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Effect of the atomic core on the fine-structure splitting for excited *nd* and *nf* states of the alkali-metal atoms

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We have calculated the second-order interaction between the spin-orbit coupling perturbation $H_{SO} \propto r^{-1}(dV/dr)\vec{1}\cdot\vec{s}$ acting on the core electrons and the exchange Coulomb interaction between the valence and core electrons. This calculation was previously carried out for two alkali *nd* states (Na 3*d* and Rb 4*d*), and was shown to result in the observed inversion of the fine-structure interval $\Delta\nu$ for these *d* states. In the present paper we have evaluated the second-order correction $\Delta\nu_2$ for the *nf* states of Na, and we have found that $\Delta\nu_2/\Delta\nu_1 \simeq -0.07$ for Na 11*f* and Na 14*f*, in good agreement with the experiment of Gallagher *et al.*, who have observed that the fine-structure interval of Na 11*f*, 13*f*, and 14*f* is normal, i.e., noninverted, and slightly smaller than the hydrogenic value $\Delta\nu_1$ (by $\sim 5\%$). Calculations have also been carried out for Na 3*d*, 4*d*, 5*d*, 11*d*, and 14*d*, and the results for $\Delta\nu_1 + \Delta\nu_2$ are negative, in good agreement with the observed inverted fine structure for these states. Additional calculations have been carried out for Cs 4*f*, 5*f*, and 6*f*.

I. INTRODUCTION

It has been known for a long time[1] that the fine structure of the excited *nd* states of the sodium atom is inverted, with the $^2D_{5/2}$ state lying *below* the $^2D_{3/2}$ state. Recently, as a result of improvements of the experimental techniques, important additional information has been obtained on the inverted fine-structure intervals for both Na *nd* and Rb *nd*. Among the experimental investigations, we may cite in particular that of Liao *et al.*[2] on the inverted fine structure Rb 4*d*, and, in addition, the paper of Fabre, Gross, and Haroche[3] on the inverted fine structure of Na *nd*, as well as the investigations of Gallagher, Hill, and Edelstein,[4] also on the fine structure of Na *nd*.

A partial explanation of the inverted fine structure of Na 3*d* was given by Phillips[5] in 1933. As a result of the experiment of Liao *et al.*,[2] Foley and Sternheimer[6] became interested in this problem, and they published an explanation of the effect as caused by the exchange polarization of 3*d* due to the perturbation $2p\rightarrow p$ of the core 2*p* electrons by the fine-structure interaction

$$H_{SO} = 2\frac{\mu_0^2}{e^2}\frac{1}{r}\frac{dV_0}{dr}\vec{1}\cdot\vec{s} \tag{1}$$

acting on the 2*p* electrons. Approximate agreement with experiment was found[6] for Na 3*d*. At about the same time, Lee, Rodgers, Das, and Sternheimer[7] considered the problem of the inverted fine structure for the case of Rb 4*d*. This case is more complicated numerically because of the large number of $np\rightarrow p$ and $nd\rightarrow d$ excitations of the Rb$^+$ core, as compared to the single $2p\rightarrow p$ excitation for the Na$^+$ ion. Nevertheless, these calculations gave qualitative agreement with the experimental value $\Delta\nu_{4d} = -0.44$ cm^{-1}. It should also be noted that related calculations of the inverted fine structure of excited *nd* states have been carried out by Lindgren and co-workers.[8] Calculations on the fine structure of the sodium *nd* states have also been carried out by Beck and Nicolaides.[9]

It was realized by Sternheimer that, in view of the fact that the fine structure $\Delta\nu_{np}$ is normal for the excited *np* states of the alkali atoms[10] ($^2P_{3/2}$ *above* $^2P_{1/2}$), it is of interest to carry out a similar calculation of the exchange core polarization for *np* states and to show that this effect is small for *np* states, and in any case that it does not lead to an inverted fine structure. The second-order term $\Delta\nu_2$ of the fine structure arises from the second-order interaction between H_{SO} [Eq. (1)] acting on the core electrons, and the exchange Coulomb interaction ($2/r_{ij}$ Ry) acting between the valence electron and the core electrons. By means of extensive calculations,[11] it was found that for the case of valence *np* states, the second-order term $\Delta\nu_2$ is in all cases small compared to $\Delta\nu_1$, the ordinary (first-order) fine-structure term, which is essentially given by the expectation value of H_{SO} for the unperturbed *np* wave function Ψ_{np}, i.e.,

$$\Delta\nu_1 \sim \langle\Psi_{np}|H_{SO}|\Psi_{np}\rangle. \tag{2}$$

Moreover, $\Delta\nu_2$ has the *same sign* as $\Delta\nu_1$, in contrast to the situation for *nd* states, where $\Delta\nu_2/\Delta\nu_1$ is negative. For *np* states, $\Delta\nu_2/\Delta\nu_1$ is of the order of +0.1 to +0.2, i.e., it tends to increase the value of $\Delta\nu$ $(=\Delta\nu_1+\Delta\nu_2)$ slightly above the calculated value of $\Delta\nu_1$.

The purpose of the present paper is to extend the calculations of Refs. 6, 7, and 11 to the case of additional Na *nd* states and, more importantly, to the *nf* states of sodium for which experimental data have recently been obtained by Gallagher, Cooke, Edelstein, and Hill.[12] The agreement with the results of Gallagher *et al.*[12] serves as a confirmation of our earlier calculations. It is found, both theoretically and experimentally, that the fine structure of the *nf* states of sodium is normal, i.e., noninverted (with the $^2F_{7/2}$ state lying *above* $^2F_{5/2}$). Moreover, the actual interval $\Delta\nu_{nf}$ is about 5% below the value of $\Delta\nu_1$ expected for hydrogenic wave functions, indicating that $\Delta\nu_2/\Delta\nu_1 \sim -0.05$. This is also essentially the result of our theoretical calculations.

We have also included our results for Na *nd* and Cs 4*f*, 5*f*, and 6*f*. In both cases (Na *nd* and Cs *nf*) the fine structure is inverted, both experimentally and according to our calculations. It should be pointed out that accurate calculations of $\Delta\nu$ for Na *nd* and Cs *nf* have recently been carried out by Luc-Koenig.[13]

II. CALCULATIONS OF $\Delta\nu_2$

The calculations of $\Delta\nu_2$ were carried out using the formalism developed in Ref. 11. The essential results are contained in Eq. (23) of Ref. 11, which gives

$$\Delta\nu_2 = -\frac{2l_v+1}{2}\,\alpha^2(\mathrm{Ryd}) \times \sum_{nl}\sum_{k} C_k(l;l_v)K_k(nl\to l;n_vl_v), \qquad (3)$$

where l_v is the azimuthal quantum number of the valence electron ($l_v=2$ for *nd*, $l_v=3$ for *nf*); α is the fine-structure constant, so that $\alpha^2(\mathrm{Ryd}) = 5.8434$ cm^{-1}; the coefficients $C_k(l;l_v)$ are angular coefficients which arise from the integration over angles and the summation over the magnetic quantum numbers m pertaining to the azimuthal quantum number l of the core state nl considered. We note that Eq. (3) actually differs from Eq. (23) of Ref. 11 by an additional summation sign $\sum_{nl}$ which was inadvertently omitted in Ref. 11. (However, the calculations of Ref. 11 did include the sum over nl, as is readily apparent from the results of Tables III–V and VII–IX of Ref. 11.) We may also note that for Na the sum over nl reduces to a single term, namely, 2*p*. On the other hand, for the case of Cs, the sum extends over $nl=2p$, $3p$, $4p$, $5p$, $3d$, and $4d$. In the second sum of Eq. (3), k is the multipolarity of the exchange interaction, and $K_k(nl\to l;n_vl_v)$ is the radial integral over the unperturbed wave function $u_0(nl)$, the perturbation $w_1(nl\to l)$, and the valence-electron wave function $v_0(n_vl_v)$. The expression for the double integral $K_k(nl\to l;n_vl_v)$ is given by Eq. (19) of Ref. 11, namely,

$$K_k(nl\to l;n_vl_v) = \int_0^\infty dr\,u_0(nl)v_0(n_vl_v)\left(\frac{1}{r^{k+1}}\int_0^r w_1(nl\to l)v_0(n_vl_v)r'^k\,dr' + r^k\int_r^\infty w_1(nl\to l)v_0(n_vl_v)r'^{-k-1}\,dr'\right). \qquad (4)$$

In Eq. (4), the perturbed wave function $w_1(nl\to l)$ is determined by the equation [cf. Eqs. (21) and (22) of Ref. 11]

$$\left(-\frac{d^2}{dr^2}+\frac{l(l+1)}{r^2}+V_0-E_0\right)w_1(nl\to l) = [\langle f(r)\rangle_{nl} - f(r)]u_0(nl), \qquad (5)$$

and the orthogonality condition

$$\int_0^\infty w_1(nl\to l)u_0(nl)\,dr = 0. \qquad (6)$$

In Eq. (5), the function $f(r)$ is defined by

$$f(r) \equiv \frac{1}{r}\frac{dV_0}{dr}, \qquad (7)$$

where V_0 is the effective central potential for the valence electron.

In Eq. (3), the coefficients $C_k(l;l_v)$ are determined by the equation [cf. Eq. (18) of Ref. 11]

$$C_k(l;l_v) = \sum_{m=-l}^{l} m[c^k(lm;l_vl_v)]^2, \qquad (8)$$

where $c^k(lm,l'm')$ is a coefficient defined in the book of Condon and Shortley.[14] The values of $C_k(l;l_v)$ for the relevant cases (namely, $l=1$ and 2, $l_v=2$ and 3) have been evaluated in Ref. 11, and are listed in Table I of this reference.

In the present work, we have evaluated $\Delta\nu_2$ (and $\Delta\nu_1$) for the following three types of states: (i) Na *nd*, with $n=3$, 4, 5, 11, and 14; (ii) Na *nf*, with $n=4$, 5, 6, 11, and 14; (iii) Cs *nf*, with $n=4$, 5, and 6.

The valence-electron wave functions $v_0(n_vl_v)$ which were used in this work were obtained as follows: (i) For the low-lying states Na 3*d*, 4*d*, 5*d*, Na 4*f*, 5*f*, and 6*f*, and for Cs 4*f*, 5*f*, 6*f*, we used Hartree-Fock wave functions using the appropriate

Na^+ and Cs^+ cores. These functions were obtained from a self-consistent procedure, which was a modification of the computing program introduced by Froese-Fischer.[15] The appropriate modifications were made by one of us (J.E.R.). (ii) For the highly excited states of Na, namely, 11*d*, 14*d*, 11*f*, and 14*f*, we used hydrogenic wave functions. This procedure is easily justifiable on the basis that these wave functions are extremely external to the relatively small Na^+ core.

With these valence-electron wave functions, we have calculated both the first-order fine-structure term $\Delta\nu_1$ and the second-order term $\Delta\nu_2$, which is given by Eqs. (3)–(8). The first-order term $\Delta\nu_1$ is given by[11]

$$\Delta\nu_1 = \tfrac{1}{4}(2l_v+1)\alpha^2(\mathrm{Ryd})I, \tag{9}$$

where I is the integral

$$I \equiv \int_0^\infty f(r)[v_0(n_v l_v)]^2\,dr$$
$$= \int_0^\infty \frac{1}{r}\frac{dV_0}{dr}[v_0(n_v l_v)]^2\,dr. \tag{10}$$

For the core electrons, we used the Hartree-Fock wave functions $u_0(nl)$ for the Na^+ and Cs^+ ions. For Na^+, the Hartree-Fock wave function for the 2*p* electrons was obtained from the tables of Clementi.[16] For the case of Cs^+, where the 2*p*, 3*p*, 4*p*, 5*p*, 3*d*, and 4*d* wave functions were required for use in Eqs. (4) and (5), these wave functions were obtained from the calculations of Freeman and Watson.[17] Obviously, the sum over *nl* in Eq. (3) contains a single term (2*p*) for Na, since we must have $l \geq 1$ in order to obtain an effect ($nl \to l$ excitation). On the other hand, the sum over *nl* in Eq. (3) contains six terms for the case of Cs^+, which have been enumerated above. However, the most important terms numerically are those due to the $5p \to p$ and $4p \to p$ excitations of the core by the fine-structure interaction, as described by Eq. (5) for the radial perturbations $w_1(nl \to l)$.

The resulting calculated values of $\Delta\nu_1$, $\Delta\nu_2$, the sums $\Delta\nu_1 + \Delta\nu_2$, and the ratios R,

$$R \equiv -\Delta\nu_2/\Delta\nu_1, \tag{11}$$

are listed in Table I. Here we have expressed both $\Delta\nu_1$ and $\Delta\nu_2$ in units of $mK = 10^{-3}\ \mathrm{cm}^{-1}$. The corresponding experimental values $\Delta\nu_{\mathrm{expt}}$ are listed in the fifth column of the table. These experimental values were obtained from Ref. 3 for Na *nd*, from the tables of Moore[1] for Cs 4*f*, 5*f*, 6*f*, and from Ref. 12 for Na 11*f* and 14*f*. To our knowledge, accurate spectroscopic values of the fine-structure intervals $\Delta\nu_{\mathrm{expt}}$ for Na 4*f*, 5*f*, and 6*f* are not available at present.

We wish to discuss first the results obtained here for the Na *nf* states, in particular 11*f* and 14*f*, and their agreement with experiment. As has been pointed out by Gallagher *et al.*,[12] the *nf* state fine structure is noninverted, and the value of $\Delta\nu$ is slightly below the value calculated for hydrogen. In fact the percentage difference from the hydrogenic value is −4.2 (±2.1)% for 11*f* and −5.2 (±1.6)% for 14*f*. These results are reproduced to a large extent by our calculations for 11*f* and 14*f*.

TABLE I. Calculated values of $\Delta\nu_1$ and $\Delta\nu_2$ for several *nd* and *nf* states of sodium, and for three *nf* states of cesium. All values of $\Delta\nu$ are in units of mK ($=10^{-3}\ \mathrm{cm}^{-1}$). The total theoretical values $\Delta\nu_1 + \Delta\nu_2$ are listed in the fourth column, and can be compared with the experimental values $\Delta\nu_{\mathrm{expt}}$. The values of the ratio $R \equiv -\Delta\nu_2/\Delta\nu_1$ are listed in the last column.

	State	$\Delta\nu_1$ (mK)	$\Delta\nu_2$ (mK)	$\Delta\nu_1 + \Delta\nu_2$	$\Delta\nu_{\mathrm{expt}}$	$R = -\Delta\nu_2/\Delta\nu_1$
Na	3*d*	45.9	−82.3	−36.4	−49.4(17) [a]	1.793
	4*d*	21.04	−47.42	−26.38	−34.3(1) [a]	2.254
	5*d*	11.18	−27.30	−16.12	−20.6(4) [a]	2.442
	11*d*	0.890	−2.318	−1.428	−2.33(2) [a]	2.604
	14*d*	0.433	−1.139	−0.706	−1.14(3) [a]	2.630
Na	4*f*	7.636	−0.199	7.437	⋯	0.0261
	5*f*	3.913	−0.169	3.744	⋯	0.0432
	6*f*	2.271	−0.121	2.150	⋯	0.0533
	11*f*	0.3689	−0.0257	0.3432	0.351(7) [b]	0.0697
	14*f*	0.1789	−0.0130	0.1659	0.167(3) [b]	0.0727
Cs	4*f*	17.0	−374.9	−357.9	−176 [c]	22.05
	5*f*	12.3	−354.8	−342.5	−147 [c]	28.85
	6*f*	8.5	−217.3	−208.8	−102 [c]	25.56

[a] Reference 3.

[b] Reference 12.

[c] Reference 1 (Vol. III).

The calculated ratio $R = -\Delta\nu_2/\Delta\nu_1$ is shown in Fig. 1 as a function of the principal quantum number n. It is seen that we have obtained a reduction of $\Delta\nu$ of 7.0% for 11*f* and 7.3% for 14*f*, in essential agreement with the experimental results of Gallagher *et al.*,[12] which have been quoted above. In concordance with this result, our calculated values of $(\Delta\nu_1 + \Delta\nu_2)$ are in good agreement with the experimental results, namely,

$$(\Delta\nu_1 + \Delta\nu_2)(11f) = 0.343\,mK\,, \tag{12}$$

$$(\Delta\nu_1 + \Delta\nu_2)(14f) = 0.166\,mK\,, \tag{13}$$

as compared to the experimental values, which are $0.351 \pm 0.007\,mK$ and $0.167 \pm 0.003\,mK$, respectively. For both Na 11*f* and 14*f*, it can be seen from the results of Table I that the experimental data of Gallagher *et al.*[12] are in disagreement with the hydrogenic values $\Delta\nu_1$, and are brought into agreement with the theory only by the inclusion of the second-order exchange core-polarization term $\Delta\nu_2$, which has been calculated in the present paper. The agreement is particularly close for Na 14*f* [see Eq. (13)]. It may be mentioned that an experiment on Na 4*f* by Liao and Bjorkholm[18] seemed to show no departure from the hydrogenic value, but this experiment is now being repeated with higher accuracy,[19] and the improved experiment may well show the small discrepancy, namely, −2.6%, from the value of $\Delta\nu_1$ which is predicted by our calculations (see Table I).

By contrast with the values of R for *nf* states, which are of the order of 0.03 to 0.07, the values of R for *nd* states of Na lie in the range from 1.79 to 2.63. The fact that these values of R are larger than 1 accounts, of course, for the inversion of the fine-structure interval, i.e., $\Delta\nu_1 + \Delta\nu_2 \equiv \Delta\nu_1(1-R)$ is negative for these states. Although we have not obtained very close agreement with the experimental values of Fabre, Gross and Haroche,[3] nevertheless the sign of $\Delta\nu_{\text{theor}}$,

$$\Delta\nu_{\text{theor}} = \Delta\nu_1 + \Delta\nu_2 = \Delta\nu_1(1-R)\,, \tag{14}$$

and the order of magnitude of $\Delta\nu_{\text{theor}}$ are correctly given by the present theory. The second-order term $\Delta\nu_2$ essentially "overshields" the first-order term $\Delta\nu_1$, resulting in an inversion of the fine-structure interval, with the $^2D_{5/2}$ state lying *below* the $^2D_{3/2}$ state. The residual discrepancies between $\Delta\nu_{\text{theor}}$ and $\Delta\nu_{\text{expt}}$ may be caused by the use of Hartree-Fock valence-electron wave functions, since it is well known that these functions are too external because of the neglect of the effects of electrostatic correlation with the core electrons having antiparallel spin.[20] Hence they tend to give values of both $\Delta\nu_1$ and $\Delta\nu_2$ that are numerically too small. Since $|\Delta\nu_2| > \Delta\nu_1$, this situation would result in a value of $\Delta\nu_1 + \Delta\nu_2$ that is negative but is somewhat smaller in magnitude than the experimental value $\Delta\nu_{\text{expt}}$. This is exactly the type of discrepancy which is shown by the values of Table I.

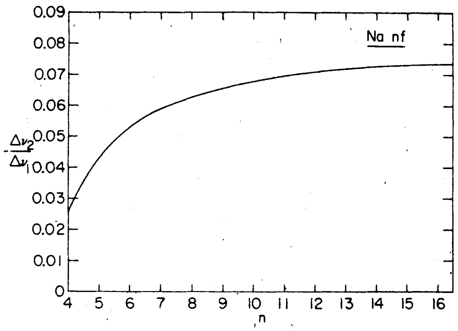

FIG. 1. Calculated ratio $-\Delta\nu_2/\Delta\nu_1$ for the *nf* states of sodium as a function of the principal quantum number n of the *nf* state. $\Delta\nu_2$ is the second-order term of the fine-structure interval due to the exchange core polarization [Eq. (3)]; $\Delta\nu_1$ is the usual first-order term [Eq. (9)]. The theoretical values for $n = 11$, 13, and 14 are in good agreement with the corresponding experimental values of Gallagher *et al.* (Ref. 12).

However, it should be pointed out that it is also possible that the third-order terms $\Delta\nu_3$, which have not been calculated here, are partly responsible for the limited discrepancy between the calculated and the observed values of $\Delta\nu$ for the Na *nd* states. It is not possible for us to calculate these third-order correction terms because of the complicated nature of the calculations, which would require extensive computer programs that are not available at present. However, it should be emphasized that these shortcomings do not affect the calculations of the correction term $\Delta\nu_2$ for the *nf* states of sodium, since $\Delta\nu_2/\Delta\nu_1$ is very small compared to 1 (i.e., $\Delta\nu_2/\Delta\nu_1 \leq 0.07$) for all of the *nf* states which have been investigated. Moreover, these values of $\Delta\nu_2$ give rise to good agreement with the experimental values $\Delta\nu_{\text{expt}}$ of Gallagher *et al.*,[12] as has been previously discussed [see Eqs. (12) and (13)]. The fact that $\Delta\nu_2/\Delta\nu_1 \ll 1$ for the Na *nf* states indicates that we may expect that $\Delta\nu_3/\Delta\nu_2$ will be similarly small, and therefore that $\Delta\nu_3$ will not affect the good agreement with experiment which has been obtained for the sodium excited *f* states.

In connection with the calculations of Ref. 8 quoted above, we wish to make the following comparison with our results of Table I for Na 3*d*, 4*d*, and 5*d*. Considering the results of Table I of Ref. 8, we see that the results of Holmgren, Lindgren, Morrison, and Mårtensson[8] (HLMM) for $\Delta\nu$ (Hartree-Fock plus polarization) amount to $\Delta\nu_{\text{HLMM},3d} = -37.7\,\text{mK}$, $\Delta\nu_{\text{HLMM},4d} = -26.9\,\text{mK}$, and $\Delta\nu_{\text{HLMM},5d} = -16.2\,\text{mK}$. These results are in almost complete agreement with those which the authors (SRD) have obtained, namely, $\Delta\nu_{\text{SRD},3d} = -36.4\text{mK}$, $\Delta\nu_{\text{SRD},4d} = -26.4\text{mK}$, and $\Delta\nu_{\text{SRD},5d} = -16.1\text{mK}$. Both sets of values are, however, significantly smaller in absolute magnitude than the corresponding experimental fine-structure splittings, namely, $\Delta\nu_{\text{expt},3d} = -49.4\text{mK}$, $\Delta\nu_{\text{expt},4d} = -34.3\text{mK}$, and $\Delta\nu_{\text{expt},5d} = -20.6\text{mK}$. The ratios

$$\rho_{\text{HLMM},nd} \equiv \Delta\nu_{\text{HLMM},nd} / \Delta\nu_{\text{expt},nd} \tag{15}$$

have the values $37.7/49.4 = 0.763$ for $3d$, $26.9/34.3 = 0.784$ for $4d$, and $16.2/20.6 = 0.786$ for $5d$. Obviously, the ratios

$$\rho_{\text{SRD},nd} \equiv \Delta\nu_{\text{SRD},nd} / \Delta\nu_{\text{expt},nd} \tag{16}$$

are almost the same as the corresponding ratios ρ_{HLMM}(0.737 for $3d$, 0.770 for $4d$, and 0.782 for $5d$).

This essential agreement seems to confirm the agreement of our polarization correction term $\Delta\nu_2$ with that of Holmgren *et al.*[8] The remaining effect, which is ~25% of $\Delta\nu_{\text{expt},nd}$, appears to be due to correlation effects, as we have concluded above (cf. Ref. 20) and as has also been concluded by Holmgren *et al.*[8] (see Fig. 9 of Ref. 8, which refers specifically to the correlation contribution to $\Delta\nu_{\text{expt}}$).

Concerning the limited agreement with experiment which has been obtained in a similar calculation, we refer to the paper of Beck and Odabasi (BO).[5] Considering Table VI of that paper (see p. 309), we note that the authors have obtained the following calculated value for $h\Delta\nu$ of the $3d$ state of Na: $h\Delta\nu = \Delta E = -3.454\times10^{-7}$ Ry, as compared to the experimental value -4.6×10^{-7} Ry, giving a ratio $\rho_{\text{BO},3d} = 3.454/4.6 = 0.751$, which is very close to the corresponding values of ρ_{3d} obtained in the present work (0.737) and from the paper of Holmgren *et al.*[8] (0.763).

In comparison with the other calculations, we should emphasize that the present results, which are based on the theory of Refs. 6 and 7, include the effect of all of the continuum states, in addition to the complete set of discrete states, through the use of the differential equation (5) for the complete perturbation $w_1(2p\rightarrow p)$. (A similar differential equation for the effect of a nuclear quadrupole-moment perturbation was first introduced by Sternheimer.[21])

We wish to make some comments on the striking difference between the large values of R for nd states in Na and the much smaller values of R for nf states. In fact, if we use the representative values $R(5d) = 2.442$ and $R(5f) = 0.0432$, the ratio is 56.5. Of course, this drastic difference between $R(nd)$ and $R(nf)$ is reflected in the fact that, while the nd fine structure is stongly inverted, the nf fine structure is normal, i.e., noninverted, and moreover nearly hydrogenic. We believe that this drastic change in the behavior of the fine structure is related to two other phenomena, which will be briefly described.

(i) The quantum defects δ_l decrease drastically in going from p and d states to f states, as is evident from the paper of Gallagher, Hill, and Edelstein[22] (see Fig. 8 and the discussion in Sec. VI of that paper). As was pointed out by Gallagher *et al.*,[22] the fact that the d states are inverted is probably the result of core penetration effects. More specifically, we have shown that unless the valence electron has a minimum overlap with the $2p$ core electrons, so that the exchange core-polarization effect is important, the fine structure will be normal, as is found for the nf states for which $|\Delta\nu_2| \ll \Delta\nu_1$. In connection with this argument, a special treatment is necessary for the np valence electrons, such as was carried out in Ref. 11. In this case, $\Delta\nu_2$ is not small, but $\Delta\nu_1$ is proportionately much larger because of the deep penetration of the valence p electrons (large quantum defects), so that we have again $\Delta\nu_2 \ll \Delta\nu_1$, and moreover $\Delta\nu_2 > 0$. Therefore, the fine structure of np states is normal and close to the value[10] calculated for $\Delta\nu_1$.

(ii) In three papers,[23-25] Sternheimer has discussed the existence of an ordering principle for the sequence of the excited-state energy levels of atoms and ions having one electron outside closed shells. This principle (which was called the "k ordering") applies in particular to the alkali-metal atoms and the singly ionized alkaline-earth ions. Here k is the sum $n+l$ of the principal and azimuthal quantum numbers of the state considered. On a scale of increasing energies E_{nl}, the states are ordered in groups having successively larger values of k $(=n+l)$. For a given value of k, the states are energy ordered according to a definite sequence of l values, which is called the "l pattern." As an example, the l pattern of rubidium is $pdsf$, and a typical sequence (for $k=7$) is $6p, 5d, 7s, 4f$. The k-ordering property and the constant l patterns persist up to $k=55$ for the case of rubidium.[23,25]

For the case of Na, the l pattern is $fdps$, e.g., $10f, 11d, 12p, 13s$ for $k=13$. However, the f level with $k=13$ lies in the region occupied by most of the $k=12$ levels. This exception to the k ordering has been called a "$k+\lambda$ exception," where λ in the present case equals -1, i.e., the $k=13$ level $10f$ lies in the region of $k=13-1=12$.

In Ref. 25, the nature of the $k+\lambda$ exceptions has been discussed in detail, and it was shown that they arise from the existence of a limiting angular momentum l_1 such that, for $l > l_1$, hydrogenic ordering prevails, i.e., the levels are arranged in groups having constant n values, and with the energy E_{nl} increasing slightly with increasing l, in the region from l_1 to $l_{\max}=n-1$. For the case of Na, it was shown that $l_1=2$. In Refs. 23–25 a tentative explanation of the k ordering for $l \leq l_1$ has been given in terms of a core-polarization effect of the same type as that which occurs in the calculation of the quadrupole antishielding factors[26,27] γ_∞ and R, and also in the calculation of the inverted fine structure for the nd states of Na and Rb.[6,7] In all three cases, it is necessary to have at least a minimum overlap of the valence-electron wave functions with the core-electron wave functions, so that core excitations of the type $v_1(nl \rightarrow l)$ or $w_1(nl \rightarrow l)$ [Eq. (5)] produce a significant overlap integral of the type of $K_k(nl \rightarrow l; n_v l_v)$ [Eq. (4)].

For the fine structure of Na nd and nf states, where $R_{nd} \sim 2.5$ whereas R_{nf} is only of the order of 0.05, the results for R_{nd} compared with those for R_{nf} strongly confirm the hypothesis in Ref. 25 that the existence of the k ordering for Na for states $l \leq 2$ is an effect which is indirectly related to the existence of the inverted fine structure for nd states, whereas for nf states the fine structure is normal (noninverted) and nearly hydrogenic. Correspondingly, for nf states $(l=3)$ and states of higher angular momentum $(l \geq 4)$, the energy ordering of the states is hydrogenic. The sharp break at $l=2$ in the energy differences between the states $E_{15,l}$ and $E_{15,l+1}$ of Na, i.e.,

$$\Delta E_{nl,l+1} \equiv E_{n,l+1} - E_{nl}, \qquad (17)$$

has also been discussed in Sec. II of Ref. 25.

Concerning the results of our calculations for Cs 4f, Cs 5f, and Cs 6f, as presented in the last three rows of Table I, we note that our theoretical values are in agreement concerning the sign with the observed inversion, although our numerical values are too large by about a factor of 2. Nevertheless, the sign and the decrease in the value of $\Delta\nu_1 + \Delta\nu_2$ with increasing n (in going from 4f to 6f) are in agreement with the trend of the experimental values of Moore,[1] which are listed in the fifth column of Table I.

However, in connection with the preceding discussion, it should be emphasized that the results for Cs 4f, 5f, and 6f in Table I cannot be considered very reliable since $|\Delta\nu_2/\Delta\nu_1|$ is so large (~25), which indicates that the third-order terms $\Delta\nu_3$ discussed above for Na nd are probably important in the present case. However, even if these terms should actually be positive, they are not likely to reverse the sign of the calculated $\Delta\nu = \Delta\nu_1 + \Delta\nu_2 + \Delta\nu_3$. In other words, the large negative second-order terms $\Delta\nu_2$ are clearly in the right direction, and we believe that they basically explain the observed negative (inverted) fine structure of the Cs 4f, 5f, and 6f states.[1] Nevertheless, in the absence of the relevant calculations of the third-order terms $\Delta\nu_3$, the present results for Cs nf must be viewed with caution, and they are certainly less reliable than those obtained above for Na nd and Na nf.

From the point of view of our previous discussion concerning Na nf, we note that for cesium, which is a much heavier atom $(Z=55)$, the fine structure of nf states is inverted, whereas for Na it is normal, i.e., noninverted, and nearly hydrogenic. The reason for this difference in behavior is that for the nf states of cesium the valence wave functions are still sufficiently internal to give a sizable exchange polarization, as is shown by the large negative values of $\Delta\nu_2$ in Table I. In other words, the overlap of the nf wave functions with the expanded core of Cs$^+$ (as compared with that of Na$^+$) is sufficient to reverse the sign of the fine structure. In this connection, we may note that the fine structure for d states in cesium is normal, i.e., noninverted, in similarity to the fine structure for p states in sodium. Thus the l value at which the inversion occurs is increased by one unit in going from Na to Cs.

This change of l value can be correlated to some extent with the increase of the limiting angular momentum l_1 for k ordering, which is ~2 units, since (as shown by Table I of Ref. 25), we have $l_1=2$ for Na and $l_1=4$ or 5 for Cs. The fact that l_1 is at least 4 for Cs indicates that possibly not only the nf states, but also the ng states for Cs will show an inverted fine structure. Experimental data on $\Delta\nu$ for ng states are not given in Moore's tables for cesium. However, in connection with the preceding discussion, it would be of interest to measure the fine structure of ng states of cesium.

In summary, the results for $\Delta\nu_{nf}$ of cesium provide additional confirmation of our two hypotheses, namely: (i) the negative fine-structure intervals for both Na nd and Cs nf are caused by the exchange core polarization involving the $np \rightarrow p$ and $nd \rightarrow d$ excitations of the core; and (ii) the existence of the limiting angular momentum l_1 and the k ordering itself are the result of the same exchange core polarization which is responsible for the inverted fine structure of certain high-angular-momentum states (nd for sodium, and nf and possibly ng for cesium). In addition, as pointed out in Refs. 23–25, the same type of $np \rightarrow p$ and $nd \rightarrow d$ excitations [see Eq. (5), with $f(r)$ replaced by $1/r^3$] are also responsible for the effects associated with the quadrupole antishielding factors[26,27] R and γ_∞.

III. SUMMARY

The main purpose of this paper is to present the results of additional calculations of the fine structure of excited states of sodium (Na) and cesium (Cs). The calculations for Na concern primarily the *nf* states, for which the fine structure is normal, i.e., noninverted ($^2F_{7/2}$ state *above* $^2F_{5/2}$ state), and the interval $\Delta\nu$ is slightly less than the hydrogenic value. It has been shown that the deviation from the hydrogenic value, as observed by Gallagher *et al.*,[12] can be explained as due to the negative exchange-core-polarization term $\Delta\nu_2$, for which values have been obtained for 4*f*, 5*f*, 6*f*, 11*f*, and 14*f*. The values of the ratio $-\Delta\nu_2/\Delta\nu_1$ are shown in Fig. 1 as a function of the principal quantum number *n*. The values of $\Delta\nu_2/\Delta\nu_1$ for Na 11*f* and Na 14*f*, namely, –7.0% and –7.3%, respectively, bring the calculated values of $\Delta\nu_1 + \Delta\nu_2$ into good agreement with the fine-structure intervals $\Delta\nu_{\text{expt}}$ observed by Gallagher, Cooke, Edelstein, and Hill.[12] This comparison is shown in Table I. This is particularly true for $\Delta\nu$(Na 14*f*) for which the agreement between the calculated value (0.1659mK) and the experimental value (0.167 ± 0.003mK) is almost perfect, as contrasted to the value 0.1789mK which would be obtained without the correction term $\Delta\nu_2$.

The results obtained for the Na *nd* states (3*d*, 4*d*, 5*d*, 11*d*, and 14*d*) are given in the first five rows of Table I. The agreement with the experimental values of Fabre, Gross, and Haroche[3] is not as close as in the corresponding situation for the Na 11*f* and 14*f* states. Nevertheless, the main feature of the fine structure inversion, $\Delta\nu < 0$ [i.e., the $^2D_{5/2}$ state lies *below* the $^2D_{3/2}$ state] is accurately reproduced, as is also the decrease of the experimental values of $|\Delta\nu_{\text{expt}}|$ with increasing principal quantum number *n*.

We have calculated the fine-structure intervals $\Delta\nu$ for the 4*f*, 5*f*, and 6*f* states of cesium. The calculated values are in agreement with the experimental inversion of the *nf*-state fine structure for Cs, although the numerical values of $|\Delta\nu_1 + \Delta\nu_2|$ are too large by a factor of ~2. However, these values cannot be considered as very reliable, because possibly important third-order terms have not been evaluated in the present work.

Finally, we have examined the relation between the inverted fine structure of the Na *nd* and Cs *nf* states, and the *k* ordering of the excited states of the alkali-metal atoms,[23-25] and, in particular, the limiting angular momentum l_1 for the existence of *k* ordering, as discussed in Ref. 25.

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