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

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We have calculated the second-order interaction between the spin-orbit coupling perturbation $H_{\rm so} \propto r^{-1}(dV/dr)\vec{l}\cdot\vec{s}$ 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. This calculation is extended to excited *np* states, and it is shown that the radial integrals have opposite sign to those for *nd*, resulting in a small increase of the calculated $\Delta\nu$ (by $\sim$ 10–20% in all cases). Specific results have been obtained for several excited *np* states of Na, K, Rb, and Cs, and give agreement to within 20–30% with the experimental fine-structure splittings $\Delta\nu_{\rm expt}$.

I. INTRODUCTION

We have calculated the second-order interaction arising from the spin-orbit coupling perturbation

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

acting on the core electrons and the exchange part of the Coulomb interaction $2/r_{12}$ Ry between the valence electron and the core electrons. This calculation was previously carried out for two alkali *nd* states (Na 3*d* and Rb 4*d*),[1,2] and was shown to result in an inversion or near cancellation of the fine-structure interval $\Delta\nu$, such as is actually observed.[3] Specifically,[1] for Na 3*d*, the observed $\Delta\nu_{\rm expt}$ is -0.049 cm^{-1}; the first-order ("normal") term $\Delta\nu_1$ is $+0.052$ cm^{-1}, and the calculated second-order term $\Delta\nu_2 = -0.133$ cm^{-1}, giving a total $\Delta\nu = -0.081$ cm^{-1}, in reasonable agreement with $\Delta\nu_{\rm expt}$.[4] Similar results were obtained[2,5] for Rb 4*d*. Two calculated values were obtained,[5] namely, -9.1 and $+7.0$ cm^{-1}, using the Hartree-Fock (HF) and energy-adjusted[6] (EA) valence (4*d*) wave functions, respectively. These results bracket the experimental value,[3] -0.44 cm^{-1}. More accurate calculations for Rb 4*d* are in progress.[7]

Since for the alkali *np* states the observed $\Delta\nu$ is positive ($^2P_{3/2}$ state *above* the $^2P_{1/2}$ level), and its value is approximately equal to the first-order result[8] $\Delta\nu_1$, it is of interest to calculate the second-order terms $\Delta\nu_2$ for these excited *np* states.[9] We note that the second-order interaction involves the $np \to p$ and $nd \to d$ excitations of the core *np* and *nd* electrons by the magnetic spin-orbit interaction $H_{\rm SO}$. (Hence there is no effect for Li, which has no internal *np* electrons.) It was found that the radial integrals involved for $\Delta\nu_2$ have sign opposite to those for valence *nd* states, resulting in a modest *increase* of the calculated $\Delta\nu$, i.e., $\Delta\nu_2 > 0$, so that $\Delta\nu_1 + \Delta\nu_2 \sim 1.2\Delta\nu_1$, and no cancellation occurs of the type found for *nd* states, in agreement with experiment.[3]

In Sec. II, the equations for $\Delta\nu_2$ will be derived for the general case of a valence electron in an arbitrary l state, denoted by l_v. Specific results for the angular coefficients will be given for valence *np*, *nd*, and *nf* electrons ($l_v = 1$, 2, and 3, respectively). The general equation for the radial integrals will also be derived.

In Sec. III, the results of Sec. II for $l_v = 1$ will be applied to calculate $\Delta\nu_2$ for the alkali-metal–atom *np* states, using both the HF valence wave functions for the valence electrons and the corresponding EA wave functions. The latter functions are derived from a potential which reproduces the observed energy eigenvalues, i.e., the observed ionization potentials. The derivation of the EA wave functions, which have been used extensively in earlier work,[6] will be discussed in some detail.

Finally, in Sec. IV, the results for $\Delta\nu_1 + \Delta\nu_2$ obtained in the present work will be summarized and discussed.

II. EQUATIONS FOR $\Delta\nu_2$

As an example of the calculation of $\Delta\nu_2$, we will consider the second-order term $\Delta\nu_2$ for the 3*p* state of sodium, where the interaction is with the 2*p* shell only, i.e., with the excitations $2p \to p$ produced by the second-order perturbation described below.

We are considering the second-order interaction between the exchange part of the electrostatic interaction of the electrons H_Q and the spin-orbit Hamiltonian H_{SO}, both taken in first order. The corresponding second-order energy ΔE_2 is given by[1,2]

$$\Delta E_2 = -2 \sum_n \frac{\langle 3p, 2p \,|H_Q|\, np, 3p\rangle \langle np, 3p \,|H_{\mathrm{SO}}|\, 2p, 3p\rangle}{E_{3p,2p} - E_{3p,np}}, \tag{1}$$

where the sum $\sum_n$ signifies a sum over the excited *np* states plus an integral over the continuum *kp* states.

The perturbation Hamiltonians H_Q and H_{SO} are given by

$$H_Q = 2/r_{12} \text{ Ry}, \tag{2}$$

$$H_{\mathrm{SO}} = \frac{2\mu_0^2}{e^2} \frac{1}{r} \frac{dV}{dr} \vec{1} \cdot \vec{s}, \tag{3}$$

where μ_0 is the Bohr magneton, V is the central atomic potential, r_{12} is the distance between electrons 1 and 2 [which are involved in Eq. (1)], and $\vec{l}$ and $\vec{s}$ have their usual meaning.

The exchange interaction in the first factor of Eq. (1) can be written out in more detail as

$$\langle 3p(1), 2p(2) \,|H_Q|\, np(1), 3p(2)\rangle,$$

where the parentheses correspond to electrons 1 and 2.

In Eq. (1), the sum over n (and the integral over continuum states) can be carried out by considering the function

$$W \equiv \sum_n \frac{\langle np, 3p \,|H_{\mathrm{SO}}|\, 2p, 3p\rangle \Psi(np, 3p)}{E_{3p,2p} - E_{3p,np}}. \tag{4}$$

The function W can be written

$$W = (\text{angular factor}) \times (1/r) \times w_1(2p \to p), \tag{5}$$

where $w_1(2p \to p)$ is determined by the differential equation

$$\left(-\frac{d^2}{dr^2} + \frac{2}{r^2} + V_0 - E_0\right) w_1(2p \to p) = [\langle f(r)\rangle_{2p} - f(r)] u_0(2p). \tag{6}$$

In Eq. (6), $f(r)$ is defined as

$$f(r) \equiv \frac{1}{r} \frac{dV}{dr} \sim \frac{2Z}{r^3} \text{ Ry}. \tag{7}$$

V_0 and E_0 are the unperturbed (spherical) potential and energy eigenvalue, respectively.

The combination $V_0 - E_0$ is determined from the unperturbed wave function (times r) $u_0(2p)$ by means of the equation[10]

$$V_0 - E_0 = \frac{1}{u_0(2p)} \frac{d^2 u_0(2p)}{dr^2} - \frac{2}{r^2}. \tag{8}$$

Equation (6) is completely similar to the equation which has been introduced by one of us[10] to describe quadrupole shielding and antishielding effects for the quadrupole hyperfine structure. In the corresponding equation, $1/r^3$ replaces $f(r)$.

We also note that in complete analogy to the antishielding case we must demand that $w_1(2p \to p)$ satisfy the orthogonality condition

$$\int_0^\infty w_1(2p \to p) u_0(2p)\, dr = 0. \tag{9}$$

From the expansion of $2/r_{12}$ in spherical harmonics, we obtain

$$H_Q = \frac{2}{r_{12}} = 8\pi \sum_k \frac{1}{2k+1} \frac{r_<^k}{r_>^{k+1}} \sum_{m=-k}^{+k} (-1)^m Y_k^m(1) Y_k^{-m}(2), \tag{10}$$

where Y_k^m is the usual normalized spherical harmonic and $r_<$ and $r_>$ are the smaller and larger, respectively, of r_1 and r_2.

In terms of $f(r)$, the term H_{SO} can be written

$$H_{\mathrm{SO}} \propto f(r) l_z s_z = \tfrac{1}{2} f(r) m, \tag{11}$$

where $s_z = \frac{1}{2}$, and m is the magnetic quantum number ($m = l_z$) of the inner-shell ($2p$) electron.

Upon inserting Eqs. (10) and (11) into Eq. (1), we obtain an angular factor here denoted by $C_k(l; l_v)$ (l_v is the angular momentum quantum number of the valence electron; here $l_v = 1$):

$$C_k(l; 1) = \frac{4\pi}{2k+1} \sum_{m=-l}^{l} m(\langle lm \,|Y_k^q|\, 11\rangle)^2, \tag{12}$$

where we have considered the "stretched" state of the valence electron; i.e., the state $m = +1$, $s_z = +\frac{1}{2}$ of $3p$ for Na. In Eq. (12), the value of the magnetic quantum number q of Y_k^q is given by $m = q + 1$, i.e., $q = m - 1$.

In terms of $w_1(2p \to p)$, ΔE_2 [Eq. (1)] involves the following double radial integral

$$K_k(2p \to p; 3p) = \int_0^\infty u_0(2p) v_0(3p)\, dr \left(\frac{1}{r^{k+1}} \int_0^r w_1(2p \to p) v_0(3p) r'^k\, dr' + r^k \int_r^\infty w_1(2p \to p) v_0(3p) r'^{-k-1} dr'\right). \tag{13}$$

With $l = 1$ in the present case (exchange with the $2p$ electrons), it can be readily seen from Eq. (12) that only the terms $k = 0$ and $k = 2$ can contribute to $\Delta\nu_2$.

The second-order energy splitting $\Delta\nu_2$ (contribution to the fine structure $\Delta\nu$) is given by

$$\Delta\nu_2 = -\tfrac{3}{2}\alpha^2 R[C_0(1; 1) K_0(2p \to p; 3p) + C_2(1; 1) K_2(2p \to p; 3p)]. \tag{14}$$

The factor $-\frac{3}{2}\alpha^2 R = -8.7650$ cm^{-1}. For $C_0(1;1)$ only the term $m=1$ contributes, and it can be readily shown that $C_0(1;1)=1$. For $C_2(1;1)$ both the $m=+1$ and $m=-1$ core states contribute.

In order to evaluate the integrals $\langle lm|Y_2^q|11\rangle$, we note that by virtue of the definition of the Condon-Shortley coefficients[11] $c^k(lm_l;l'm_l')$ we find

$$[4\pi/(2k+1)](\langle lm|Y_k^q|l'm'\rangle)^2 = [c^k(lm;l'm')]^2 . \tag{15}$$

This equation follows simply if we note that $Y_k^q = (2\pi)^{-1/2}\Theta(k,q)e^{iq\phi}$, where $q = m_l - m_l'$ in the Condon and Shortley (CS) notation.[11] Combining the factor $(2\pi)^{1/2}$ with $[2/(2k+1)]^{1/2}$, Eq. (6) of CS, and squaring gives the desired factor $4\pi/(2k+1)$.

The values of $c^k(lm;l'm')$ are tabulated on pp. 178 and 179 of Ref. 11. In view of Eq. (15), Eq. (12) can be rewritten

$$C_k(l;1) = \sum_{m=-l}^{l} m[c^k(lm;11)]^2 . \tag{16}$$

Now we find[11] $[c^2(11;11)]^2 = \frac{1}{25}$ and $[c^2(1,-1;11)]^2 = \frac{6}{25}$, giving

$$C_2(1;1) = \tfrac{1}{25}(+1) + \tfrac{6}{25}(-1) = -\tfrac{1}{5} . \tag{17}$$

As a generalization of Eq. (16), we can write for the case of a valence electron with angular momentum l_v, and considering again the "stretched" state for which the magnetic quantum number m_v equals l_v,

$$C_k(l;l_v) = \sum_{m=-l}^{l} m[c^k(lm;l_v l_v)]^2 . \tag{18}$$

The radial integral $K_k(nl\to l;n_v l_v)$ which appears in the case of arbitrary l_v is given by

$$K_k(nl\to l;n_v l_v) = \int_0^\infty dr\, u_0(nl)v_0(n_v l_v)\left(\frac{1}{r^{k+1}}\int_0^r w_1(nl\to l)v_0(n_v l_v)r'^k dr' + r^k\int_r^\infty w_1(nl\to l)v_0(n_v l_v)r'^{-k-1}dr'\right) . \tag{19}$$

Here n_v is the principal quantum number of the valence electron; $v_0(n_v l_v)$ is the radial part of the valence wave function (times r), normalized to 1, in the same manner as the core wave function $u_0(nl)$, i.e.,

$$\int_0^\infty [v_0(n_v l_v)]^2 dr = \int_0^\infty [u_0(nl)]^2 dr = 1 . \tag{20}$$

We also note that the core electron perturbation (times r) $w_1(nl\to l)$ satisfies an equation which is the generalization of Eq. (6),

$$\left(-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_0 - E_0\right)w_1(nl\to l) = [\langle f(r)\rangle_{nl} - f(r)]u_0(nl), \tag{21}$$

and the orthogonality condition [cf. Eq. (9)],

$$\int_0^\infty w_1(nl\to l)u_0(nl)\,dr = 0 . \tag{22}$$

The appropriate general equation which replaces Eq. (14) is

$$\Delta\nu_2 = -\frac{2l_v+1}{2}\alpha^2 R\sum_k C_k(l;l_v)K_k(nl\to l;n_v l_v), \tag{23}$$

where $\alpha^2 R = 5.8434$ cm^{-1}. For comparison, the first-order term $\Delta\nu_1$ of the fine-structure splitting is given by

$$\Delta\nu_1 = \tfrac{1}{4}(2l_v+1)\alpha^2 R I, \tag{24}$$

where the integral I is given by

$$I \equiv \int_0^\infty f(r)[v_0(n_v l_v)]^2 dr = \int_0^\infty \frac{1}{r}\frac{dV}{dr}[v_0(n_v l_v)]^2 dr, \tag{25}$$

with V in Rydberg units and r in atomic units of the Bohr radius a_H.

The values of $C_k(l;l_v)$ have been calculated for p, d, and f valence electrons ($l_v = 1,2,3$), interacting with the $np\to p$ and $nd\to d$ ($l=1$, $l=2$) excitations of the core produced by the spin-orbit coupling interaction H_{SO}.

The resulting values, obtained using the CS tables of $c^k(lm;l'm_l')$, are presented in Table I. We have previously calculated the results for $l_v=2$,[5] where Eq. (18) had also been stated for the case $l_v=2$ (valence d electron), and the present derivation is patterned on the derivation given there. The radial integrals and resulting $\Delta\nu_2$ values for Rb $4d$ were also evaluated there and elsewhere.[2] The value $\frac{2}{5}$ for $C_1(1;2)$ has also been independently evaluated in Ref. 1. We note that in Table I of the present paper the values of $C_{k_i}(l;l_v)$ for the various

TABLE I. Values of the angular coefficients $C_{k_i}(l;l_v)$ for $l=1,2$ and $l_v=1,2,3$. The appropriate value of k_i for each contributing multipolarity is listed in parentheses after the value of C_{k_i}.

l_v	l	$C_{k_1}(k_1)$	$C_{k_2}(k_2)$	$C_{k_3}(k_3)$
1	1	1 (0)	$-\frac{1}{5}$ (2)	
1	2	1 (1)	$-\frac{3}{7}$ (3)	
2	1	$\frac{2}{5}$ (1)	$-\frac{6}{35}$ (3)	
2	2	2 (0)	$\frac{2}{7}$ (2)	$-\frac{8}{21}$ (4)
3	1	$\frac{9}{35}$ (2)	$-\frac{1}{7}$ (4)	
3	2	$\frac{6}{7}$ (1)	$\frac{1}{7}$ (3)	$-\frac{275}{847}$ (5)

contributing multipolarities k_i are listed in separate columns, with the value of k_i given in parentheses in each case after the value of $C_{k_i}(l; l_v)$.

Concerning the radial integrals $K_k(nl \rightarrow l; n_v 1)$ for *np* states ($l_v = 1$), the essential result is that for *np* states the integrals K_0 and K_2 are *negative* and relatively small (compared to I), so that with the negative sign in front of Eq. (14) we find $\Delta\nu_2 > 0$, i.e., $\Delta\nu_2$ has the same sign as $\Delta\nu_1$ [which is intrinsically positive; see Eq. (25), in which $dV/dr > 0$]. This result is in sharp contrast to the situation for *nd* states, where the corresponding integrals K_1 and K_3 are positive and relatively large, so that $\Delta\nu_2 < 0$, and is of the same order as $\Delta\nu_1$, leading to the approximate cancellation of $\Delta\nu_1$, or even an inversion of the fine structure ($\Delta\nu_1 + \Delta\nu_2 < 0$), such as is actually observed in several cases.[3] The evaluation of the integrals K_0 and K_2 for valence *np* states will be discussed in some detail in Sec. III. Here we merely note that the preceding discussion has tacitly assumed that the dominant coefficients $C_k(l; l_v)$ are positive, and this is indeed the case, as can be seen from Table I. In connection with the negative values of $C_2(1;1) = -\frac{1}{5}$ and $C_3(2;1) = -\frac{3}{7}$, we should mention that these are considerably smaller numerically than $C_0(1;1) = 1$ and $C_1(2;1) = 1$, respectively, and moreover, the radial integrals $K_k(nl \rightarrow l; n_v l_v)$ have a tendency to decrease somewhat with increasing k. A similar comment applies to the situation for $l_v = 2$, $l = 1$ (external *d* electron), where $C_3(1;2) = -\frac{6}{35}$ is appreciably smaller than $C_1(1;2) = \frac{2}{5}$, although having opposite sign. In fact, the ratios $C_3(2;1)/C_1(2;1)$ and $C_3(1;2)/C_1(1;2)$ are both equal to $-\frac{3}{7}$.

III. CALCULATIONS FOR THE ALKALI ATOM *np* STATES

We have carried out the calculations of $\Delta\nu_1$ and $\Delta\nu_2$ for the first few excited *np* states of the alkali-metal atoms Na, K, Rb, and Cs, using two types of radial valence (*np*) wave functions. First we note that since lithium has a $1s^2$ electron core, with no *p* electrons, $\Delta\nu_2$ for this case will be zero, in as much as only $np \rightarrow p$ (and $nd \rightarrow d$) excitations of the core can contribute to the effect.

In the first part of the calculations, we have used the HF wave functions of the valence electron for Na 3*p*, 4*p*, 5*p*, K 4*p*, 5*p*, 6*p*, Rb 5*p*, 6*p*, and Cs 6*p*, 7*p*. The HF wave functions were obtained by using a modification of the Froese-Fischer computing program.[12] The resulting values of $\Delta\nu_1$, $\Delta\nu_2$, and $(\Delta\nu_1 + \Delta\nu_2)/\Delta\nu_{\text{expt}}$ are presented in Table II. The values of $\Delta\nu_1 + \Delta\nu_2$, the ratios $(\Delta\nu_1 + \Delta\nu_2)/\Delta\nu_1$, and the experimental values $\Delta\nu_{\text{expt}}$ are listed in Table II. The values of $\Delta\nu_{\text{expt}}$ were obtained from the tables of Moore.[3]

For K, Rb, and Cs, more than one shell of the core contributes to $\Delta\nu_2$. For this reason, we have tabulated in Tables III–V the individual core contributions $\Delta\nu_2(nl \rightarrow l)$ for K, Rb, and Cs, respectively. (For Na, the only contribution arises from $2p \rightarrow p$). In all cases, except for the small terms arising from $4d \rightarrow d$ of Cs and $3d \rightarrow d$ of Rb, the integrals $K_k(nl \rightarrow l; n_v l_v)$ are negative, leading to a positive sign of $\Delta\nu_2(nl \rightarrow l)$, on account of the negative sign in Eq. (23) for $\Delta\nu_2$.

As can be seen from Table II, $\Delta\nu_2/\Delta\nu_1$ lies in the range 0.12–0.18 in all cases. Thus the second-order term produces a modest *increase* of the fine-structure splitting. This result is in marked contrast to the results previously obtained for two *nd* states, namely, Na 3*d* (Ref. 1) and Rb 4*d* (Refs. 2 and 5), in which $\Delta\nu_2$ is negative and counteracts strongly the effect of the (positive) first-order term $\Delta\nu_1$, i.e., $\Delta\nu_2 \sim -2\Delta\nu_1$ for Na 3*d* and $\Delta\nu_2 \sim -\Delta\nu_1$ for Rb 4*d*. These results provide an explanation of the negative fine-structure interval which has been observed for these two *nd* states.[3]

TABLE II. Values of $\Delta\nu_1$, $\Delta\nu_2$, and the total $\Delta\nu_1 + \Delta\nu_2$ (in units of cm^{-1}) for HF valence electron wave functions. The experimental values $\Delta\nu_{\text{expt}}$ (Ref. 3) and the ratios $(\Delta\nu_1 + \Delta\nu_2)/\Delta\nu_1$ and $(\Delta\nu_1 + \Delta\nu_2)/\Delta\nu_{\text{expt}}$ are also listed.

State	$\Delta\nu_1$	$\Delta\nu_2$	$\Delta\nu_1 + \Delta\nu_2$	$\frac{\Delta\nu_1 + \Delta\nu_2}{\Delta\nu_1}$	$\Delta\nu_{\text{expt}}$	$\frac{\Delta\nu_1 + \Delta\nu_2}{\Delta\nu_{\text{expt}}}$
Na 3*p*	13.445	2.022	15.467	1.150	17.196	0.899
4*p*	4.483	0.661	5.144	1.147	5.63	0.914
5*p*	2.000	0.293	2.293	1.147	2.52	0.910
K 4*p*	38.70	6.83	45.53	1.176	57.72	0.789
5*p*	13.19	2.25	15.44	1.171	18.76	0.823
6*p*	6.03	1.01	7.04	1.167	8.41	0.837
Rb 5*p*	146.41	24.78	171.19	1.169	237.60	0.720
6*p*	50.55	8.15	58.70	1.161	77.50	0.757
Cs 6*p*	305.70	54.53	360.23	1.178	554.11	0.650
7*p*	107.70	12.84	120.54	1.119	181.01	0.666

TABLE III. Contributions $\Delta\nu_2(nl \rightarrow l)$ of the core states $nl = 2p$ and $3p$ to the total $\Delta\nu_2$ of K $4p$, $5p$, and $6p$ for HF valence wave functions.

State	$3p$	$2p$	Total
K $4p$	5.22	1.61	6.83
$5p$	1.692	0.556	2.248
$6p$	0.761	0.249	1.010

TABLE V. Contributions $\Delta\nu_2(nl \rightarrow l)$ of the various core states (nl) to the total $\Delta\nu_2$ of Cs $6p$ and $7p$ for HF valence wave functions

State	$5p$	$4p$	$3p$	$2p$	$4d$	$3d$	Total
Cs $6p$	37.13	12.01	3.65	2.54	−0.811	+0.010	54.53
$7p$	8.09	2.85	1.28	0.90	−0.280	+0.004	12.84

Concerning the detailed agreement of the theoretical values $\Delta\nu_1 + \Delta\nu_2$ with the experimental values $\Delta\nu_{\text{expt}}$, we can conclude from Table II that the results $\Delta\nu_1$ obtained with the HF wave functions are far too small, with the discrepancy increasing with increasing Z. This situation arises from the fact that the HF functions are appreciably too external, since they do not include the correlation effects with core electrons of antiparallel spin. Correspondingly, the HF wave functions give a binding energy which is too small by an amount which increases as we go to the heavier alkali-metal atoms. This shortcoming of the HF valence wave functions has been previously discussed on a number of occasions by one of us,[6] in particular in connection with the calculation of the electronic dipole and quadrupole polarizabilities α_d and α_q of the alkali-metal atoms[13] and the calculation of the quadrupole antishielding factor R for these atoms.[14] For this reason, we have frequently used in our past work EA wave functions which reproduce the observed ionization potentials of the outermost (valence) electron in various ns, np, and nd states.[6,13,14] These EA wave functions will be used in the second part of the present calculations (see below).

It can also be seen from Table II that the additional terms $\Delta\nu_2$, although they are positive, are insufficient to produce agreement with the experimental values $\Delta\nu_{\text{expt}}$. This is particularly true for the heavier alkali-metal atoms Rb and Cs. In fact, the last column of Table II shows that the disagreement with experiment increases regularly with increasing Z; thus $(\Delta\nu_1 + \Delta\nu_2)/\Delta\nu_{\text{expt}}$ decreases from ~0.90 for Na to ~0.66 for Cs. Of course, it should be mentioned that a part of this disagreement may be due to the neglect of relativistic effects. However, such effects would hardly be expected to be large enough for Na np and K np.

TABLE IV. Contributions $\Delta\nu_2(nl \rightarrow l)$ of the various core states (nl) to the total $\Delta\nu_2$ of Rb $5p$ and $6p$ for HF valence wave functions.

State	$4p$	$3p$	$2p$	$3d$	Total
Rb $5p$	18.54	4.330	2.181	−0.276	24.775
$6p$	5.995	1.490	0.753	−0.093	8.145

The main result of Tables III–V for the terms $\Delta\nu_2(nl \rightarrow l)$ is that the predominant term in every case is $\Delta\nu_2(n_0 p \rightarrow p)$, where n_0 is the principal quantum number of the outermost filled p shell of the core, i.e., $3p \rightarrow p$ for K, $4p \rightarrow p$ for Rb, and $5p \rightarrow p$ for Cs. It should also be noted that for the $np \rightarrow p$ terms, $\Delta\nu_2(np \rightarrow p)$ decreases regularly with decreasing n, for all of the excited states considered in Tables III–V. For the most external d state of the core, as already mentioned, $\Delta\nu_2(nd \rightarrow d)$ is negative for both Rb $(3d \rightarrow d)$ and Cs$(4d \rightarrow d)$. However, these negative terms are small in absolute magnitude compared even to the small $\Delta\nu_2(2p \rightarrow p)$ terms in all four cases (Rb $5p$, and $6p$ and Cs $6p$, and $7p$). Finally, the $\Delta\nu_2(3d \rightarrow d)$ terms are negligible for Cs $6p$ and $7p$.

The results obtained using EA wave functions are presented in Tables VI–IX. The results for $\Delta\nu_1$ in Table VI have been previously obtained by one of us and Peierls in Ref. 8 (see Table I of Ref. 8). The values of $\Delta\nu_2$ obtained in the present work are listed in the third column of Table VI. These values are positive (as for the HF functions), and rather small compared to $\Delta\nu_1$. Thus the ratios $\Delta\nu_2/\Delta\nu_1$ lie between 0.09 and 0.20 in all cases. In this case, in contrast to the results for HF functions, the calculated results, namely, the values of $\Delta\nu_1 + \Delta\nu_2$, are somewhat larger than $\Delta\nu_{\text{expt}}$, with the ratios $(\Delta\nu_1 + \Delta\nu_2)/\Delta\nu_{\text{expt}}$ ranging from 1.22 to 1.36.

The individual terms $\Delta\nu_2(nl \rightarrow l)$ which contribute to $\Delta\nu_2$ are tabulated in Tables VII–IX. The results are very similar to those obtained with HF wave functions in Tables III–V. The predominant terms are again $\Delta\nu_2(n_0 p \rightarrow p)$, where n_0 is the principal quantum number of the outermost filled p shell of the core. The terms $\Delta\nu_2[(n_0 - 1)p \rightarrow p]$ and $\Delta\nu_2[(n_0 - 2)p \rightarrow p]$ are progressively smaller, in similarity to Tables III–V. Also for the $nd \rightarrow d$ excitations, $\Delta\nu_2(3d \rightarrow d)$ of Rb np and $\Delta\nu_2(4d \rightarrow d)$ of Cs np are small and negative, due to the positive values of the corresponding radial integrals and the minus sign of Eq. (23). However, these $|\Delta\nu_2(nd \rightarrow d)|$ terms are essentially negligible, being smaller than $\Delta\nu_2(2p \rightarrow p)$ in all cases. Finally, the $\Delta\nu_2(3d \rightarrow d)$ terms of Cs are exceedingly small and posi-

TABLE VI. Values of $\Delta\nu_1$, $\Delta\nu_2$, and the total $\Delta\nu_1+\Delta\nu_2$ (in units of cm^{-1}) for the EA valence electron wave functions of Ref. 14. The experimental values $\Delta\nu_{\text{expt}}$ (Ref. 3) and the ratios $(\Delta\nu_1+\Delta\nu_2)/\Delta\nu_1$ and $(\Delta\nu_1+\Delta\nu_2)/\Delta\nu_{\text{expt}}$ are also listed.

State	$\Delta\nu_1$	$\Delta\nu_2$	$\Delta\nu_1+\Delta\nu_2$	$\frac{\Delta\nu_1+\Delta\nu_2}{\Delta\nu_1}$	$\Delta\nu_{\text{expt}}$	$\frac{\Delta\nu_1+\Delta\nu_2}{\Delta\nu_{\text{expt}}}$
Na 3p	18.731	3.322	22.053	1.177	17.196	1.282
4p	6.099	1.073	7.172	1.176	5.63	1.274
5p	2.729	0.487	3.216	1.178	2.52	1.276
K 4p	62.90	12.74	75.64	1.203	57.72	1.310
5p	20.14	3.94	24.08	1.196	18.76	1.284
6p	9.00	1.75	10.75	1.194	8.41	1.278
Rb 5p	265.36	24.72	290.08	1.093	237.60	1.221
6p	87.88	8.59	96.47	1.098	77.50	1.245
7p	40.18	4.03	44.21	1.100	35.09	1.260
Cs 6p	652.86	103.12	755.98	1.158	554.11	1.364
7p	203.89	29.24	233.13	1.143	181.01	1.288
8p	93.35	13.19	106.54	1.141	82.64	1.289

tive (Table IX), in the same manner as the corresponding $\Delta\nu_2(3d\to d)$ terms calculated using HF wave functions (Table IV).

In connection with Tables V–IX, we note that we have obtained results for the EA wave functions $v_0(np)$ for the first three excited np states of the four alkali-metal atoms Na, K, Rb, and Cs. These EA wave functions were first obtained by one of us and Peierls in Ref. 14. The wave functions were obtained from the condition[6] that the calculated energy E_0 in the Schrödinger equation for the effective potential V_{eff} must reproduce the observed atomic eigenvalue, i.e., the ionization potentials for the various np states. Thus the equation solved to obtain V_{eff} is given by

$$\left(-\frac{d^2}{dr^2}+\frac{2}{r^2}+V_0+a\left|V_{\text{exch}}\right|-E_0\right)v_0(np)=0, \qquad (26)$$

where E_0 is the *experimental* energy eigenvalue[3] pertaining to np, and Eq. (26) is treated as an eigenvalue equation for the parameter a. We have

$$V_{\text{eff}}=V_0+a\left|V_{\text{exch}}\right|. \qquad (27)$$

The exchange potential is used merely as a shape function for the correction term $\delta V\equiv V_{\text{eff}}-V_0$. For V_{exch}, we took the Slater exchange[15] (with the Gáspár-Kohn-Sham[16] correction factor of $\frac{2}{3}$):

$$V_{\text{exch}}=-4[(3/8\pi)\rho]^{1/3}\ \text{Ry}, \qquad (28)$$

where ρ is the HF density of the electrons of the core. In Eq. (26), V_0 is taken as a potential which reproduces the energy of the valence s state, $(n_0+1)s$, so that the correction term $a\left|V_{\text{exch}}\right|$, and hence the parameter a, is usually quite small, i.e., $|a|\lesssim 0.05$. For Na, we used the empirical potential V_0 obtained by Prokofjew[17]; for K, a potential derived by one of us[18] was employed; for Rb, the potential of Callaway and Morgan[19] was used; while for Cs, we utilized a potential derived by one of us.[6]

From the results of Tables II and VI, in particular the values of $(\Delta\nu_1+\Delta\nu_2)/\Delta\nu_{\text{expt}}$, it can be concluded that (i) the calculations reproduce on the whole the vast changes of $\Delta\nu_{\text{expt}}$ in going from Na 5p (2.52 cm^{-1}) to Cs 6p (554.11 cm^{-1}); (ii) however, if we are looking for detailed agreement, i.e., to better than 20–30%, neither the HF nor the EA calculations are able to give this degree of agreement. The HF wave functions underestimate the observed fine-structure splittings, in particular, for Rb and Cs. Thus if we denote the ratio $(\Delta\nu_1+\Delta\nu_2)/\Delta\nu_{\text{expt}}$ by $\mathcal{R}$, we find $\mathcal{R}_{\text{HF}}(\text{Rb }5p)=0.720$ and $\mathcal{R}_{\text{HF}}(\text{Cs }6p)=0.650$. On the other hand, the EA wave functions overestimate $\Delta\nu_{\text{expt}}$ by about the same relative amount. In particular, we find $\mathcal{R}_{\text{EA}}(\text{Rb }5p)$

TABLE VII. Contributions $\Delta\nu_2(nl\to l)$ of the core states $nl=2p$ and $3p$ to the total $\Delta\nu_2$ of K 4p, 5p, and 6p for EA valence wave functions.

State	3p	2p	Total
K 4p	10.62	2.12	12.74
5p	3.255	0.682	3.937
6p	1.442	0.306	1.748

TABLE VIII. Contributions $\Delta\nu_2(nl\to l)$ of the various core states (nl) to the total $\Delta\nu_2$ of Rb 5p, 6p, and 7p for EA valence wave functions.

State	4p	3p	2p	3d	Total
Rb 5p	15.24	6.138	3.770	−0.425	24.723
6p	5.392	2.075	1.254	−0.136	8.585
7p	2.561	0.959	0.575	−0.062	4.033

TABLE IX. Contributions $\Delta\nu_2(nl \rightarrow l)$ of the various core states (nl) to the total $\Delta\nu_2$ of Cs $6p$, $7p$, and $8p$ for EA valence wave functions.

State	$5p$	$4p$	$3p$	$2p$	$4d$	$3d$	Total
Cs $6p$	75.76	15.06	7.73	6.00	−1.48	+0.05	103.12
$7p$	20.73	4.66	2.41	1.87	−0.45	+0.016	29.24
$8p$	9.29	2.14	1.10	0.86	−0.20	+0.007	13.20

$= 1.221$ and $\mathcal{R}_{\mathrm{EA}}(\mathrm{Cs}\ 6p) = 1.364$.

It thus appears that in order to obtain complete agreement with $\Delta\nu_{\mathrm{expt}}$, we require for both HF and EA valence wave functions (i) relativistic corrections (especially for the case of Cs) and (ii) higher-order terms $\Delta\nu_3(n_1l_1 \rightarrow l_1\ n_2l_2 \rightarrow l_2)$, involving the excitation of two core electrons n_1l_1 and n_2l_2, by the combination of the spin-orbit interaction H_{SO} and the electron-electron interaction $H_Q = 2/r_{ij}$, acting both between two core electrons and either core electron and the valence electron.

IV. SUMMARY AND DISCUSSION

We have calculated the second-order terms $\Delta\nu_2$ for several excited np states of the alkali-metal atoms (Na, K, Rb, and Cs). It was found that these terms are positive and small compared to the first-order terms $\Delta\nu_1$ (~10–20%), thus resulting in a modest increase of the calculated fine-structure splitting $\Delta\nu = \Delta\nu_1 + \Delta\nu_2$. The HF valence electron (np) wave functions give calculated values of $\Delta\nu$ which are smaller than the experimental values by an amount ranging from ~10% for Na np to 35% for Cs $6p$ and $7p$. On the other hand, the EA valence wave functions[14] give values of $\Delta\nu$ which are too large (as compared to $\Delta\nu_{\mathrm{expt}}$) by ~20–30% in all cases. Nevertheless, the general trend of the experimental results is well reproduced by the calculations. This trend consists of an increase by a factor >200 between the smallest $\Delta\nu_{\mathrm{expt}} = 2.52$ cm^{-1} for Na $5p$ and the largest $\Delta\nu_{\mathrm{expt}} = 554.11$ cm^{-1} for Cs $6p$.

It has been concluded from these results that while general agreement with the trend of the $\Delta\nu_{\mathrm{expt}}$ values has been obtained, nevertheless, in order to obtain detailed agreement with the individual $\Delta\nu_{\mathrm{expt}}$ values, it is necessary to include third-order terms $\Delta\nu_3$ for both the HF and the EA wave functions. The HF valence wave functions $[v_0(nl)]_{\mathrm{HF}}$ are considerably too external, because the electrostatic correlation effects with core electrons of antiparallel spin are not included in the HF calculations. This point has already been extensively discussed by one of us in connection with calculations of the dipole and quadrupole polarizabilities[13] α_d and α_q and of the quadrupole antishielding factors[14] R of the alkali-metal atoms.

On the other hand, earlier work on the first-order fine-structure splittings $\Delta\nu_1$ (Ref. 8), as well as the present calculations, shows that the EA wave functions derived in Ref. 14 are somewhat too internal, and as a result the calculated fine-structure splittings $\Delta\nu_1 + \Delta\nu_2$ are somewhat larger than the experimental values. This situation may arise from a slight overestimate of the correlation effects which is implicit in the calculation of the EA wave functions by the method of Eqs. (26)–(28).

After the preceding calculations had been completed, it came to our attention that a similar calculation of the fine-structure intervals of several Na np and nd levels has been recently carried out by Holmgren, Lindgren, Morrison, and Mårtensson,[20] using the many-body-theory formalism previously developed for hyperfine-structure calculations in an earlier paper by Garpman *et al.*[21]

In connection with the previous calculation of Ref. 1 for the inverted fine structure of Na $3d$, it should also be mentioned that the inverted fine structure for excited nd states of sodium has recently been confirmed in three separate investigations by Fabre, Gross, and Haroche,[22] by Fredericksson and Svanberg,[23] and by Gallagher, Hill, and Edelstein.[24] In Ref. 24, accurate values of the fine-structure intervals for the Na nd and nf levels have been obtained for n values ranging from $n = 11$ to $n = 17$.

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