momental, respectively, in $\hbar$ units ($\alpha_d{}'$ is in units of $a_o{}^3$, $\alpha_q{}'$ is in units of $a_o{}^5$, and r is in units of a_o). The quantities ζ, $\alpha_d{}'$, and $\alpha_q{}'$ (collectively denoted as γ henceforth) can vary over the orbit and are therefore left inside the averages for the powers of the radius. For purposes of this model, these averages are interpreted as the classical analogs of the quantum mechanical expectation values, which are time averages over the Keplerian orbits

$$\langle \gamma r^p \rangle = \oint dt \, \gamma(r) r^p / \oint dt. \quad (2)$$

Using Bohr–Sommerfeld–Wilson quantization rules, these orbits are specified by the principal and orbital angular-momentum quantum numbers n and l. If the core is modeled as a thin hollow shell of charge $\zeta - \zeta_c$ with a radius ρ (in units of a_o), then these integrals break up into separate portions along the external and internal orbital segments

$$\langle \gamma r^p \rangle = \frac{\gamma_{\text{inner}} \displaystyle\int_{r < \rho} dt \, r^p + \gamma_{\text{outer}} \displaystyle\int_{r > \rho} dt \, r^p}{\displaystyle\int_{r < \rho} dt + \displaystyle\int_{r > \rho} dt}. \quad (3)$$

Here ζ is the hydrogenic core charge and ζ_c is a variable dependent on n and l. We assume that the stepwise discontinuous values of ζ, $\alpha_d{}'$, and $\alpha_q{}'$ pass to $\zeta \to \zeta_c$, $\alpha_d{}' \to 0$, and $\alpha_q{}' \to 0$ for $r < \rho$. Details of the integrations involved in Eq. (3) are given in Ref. 3, assuming that the external quantum numbers n and l remain integers and that the internal orbits are described by conservation of energy and angular momentum. For $r > \rho$, the quantities $\alpha_d{}'$, $\alpha_q{}'$, ζ, and ζ_c are

treated as empirical parameters that can be least-squares adjusted to fit Eq. (1) to the measured term values.

This model pictures the core as a hollow shell of charge that can be displaced, distorted, and transited by an orbiting electron. This is the simplest usable model that includes penetration and polarization. An extended core, in which the more deeply penetrating orbits encounter a greater overburden of core charge, would be more realistic, but the complicated dynamics of the internal orbit would sacrifice the main advantage of the classical approach, which is its simplicity. A compromise was utilized in Ref. 3, in which the hollow shell model was retained but the amount of charge on the shell was allowed to depend weakly on the depth of penetration. The functional dependence used in Ref. (3) for Si III data was

$$\zeta_c = \zeta + A \exp(B/P), \qquad (4)$$

where A and B are empirically determined constants and P is the externally computed orbit perihelion. A number of other charge models were attempted for the Cs I data, but Eq. (4) was the most successful in parameterizing the data.

3. NONHYDROGENIC ASPECTS OF Cs I

There are a number of important characteristics of Cs I that are not accounted for in the simple classical model described above. These include the inversion of fine structure, tunneling penetration, and exchange effects.

The f series in Cs I has inverted fine structure for all n values.[4] This cannot be described by electrostatic penetration of a charged (but magnetically inert) core. Semiclassical descriptions of fine-structure inversions in alkali systems[5] usually invoke perturbations caused by high-lying excited core configurations that affect only the spin–orbit contributions to Eq. (1). Since the spin–orbit contributions cancel from the statistically weighted centroid of the fine-structure levels, all fitting was done to these centroids.

Neutral cesium, with a nuclear charge $Z = 55$, is very close to the region of collapse of the $4f$ orbital at $Z = 57$.[6] Thus, although the $4f$ radial wave function peaks outside the $5p$ in Cs I, the $4f$ peaks inside the $5p$ for both La I and Ba II.[7] Thus it has been suggested by Fröman et al.[8] that the f series in Cs I is subject to two separate types of core penetration: the familiar effect arising from the intersection of the orbit with the core near the classical orbit perihelion and a second phenomenon that might be termed tunneling penetration. As is typical of atoms in the vicinity of $4f$ orbital collapse, the radial dependence of the effective potential energy of the active electron in Cs I has two regions of negative energy separated by a barrier and hence two families of classical orbits for a given energy. The outer region corresponds to alkalilike screened hydrogenic orbits (external to the $n = 5$ shell), whereas the inner region corresponds to rare-earth-like shielded orbits (internal to the $n = 5$ shell). The classical model of Ref. 3 describes the former but not the latter. Fröman et al.[8] have reported WKB approximation calculations of the tunneling through this barrier that indicated that the $4f$ is much more severely affected by this process than are the other f orbitals. Therefore the $4f$ was excluded from our analysis.

Sansonetti et al.[1] have emphasized the importance of exchange effects between the valence electron and the core in a polarization analysis of Cs I and have made Hartree–Fock

estimates of the magnitude and n and l dependences of these effects. It can be seen from Table 4 of Ref. 1 that for Cs I the calculated exchange corrections are very nearly proportional to the calculated penetration corrections as a function of n for a given l. Table 4 of Ref. 1 also lists calculated values for the nonhydrogenic relativistic corrections for Cs I, which exhibit a similar n and l behavior to the exchange and penetration corrections, although of much smaller magnitude. If this tendency has quantitative validity, then all three of these corrections should reside to a large degree in the empirical values for ρ and ζ_c of the classical penetration model. The experimental dependences that are due to exchange and relativistic effects would be expected to distort the penetration parameters deduced from a single l series because of the similarity of their n dependences, but they would not distort the polarization parameters determined jointly from more than one l series.

4. RESULTS

The available observed excitation-energy-level values with $n \geq 5$ and $l \geq 3$ for Cs I are presented in Table 1 with their quoted uncertainties and literature sources, along with the results of our semiclassical parameterization. It should be noted that the 10–12f fine-structure separations of Eriksson and Wenåker[2] are systematically smaller than the corresponding precision measurements of Fredriksson et al.[4] by amounts exceeding the quoted uncertainties. The 13f and 14f centroids in Table 1 were assigned larger uncertainties since they were computed from the only fine-structure component given in Ref. 2 and the fine-structure separation given in Ref. 4. The discrepancy between Refs. 2 and 4 suggests that the centroids of the other f levels could have uncertainties larger than those quoted.

Table 1. Available Observed Excitation-Energy-Level Values with $n \geq 5$ and $l \geq 3$ for Cs I

nl	E_{obs} (uncert)	$E_{\mathrm{obs}} - E_{\mathrm{fit}}{}^{a}$	$\zeta_c - \zeta$	P
5f	26 971.2192(10)[b]	+0.0003	0.03128	6.972
6f	28 329.4509(10)[b]	+0.0016	0.03651	6.606
7f	29 147.9381(10)[b]	−0.0021	0.03976	6.421
8f	29 678.7108(10)[b]	−0.0000	0.04191	6.311
9f	30 042.2868(10)[b]	−0.0002	0.04340	6.240
10f	30 302.1426(10)[b]	+0.0008	0.04448	6.192
11f	30 494.2680(10)[b]	+0.0011	0.04528	6.157
12f	30 640.3021(10)[b]	+0.0009	0.04589	6.130
13f	30 753.8811(100)[c]	−0.0058	0.04638	6.110
14f	30 843.9594(100)[c]	−0.0097	0.04676	6.095
5g	27 008.0557(7)[d]	+0.0000	0	13.820
6g	28 352.4442(9)[d]	+0.0001	0	12.000
7g	29 163.0705(14)[d]	+0.0009	0	11.304
8g	29 689.1342(11)[d]	+0.0001	0	10.934
9g	30 049.7475(16)[d]	−0.0008	0	10.708
10g	30 307.6535(21)[d]	−0.0018	0	10. 557
11g	30 498.4521(35)[e]	+0.0012	0	10.451

^{a} $\alpha_d = 15.759$, $\alpha_q = 47.990$, $\rho = 8.136$, $\zeta_c = \zeta + (1.916 \times 10^{-3})\exp(19.472/P)$, $IP = 31\,406.460$ cm^{-1}.
^{b} Ref. 2.
^{c} Ref. 2, using fine structure of Ref. 4.
^{d} Ref. 1.
^{e} A misprint in Table 2 of Ref. 1 has been corrected.

A six-parameter fit was made to 17 data points by a weighted nonlinear least-squares adjustment[9] of $\alpha_d{}'$ and $\alpha_q{}'$ [cf. Eq. (1)], ρ [cf. Eq. (3)], A and B [cf. Eq. (4)], and the ionization potential IP. The ionization potential was left as a free parameter to avoid introducing the uncertainties that are inherent in published values for the IP and the $4f$ excitation energies into the fit. The differences between the observed and fitted energies are given in Table 1 and indicate that the data are generally reproduced to within their quoted uncertainties. The fitted values for the parameters are also given in Table 1. The value for IP was about 0.0045 cm^{-1} higher than that of Ref. 1, but this is probably not significant in view of the uncertainties in the nf levels suggested by the fs discrepancies between Refs. 2 and 4.

The fitted value $\rho = 8.136$ places the effective radius of the core just beyond the largest f perihelion $[P(4f) = 8]$ but well inside the smallest g perihelion (the classical perihelions are also listed in Table 1), so the g levels are here considered nonpenetrating. {The classical perihelion is given by $P = a_o(1 - \epsilon)$, where $\epsilon = [1 - l(l + 1)/n^2]$}. The effective charge penetrated is also tabulated here and is small (less than 0.05 electron charge at the series limit) and slowly varying with n. A Hartree–Fock calculation of charge distribution in Cs II outside $\rho = 6$ gives $(\zeta_c - \zeta) = 0.002$ and is thus consistent with the values obtained in Table 1. Since penetration effects in the g series are neglected in this analysis, the values for $\alpha_d{}'$ and $\alpha_q{}'$ are in good agreement with those obtained in Ref. 1 from the g series alone. The theoretical interpretation of these values should, however, be considered with caution, since there is evidence for small penetration effects in the g and h series also. Safinya et al.[10] have determined the $\Delta n = 0$ g–h and h–i separations in Cs I for several high n values and have obtained $\alpha_d{}'$ and $\alpha_q{}'$ values somewhat different from those inferred from the g series alone by Sansonetti et al.[1] We attempted to parameterize these $\Delta n = 0$ intervals classically but found that they could not be reproduced to within their quoted uncertainties without including penetration effects in both the g and h series. There were not sufficient data points to determine the penetration parameters that, within the context of this model, would have to be separately defined for each l series. Such an analysis would not require a prohibitive increase in the number of fitting parameters if a systematic l dependence could be recognized, but it would require substantially more high n and l data, preferably including $\Delta n \neq 0$ transition energies.

The results of our fit were used to extrapolate the f and g series to high n values. These extrapolations were reduced to values for the high n quantum defects of $\delta(f) = 0.0336$ and $\delta(g) = 0.0068$. Pendrill et al.[11] have deduced a value $\delta(f) = 0.033(3)$ from measurements for $23 \leq n \leq 109$ and a value $\delta(g) = 0.0077(8)$ for measurements for $27 \leq n \leq 36$. They also quote an unpublished value $\delta(g) = 0.00686(3)$ attributed to Sansonetti et al. Measurements of the f series for $16 \leq n \leq 65$ have been reported by Mirza and Duley,[12] but these values are not of spectroscopic accuracy and could not be incorporated into our analysis.

A study was also made of the effect of including in Eq. (1) the retardation term proportional to $\langle r^{-5} \rangle$, which has been suggested by Kelsey and Spruch.[13] The influence of this term

was slight in this case, and the fitted results with and without it were essentially equivalent.

The results presented here indicate that the classical core polarization model, by which so many spectral term values have been studied, can be extended in a simple classical manner to account reasonably well for penetration effects. This provides a means of isolating the l-dependent component that has been observed to distort the effective $\alpha_q{}'$ values that are extracted from spectral data. It shows that Eq. (1) can be used to describe term values of high-l states accurately, provided that the averages over reciprocal powers of the radius are reinterpreted to include core penetration. This can permit more reliable predictions of high-l-term values and may lead to insights into the penetration contributions to the quantum defect.

Note added in proof. A recent measurement by Lorenzen et al.[14] reports a value of 31 406.468(6) cm^{-1} for the ionization potential of Cs. We are thankful to L. R. Pendrill for calling this reference to our attention.

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REFERENCES

1. C. J. Sansonetti, K. L. Andrew, and J. Verges, "Polarization, penetration, and exchange effects in the hydrogenlike nf and ng terms of cesium," J. Opt. Soc. Am. **71**, 423–433 (1981).
2. K. B. S. Eriksson and I. Wenåker, "New wavelength measurements in Cs I," Phys. Scr. **1**, 21–24 (1970).
3. L. J. Curtis, "A semiclassical formula for the term energy of a many-electron atom," J. Phys. B. **14**, 1373–1386 (1981).
4. K. Fredriksson, H. Lundberg, and S. Svanberg, "Fine- and hyperfine-structure investigation in the 5^2D–n^2F series of cesium," Phys. Rev. A **21**, 241–247 (1980).
5. H. E. White, *Introduction to Atomic Spectra* (McGraw-Hill, New York, 1934), pp. 393–394.
6. M. G. Mayer, "Rare-earth and transuranic elements," Phys. Rev. **60**, 184–187 (1941).
7. D. C. Griffin, R. D. Cowan, and K. L. Andrew, "Instabilities in the iterative solution of the Hartree–Fock equations for excited electrons," Phys. Rev. A **3**, 1233–1242 (1971).
8. A. Fröman, J. Linderberg, and Y. Öhrn, "Penetration effects in the ^2F series of Cs I," J. Opt. Soc. Am **54**, 1064–1065 (1964).
9. P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969), pp. 232–242.
10. K. A. Safinya, T. F. Gallagher, and W. Sandner, "Resonance measurements of f–h and f–i intervals in cesium using selective and delayed field ionization," Phys. Rev. A **22**, 2672–2678 (1980).
11. L. R. Pendrill, D. Delande, and J. C. Gay, "Quantum defect and fine-structure measurements of P, D, F, and G Rydberg states in atomic caesium," J. Phys. B **12**, L603–L608 (1979).
12. M. Y. Mirza and W. W. Duley, "Energy levels for highly excited ^2F states in Cs," J. Phys. B **11**, 1917–1920 (1978).
13. E. J. Kelsey and L. Spruch, Retardation effects on high Rydberg states: a retarded R^{-5} polarization potential, Phys. Rev. A **18**, 15–25 (1978).
14. C.-J. Lorenzen, K.-H. Weber, and K. Niemax, "Energies of the $n\,^2S_{1/2}$ and $n\,^2D_{3/2,5/2}$ states of Cs," Opt. Commun. **33**, 271–276 (1980).