[35] C. W. Allen, *Astrophysical Quantities* (Athlone, London, 1955).

[36] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer, Berlin, 1957).

[37] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge U. P., Cambridge, England, 1963).

---

PHYSICAL REVIEW A VOLUME 4, NUMBER 5 NOVEMBER 1971

# Calculation of Fine-Structure Splittings and Quadrupole Antishielding Factors for Atomic States*

R. M. Sternheimer and R. F. Peierls
*Brookhaven National Laboratory, Upton, New York 11973*

(Received 25 June 1971)

As a test of accurate valence wave functions which have been previously obtained for the excited *np* states of the alkali atoms, we have calculated the fine-structure splittings $\Delta\nu$ using these wave functions. The resulting values of $\Delta\nu_{\mathrm{theor}}$ are generally in good agreement with the corresponding experimental values $\Delta\nu_{\mathrm{expt}}$. Calculations have also been carried out for the atomic quadrupole shielding factor $R$ for the ground states of boron (B $2p$) and aluminum (Al $3p$), and the ionic antishielding factor $\gamma_\infty$ for the ions B$^+$, Al$^+$, and Al$^{3+}$. The value of $R(\mathrm{B}\,2p) = +0.048$ is in good agreement with the results of calculations using spin-polarization wave functions. The result for $R(\mathrm{Al}\,3p) = -0.063$ leads to a corrected value of the nuclear quadrupole moment $Q(\mathrm{Al}^{27}) = 0.140 \pm 0.002$ b, using the atomic-beam result of Lew and Wessel. The ionic antishielding factors $\gamma_\infty$ have the following calculated values: $\gamma_\infty(\mathrm{B}^+) = +0.773$, $\gamma_\infty(\mathrm{Al}^+) = -1.68$, and $\gamma_\infty(\mathrm{Al}^{3+}) \cong -2.4$.

## I. INTRODUCTION

In a recent paper,[1] the present authors have obtained accurate valence wave functions $v_{np}$ for the lowest three excited *np* states for each of the five alkali atoms. These wave functions were obtained from the requirement that they should be derivable from a potential $V_0$ which is such that the experimental energy eigenvalues[2] $E_{0,\mathrm{expt}}(np)$ are correctly reproduced. These wave functions were used to obtain accurate values of the quadrupole antishielding factors[3] $R(np)$ for these states. The values of $R(np)$ were used in turn to obtain the corrected values of the nuclear quadrupole moments $Q$ for 12 alkali isotopes. As a check on the wave functions $v_{np}$, we have calculated (in Ref. 1) the values of $\langle r^{-3}\rangle_{np}$ and also the oscillator strengths $f_{n_0s-n_0p}$, where $n_0$ is the principal quantum number for the lowest excited *np* state (e.g., $n_0 = 3$ for Na). Both quantities were found to be in good agreement with the corresponding experimental values. (For $\langle r^{-3}\rangle_{np}$, a comparison was possible only for Rb $6p$ and $7p$ and for Cs $7p$ and $8p$.)

It appears that a further test of the wave functions is obtained by calculating the fine-structure splittings $\Delta\nu$ for the alkali atom *np* states, and by comparing the resulting values with the corresponding experimental values $\Delta\nu_{\mathrm{expt}}$, as obtained from the tables of Moore.[2] This will be done in Sec. II of this paper. It is found that the agreement is very satisfactory (generally within 15%), except for the case of lithium, where the situation has been extensively discussed previously.[4,5]

In previous work, extensive calculations of the quadrupole antishielding factor $R$ have been carried out for the alkali atom *np* states,[1] and also for the $3d^9\,4s^2$ and $3d^{10}\,4p$ states of copper,[6] and for the rare earths Pr and Tm (both $5d$ and $4f$),[6] and also for[6] Be $2s2p\;^2P$. For the case of the alkalis and for copper, the valence wave functions were adjusted to reproduce the experimental eigenvalues[2] $E_{0,\mathrm{expt}}$, as discussed above. In addition, Hartree-Fock wave functions were used for the core electrons. It seemed desirable to extend this type of calculations to additional atomic states, and in the present paper, we have carried out calculations for the ground states of aluminum and boron, i.e., for Al $3p$ and B $2p$. The resulting values of $R$ are small, i.e., $|R|$ is less than 0.1 in both cases. The calculations of $R$ for Al $3p$ and B $2p$ are reported in Sec. III.

## II. CALCULATIONS OF FINE STRUCTURE

For the fine-structure interval $\Delta\nu$ between the $^2P_{1/2}$ state and the $^2P_{3/2}$ state, the classical formula[7] gives the following result:

$$\Delta\nu = \tfrac{3}{4}\,\alpha^2 R_\infty \int_0^\infty \frac{1}{r}\frac{dV}{dr}\, v_{np}^2\, dr\ , \qquad (1)$$

where $\alpha$ is the fine-structure constant, $R_\infty = 109\,737$ cm$^{-1}$; $dV/dr$ is the first derivative of the effective potential $V$ experienced by the $np$ electron; $dV/dr$ is in units Ry/$a_H$, where $a_H$ is the Bohr radius; and $v_{np}$ is $r$ times the radial part of the valence $np$ wave function, normalized to 1,

$$\int_0^\infty v_{np}^2 dr = 1 \; . \tag{2}$$

We note that the factor $\frac{3}{4}\alpha^2 R_\infty$ equals 4.3825 cm$^{-1}$.

The valence wave functions $v_{np}$ for the alkali atoms, together with the values of $dV/dr$, are tabulated in a separate report.[8] As we have noted in the Introduction, the wave functions $v_{np}$ were obtained in a recent paper (Ref. 1) from the requirement that they should be consistent with the experimental energy eigenvalues[2] $E_{0,\mathrm{expt}}$. The corresponding potentials $V$ and the derivatives $dV/dr$ have also been previously obtained,[9] in connection with a calculation of the Sandars dipole enhancement factor.[10]

As explained in Ref. 9 [see Eqs. (14)–(16) of Ref. 9], the derivative $dV/dr$ was obtained from the potential $V(r)$ by numerical or analytic differentiation (depending on the region of $r$).

The resulting values of $\Delta\nu_{\mathrm{theor}}$ as obtained from Eq. (1), together with the experimental values $\Delta\nu_{\mathrm{expt}}$ are given in Table I. This table also lists the values of the ratio $\rho$ defined by

$$\rho \equiv \Delta\nu_{\mathrm{theor}}/\Delta\nu_{\mathrm{expt}} \; . \tag{3}$$

We note that the discrepancy between theory and experiment, i.e., $\rho - 1$, is quite small except for the case of Li $2p$ and $3p$. For the latter case, Blume, Freeman, and Watson[4,5] have evaluated in detail the effects of exchange on the expression for $\Delta\nu$, which was not included in the present formula, i.e., Eq. (1). We note that the quantity $\zeta$ of Refs. 4 and 5 is $\frac{2}{3}$ of the splitting $\Delta\nu$ for the present case of $^2P$ states. If we use the ratio $\zeta_{cd}/\zeta_c$ of Refs. 4 and 5 as a measure of the exchange effect in reducing $\zeta$, we obtain a reduction factor[5] $\zeta_{cd}/\zeta_c = 0.48/0.16 = 3.00$ for Li $1s^2 2p$ and $\zeta_{cd}/\zeta_c = 0.149/0.044 = 3.39$ for Li $1s^2 3p$. Upon applying these reduction factors to the present results, we obtain for $\Delta\nu_{\mathrm{theor,red}}$, defined as

$$\Delta\nu_{\mathrm{theor,red}} \equiv (\zeta_{cd}/\zeta_c)^{-1} \Delta\nu_{\mathrm{theor}} \; , \tag{4}$$

the following values: $\Delta\nu_{\mathrm{theor,red}} = 0.969/3.00 = 0.323$ cm$^{-1}$ for Li $2p$ and $\Delta\nu_{\mathrm{theor,red}} = 0.311/3.39 = 0.092$ cm$^{-1}$ for Li $3p$. These results are in good agreement with the corresponding experimental values, 0.34 and 0.10 cm$^{-1}$, respectively (see Table I). This indicates that the predominant part of the discrepancy between the $\Delta\nu_{\mathrm{theor}}$ calculated from Eq. (1) and the experimental value $\Delta\nu_{\mathrm{expt}}$ for the case of lithium is indeed due to the reduction brought about by the effect of exchange, as discussed in Ref. 5.

TABLE I. Theoretical and experimental values of the fine-structure splittings $\Delta\nu$ (in cm$^{-1}$) of the first three excited $np$ states of each of the alkali atoms, and the ratios $\rho \equiv \Delta\nu_{\mathrm{theor}}/\Delta\nu_{\mathrm{expt}}$. The theoretical values $\Delta\nu_{\mathrm{theor}}$ were calculated from Eq. (1), using the valence wave functions previously determined in Ref. 1. The experimental values $\Delta\nu_{\mathrm{expt}}$ were obtained from the tables of Moore (Ref. 2). The next-to-last column of the table gives the values of the contribution $\Delta\nu_{\mathrm{nucl}}$ of the nucleus alone, as obtained from Eqs. (5) and (6). The last column gives the values of $\delta Z$, as calculated from Eq. (9).

| State | $\Delta\nu_{\mathrm{theor}}$ | $\Delta\nu_{\mathrm{expt}}$ | $\rho$ | $\Delta\nu_{\mathrm{nucl}}$ | $\delta Z$ |
|---|---|---|---|---|---|
| Li $2p$ | 0.969 | 0.34 | 2.85 | 1.708 | 1.30 |
| Li $3p$ | 0.311 | 0.10 | 3.11 | 0.521 | 1.21 |
| Li $4p$ | 0.134 | ··· | ··· | 0.222 | 1.19 |
| Na $3p$ | 18.731 | 17.196 | 1.089 | 22.474 | 1.83 |
| Na $4p$ | 6.099 | 5.63 | 1.083 | 7.255 | 1.75 |
| Na $5p$ | 2.729 | 2.52 | 1.083 | 3.238 | 1.73 |
| K $4p$ | 62.90 | 57.72 | 1.090 | 69.03 | 1.69 |
| K $5p$ | 20.14 | 18.76 | 1.074 | 22.05 | 1.65 |
| K $6p$ | 9.00 | 8.41 | 1.070 | 9.85 | 1.64 |
| Rb $5p$ | 265.36 | 237.60 | 1.117 | 280.56 | 2.01 |
| Rb $6p$ | 87.88 | 77.50 | 1.134 | 92.82 | 1.97 |
| Rb $7p$ | 40.18 | 35.09 | 1.145 | 42.43 | 1.96 |
| Cs $6p$ | 652.86 | 554.11 | 1.178 | 682.63 | 2.40 |
| Cs $7p$ | 203.89 | 181.01 | 1.126 | 213.03 | 2.36 |
| Cs $8p$ | 93.35 | 82.64 | 1.130 | 97.52 | 2.35 |

For Na and the heavier alkali atoms, the effect of exchange on $\Delta\nu$ appears to be much smaller, as is indicated by the small discrepancies $\rho - 1 \sim 0.1$ obtained using Eq. (1). The remaining discrepancies ($\sim 0.1$) may be at least partly due to the fact that the values of $\langle r^{-3}\rangle$ as obtained from the present wave functions may be slightly too large.

Since the values of $\langle r^{-3}\rangle$ are available for the alkali atom wave functions used above, it is of interest to calculate the contribution of the nuclear potential to $\Delta\nu_{\mathrm{theor}}$. This nuclear contribution is simply given by

$$\Delta\nu_{\mathrm{nucl}} = \tfrac{3}{4}\alpha^2 R_\infty 2Z \langle r^{-3}\rangle_{np} \; , \tag{5}$$

where the factor $2Z$ arises from the fact that the nuclear potential in rydberg units is $-2Z/r$. Thus we find

$$\Delta\nu_{\mathrm{nucl}} = 8.7650 Z \langle r^{-3}\rangle_{np} \ \mathrm{cm}^{-1} \; . \tag{6}$$

If the theoretical splitting $\Delta\nu_{\mathrm{theor}}$ [Eq. (1)] is written

$$\Delta\nu_{\mathrm{theor}} = 8.7650 (Z - \delta Z) \langle r^{-3}\rangle_{np} \ \mathrm{cm}^{-1} \; , \tag{7}$$

then this equation defines an effective decrease of the nuclear charge $\delta Z$, which simulates the effect of the core-electron screening on $\Delta\nu$.

The values of $\langle r^{-3}\rangle_{np}$ for the alkali atoms have been given by the present authors in Ref. 1, Table III. The calculated values of $\Delta\nu_{\mathrm{nucl}}$ are given in the next-to-last column of Table I of this paper.

Finally, the resulting values of $\delta Z$ are listed in the last column of Table I. We note that from Eqs. (6) and (7), $\delta Z$ is obtained from

$$\Delta\nu_{\text{theor}}/\Delta\nu_{\text{nucl}} = 1 - \delta Z/Z \ , \tag{8}$$

so that

$$\delta Z = Z(1 - \Delta\nu_{\text{theor}}/\Delta\nu_{\text{nucl}}) \ . \tag{9}$$

It is seen that the values of $\delta Z$ are roughly constant with increasing quantum number $n$ for a given alkali (given $Z$), and that they increase from ~1.2 for lithium to ~2.4 for cesium.

## III. CALCULATIONS OF $R$ FOR Al $3p$ AND B $2p$

The calculation of the quadrupole antishielding factor $R$ for aluminum and boron follows along the same lines as the work of Refs. 1 and 6.

For aluminum, we used the Hartree-Fock wave functions of Watson and Freeman[11] for the core electrons ($1s$, $2s$, $2p$, $3s$, and $3p$). For the $3p$ state, we used a wave function $v_{3p}$ determined from the requirement that it should reproduce the observed atomic $3p$ energy eigenvalue,[2] namely $E_0 = -0.439\,27$ Ry. The procedure of the actual determination is the same as was employed[1] in our previous calculation of the valence wave functions $v_{np}$ of the alkali atoms. Thus $V_{0,\text{HF}}$ is a preliminary estimate of the potential, obtained in this case from the Hartree-Fock $3p$ wave function[11] $v_0'$, by the equation[12]

$$V_0 - E_{0,\text{HF}} = \frac{1}{v_0'}\frac{d^2 v_0'}{dr^2} - \frac{2}{r^2} \ , \tag{10}$$

where $E_{0,\text{HF}}$ is the Hartree-Fock energy eigenvalue. The function $V_0(r)$ thus obtained is modified by the addition of a term $a\,|V_{\text{exch}}(r)|$, where $V_{\text{exch}}(r)$ is the Slater exchange potential,[13] and $a$ is a constant which is so adjusted that the eigenvalue condition (correct behavior at $r\to\infty$) is satisfied, using the experimental $E_0$ given above. We note that $V_{\text{exch}}(r)$ is used only to give the shape of the correction term needed to obtain the effective potential $V(r)$ from $V_0(r)$. Thus we have

$$V = V_0 + a\,|V_{\text{exch}}| \ . \tag{11}$$

The perturbed wave functions $v_1'(nl\to l')$ involved in the calculation are the solutions of the equation[3]

$$\left(-\frac{d^2}{dr^2} + \frac{l'(l'+1)}{r^2} + V_0 - E_0\right) v_1'(nl\to l') = u_0'(nl)[r^{-3} - \langle r^{-3}\rangle_{nl}\,\delta_{ll'}] \ , \tag{12}$$

where $u_0'(nl)$ is $r$ times the radial part of the core wave function for the shell $nl$. We have thus obtained the perturbed functions $v_1'(1s\to d)$, $v_1'(2s\to d)$, $v_1'(2p\to p)$, $v_1'(2p\to f)$, and $v_1'(3s\to d)$. These functions [together with the $u_0'(nl)$] have been tabulated in the report of Ref. 8 (see Tables 6–10 of Ref. 8 which pertain to Al). The function $v_{3p}$ is, of course, also listed, together with the derivative $dV/dr$, which was used to calculate the fine-structure splitting $\Delta\nu$ for Al $3p$, as will be discussed below.

The contributions $R_D$ due to direct interaction and $R_E$ due to exchange interaction (between the valence electron and the core) are obtained in terms of double integrals over products of the functions $u_0'(nl)$, $v_1'(nl\to l')$, and $v_{np}$. The pertinent equations are given by Eqs. (13)–(20′) of Ref. 1. We note that $\langle r^{-3}\rangle_{3p}$, which appears in the denominator of the equations for $R_D$, $R_E$, and $R(=R_D+R_E)$, has the value

$$\langle r^{-3}\rangle_{3p} = 1.2960\,a_H^{-3} \ . \tag{13}$$

It may be noted that the Hartree-Fock wave function of Ref. 11 would give $\langle r^{-3}\rangle_{3p} = 1.0554\,a_H^{-3}$, so that the requirement of consistency with the experimental energy $E_0$ results in an increase of $\langle r^{-3}\rangle_{3p}$ by a factor of $1.2960/1.0554 = 1.228$, i.e., a ~23% increase. The corresponding change in the energy is very small, i.e., only 0.0413 Ry, obtained as the difference between the experimental eigenvalue (−0.4393 Ry) and the Hartree-Fock eigenvalue of Watson and Freeman[11] (−0.3980 Ry).

The resulting values of $R_D(nl\to l';\,3p)$ and $R_E(nl\to l';\,3p)$, as well as the total contributions (direct + exchange), namely $R(nl\to l';\,3p)$, have been tabulated in Table II. Note that all values have been multiplied by a factor of 100. The angular modes of excitation, i.e., those with $l' = l+2$, have been separated in the table from the only radial mode, namely $2p\to p$, and the final total values of $10^2R_D$, $10^2R_E$, and $10^2R$ are given in the last row of the table. It is seen that the antishielding provided by the $2p\to p$ mode (negative contribution) predominates over the shielding due to the angular modes (positive contribution), leading to a small negative $R$: $R = -0.0628$. For the individual angu-

TABLE II. Values of the contributions to $R$ and $\gamma_\infty$ from the core excitations ($nl\to l'$) for Al $3p$. The values of $R(nl\to l';\,3p)$ have been multiplied by $10^2$, as indicated. The row labeled "Total (ang)" refers to the total contribution of the angular perturbations $nl\to l'$, with $l' = l+2$. The last row of the table gives the sum of Total (ang) and the $2p\to p$ contribution, i.e., the total values for the Al $3p$ state. In the fourth column, $R = R_D + R_E$.

| Excitation | $10^2R_D$ | $10^2R_E$ | $10^2R$ | $\gamma_\infty$ |
|---|---|---|---|---|
| $1s\to d$ | 2.971 | −1.820 | +1.151 | 0.0540 |
| $2s\to d$ | 1.322 | −0.190 | +1.132 | 0.1752 |
| $3s\to d$ | 1.225 | −1.314 | −0.089 | 0.7797 |
| $2p\to f$ | 2.156 | −0.477 | +1.679 | 0.2365 |
| Total (ang) | 7.674 | −3.801 | +3.873 | 1.2454 |
| $2p\to p$ | −10.130 | −0.024 | −10.154 | −2.928 |
| Total | −2.456 | −3.825 | −6.281 | −1.683 |

lar modes, it is interesting to note that the exchange terms $R_E$ can be very important, notably for $1s \rightarrow d$ and even more so for $3s \rightarrow d$, where the exchange term ($-0.013\,14$) is actually numerically larger than the direct term ($+0.012\,25$). This latter effect is probably due to the large overlap of the valence $3p$ wave function with the rather external $3s$ wave function of the $\mathrm{Al}^+$ core.

In the last column of Table II we have listed the terms of the ionic antishielding factor[14] $\gamma_\infty(nl \rightarrow l')$, which are simply given by

$$\gamma_\infty(nl \rightarrow l') = c(nl \rightarrow l') \int_0^\infty u_0'(nl) v_1'(nl \rightarrow l') r^2 dr , \quad (14)$$

where the angular factor $c(nl \rightarrow l')$ has the values $\frac{8}{5}$ for $ns \rightarrow d$, $\frac{48}{25}$ for $np \rightarrow p$, and $\frac{72}{25}$ for $np \rightarrow f$. The antishielding due to $2p \rightarrow p$ predominates over the shielding due to $ns \rightarrow d$. This leads to a negative $\gamma_\infty$ for the $\mathrm{Al}^+$ ion, namely $\gamma_\infty(\mathrm{Al}^+) = -1.683$.

We note that if we subtract from $\gamma_\infty(\mathrm{Al}^+)$ the contribution $\gamma_\infty(3s \rightarrow d)$ of the $3s$ electrons, we obtain an approximate value of $\gamma_\infty$ for the trivalent $\mathrm{Al}^{3+}$ ion, namely

$$\gamma_\infty(\mathrm{Al}^{3+}) = -1.683 - 0.780 = -2.463 . \quad (15)$$

We have also calculated the fine-structure splitting $\Delta\nu$ for Al $3p$. The value obtained from Eq. (1), using the function $v_{3p}$ obtained above, is $\Delta\nu_{\mathrm{theor}} = 127.71\ \mathrm{cm}^{-1}$, as compared to the experimental value[2] $\Delta\nu_{\mathrm{expt}} = 112.04\ \mathrm{cm}^{-1}$, giving a ratio $\rho = 1.140$, which is quite comparable with the value of $\rho$ obtained in Table I for Na and the heavier alkali atoms.

The calculation of $R$ for B $2p$ was carried out in the same manner as the calculation of $R$ for Al $3p$. We used the Hartree-Fock wave functions of Glembotskii, Kibartas, and Iutsis.[15] We used these functions directly for $u_0'(1s)$ and $u_0'(2s)$, whereas for $2p$, a potential $V_0$ was derived from the function of Ref. 15 by means of Eq. (10), and subsequently an effective potential $V$ of the type of Eq. (11) was derived, with the constant $a$ deduced again from the requirement of consistency with the experimental eigenvalue[2] $E_0 = -0.609\,81$ Ry.

The perturbed wave functions $v_1'(1s \rightarrow d)$ and $v_1'(2s \rightarrow d)$ were obtained from Eq. (12), with $l' = 2$. We note that for $v_1'(ns \rightarrow d)$, the boundary condition at $r = 0$ is that $v_1'$ at $r = 0$ equals $a_1/6$, where $a_1$ is the coefficient of the linear term in the expansion of $u_0'(ns)$ at $r = 0$, i.e.,[3]

$$u_0'(ns) = a_1 r + a_2 r^2 + \cdots \quad (r \text{ small}) , \quad (16)$$

$$v_1'(ns \rightarrow d;\ r = 0) = a_1/6 . \quad (17)$$

The resulting wave functions $v_1'(ns \rightarrow d)$, together with the unperturbed functions[15] $u_0'(ns)$ and the valence $2p$ wave function $v_{2p}$ (consistent with $E_{0,\mathrm{expt}}$) are tabulated in Tables 11 and 12 of Ref. 8. The last table of this reference (Table 13) gives the derivative $dV/dr$ which was used in the calculation of the fine-structure splitting $\Delta\nu$ for B $2p$. We note that the value of $\langle r^{-3}\rangle_{2p}$ (which enters into $R$) is $0.7798 a_H^{-3}$.

The values of $R_D(nl \rightarrow l')$, $R_E(nl \rightarrow l')$, and the total $R(nl \rightarrow l') = R_D(nl \rightarrow l') + R_E(nl \rightarrow l')$ are listed in Table III. (All of these quantities have been multiplied by a factor $10^2$, in the same manner as for Table II.) The last row of the table gives the total $R_D$ and $R_E$ values, and the total $R$ which is slightly shielding, i.e., $R(\mathrm{B}\ 2p) = +0.0478$. It is interesting to note that for both $1s \rightarrow d$ and $2s \rightarrow d$, the exchange terms $R_E$ are very important and reduce the shielding provided by the direct terms $R_D$. For the case of $2s \rightarrow d$, the situation is very similar to that for $3s \rightarrow d$ for Al. Thus the overlap of the valence wave function $v_{np}$ with $u_0'(ns)$ and $v_1'(ns \rightarrow d)$ is very extensive in both cases ($n = 2$ for B, $n = 3$ for Al), and as a result, $R_E$ has nearly the same magnitude as $R_D$, resulting in a very small total $R(ns \rightarrow d)$, i.e., $-0.000\,89$ for Al $3p$ and $+0.000\,81$ for B $2p$.

The last column of Table III gives the contributions $\gamma_\infty(ns \rightarrow d)$ to the ionic antishielding factor $\gamma_\infty(\mathrm{B}^+)$, which is given in the bottom row, i.e., $\gamma_\infty(\mathrm{B}^+) = 0.7729$.

Finally, as indicated above, we have also calculated the fine-structure splitting $\Delta\nu$ for B $2p$ from the function $v_{2p}$ obtained above. The result is $\Delta\nu_{\mathrm{theor}} = 25.4\ \mathrm{cm}^{-1}$, as compared to the experimental value $\Delta\nu_{\mathrm{expt}} = 16\ \mathrm{cm}^{-1}$, resulting in a ratio $\rho = 1.588$.

Concerning the values of $\Delta\nu_{\mathrm{theor}}$ obtained here for Al $3p$ and B $2p$, we refer to our previous discussion for the alkali excited states [see Sec. II, Eq. (4)]. Thus for both Al and B, Blume and Watson[4] have carried out calculations of both $\zeta_{cd}$ (direct term only) and $\zeta_c$ (which includes exchange terms with the core). The reduction factors $\zeta_{cd}/\zeta_c$ have the following values: for Al $3p$,

$$\zeta_{cd}/\zeta_c = 66.5/60.5 = 1.099 ; \quad (18)$$

and for B $2p$,

$$\zeta_{cd}/\zeta_c = 14.9/9.74 = 1.530 . \quad (19)$$

Upon applying these factors to $\Delta\nu_{\mathrm{theor}}$ in both cases, using Eq. (4), we obtain for the reduced $\Delta\nu$

TABLE III. Values of the contributions to $R$ and $\gamma_\infty$ from the core excitations ($ns \rightarrow d$) for B $2p$. The values of $R(ns \rightarrow d;\ 2p)$ have been multiplied by $10^2$, as indicated. The last row of the table gives the total values for the B $2p$ state. In the fourth column, $R = R_D + R_E$.

| Excitation | $10^2 R_D$ | $10^2 R_E$ | $10^2 R$ | $\gamma_\infty$ |
|---|---|---|---|---|
| $1s \rightarrow d$ | 9.366 | −4.666 | +4.700 | 0.1468 |
| $2s \rightarrow d$ | 3.847 | −3.766 | +0.081 | 0.6261 |
| Total | 13.213 | −8.432 | +4.781 | 0.7729 |

values: for Al 3*p*,

$$\Delta\nu_{\text{theor,red}} = 127.71/1.099 = 116.2\ \text{cm}^{-1}\ , \tag{20}$$

and for B 2*p*,

$$\Delta\nu_{\text{theor,red}} = 25.42/1.530 = 16.61\ \text{cm}^{-1}\ . \tag{21}$$

These values are in good agreement with the corresponding experimental values[2] $\Delta\nu_{\text{expt}} = 112.04$ cm$^{-1}$ and 16 cm$^{-1}$, respectively. The reduction factor is considerable for B 2*p*, probably due to the great amount overlap between 2*p* and 2*s* for this atomic state.

The correction factors $C = 1/(1-R)$ derived from the values of $R$ obtained above are, for Al 3*p*,

$$C = 1/(1-R) = 1/(1+0.063) = 0.941\ , \tag{22}$$

and for B 2*p*,

$$C = 1/(1-R) = 1/(1-0.048) = 1.050\ , \tag{23}$$

corresponding to the values of $R = -0.063$ for Al 3*p* and $R = +0.048$ for B 2*p*.

For the case of aluminum, the preceding value of $C$ can be used to correct the value of the quadrupole moment $Q(\text{Al}^{27})$ obtained from the atomic-beam measurement of Lew and Wessel.[16] The uncorrected value of Ref. 16 is $0.149 \pm 0.002$ b (1 b $= 10^{-24}$ cm$^2$). Thus we obtain

$$Q(\text{Al}^{27}) = 0.149 \times 0.941 = 0.140\ (\pm 0.002)\,\text{b}. \tag{24}$$

For the case of boron, both Schaefer *et al.*[17] and Nesbet[18] have obtained very accurate values of $Q(\text{B}^{10})$ and $Q(\text{B}^{11})$, using wave functions that include the effects of core polarization, which are represented by the factor $1-R$. Thus the values of $Q(\text{B}^{10})$ and $Q(\text{B}^{11})$ which they have obtained already include the effects of $1-R$. For reference, the values of Nesbet[18] are $Q(\text{B}^{10}) = 0.08472(56)$ b and $Q(\text{B}^{11}) = 0.04065(26)$ b, where the numbers in parentheses indicate the expected errors in the last two significant figures. The results of Schaefer *et al.*[17] are ~5% smaller for both isotopes.

On the other hand, we can use the results of Schaefer *et al.*[17] and those of Larsson[19] in a comparison with the present calculations of $R$ for B 2*p*. Thus from the results of Schaefer *et al.*,[17] we find that $\langle r_q^{-3}\rangle$, defined as

$$\langle r_q^{-3}\rangle \equiv (1-R)\langle r^{-3}\rangle\ , \tag{25}$$

is smaller than $\langle r^{-3}\rangle$ obtained directly from the one-electron 2*p* wave function. The authors have obtained $\langle r_q^{-3}\rangle = 0.7436 a_H^{-3}$, $\langle r^{-3}\rangle = 0.7755 a_H^{-3}$ (see Ref. 17, Table VIII), which gives

$$1-R = 0.7436/0.7755 = 0.9589\ , \tag{26}$$

so that $R = 0.0411$. Our result $R = 0.0478$ is in reasonably good agreement with this value, indicating that the small shielding effect found in the present paper is confirmed by the calculations using the more elaborate "polarization wave functions" of Ref. 17.

Additional confirmation is obtained from the paper of Larsson[19] (see his Table VII), who has obtained $R_D = 0.139$, $R_E = -0.089$, giving a total $R = 0.050$, in good agreement with our results (see Table III of this paper), namely, $R_D = 0.132$, $R_E = -0.084$, giving $R = 0.048$.

In connection with the paper of Schaefer *et al.*,[17] it is also of interest to note that not only for B 2*p*, but also for the ground states of C, O, and F, there is also a small shielding, i.e., $R$ is positive and of the order of 0.05 to 0.10. Thus from Table VIII of their paper, we find, for carbon,

$$1-R_C = 1.637/1.692 = 0.9675\ , \tag{27}$$

giving $R_C = 0.0325$; for oxygen,

$$1-R_O = 4.334/4.973 = 0.8715\ , \tag{28}$$

giving $R_O = 0.1285$; and for fluorine,

$$1-R_F = 6.880/7.545 = 0.9119\ , \tag{29}$$

giving $R_F = 0.0881$.

In connection with the present calculations of $R$ and $\gamma_\infty$ for aluminum, we have obtained $R = -0.063$ and $\gamma_\infty(\text{Al}^{3+}) = -2.46$ in the present paper [see Table II and Eq. (15)]. In the calculations of Sawatzky and Hupkes[20] and of Sharma,[21] an earlier value[3,12] $R = -0.005$ obtained by one of us (R. M. S.) was used, together with the value of $\gamma_\infty = -2.59$ obtained by Das and Bersohn,[22] using the variational method of calculation. The results of Refs. 20 and 21 would be altered slightly by the use of the present values of $R$ and $\gamma_\infty(\text{Al}^{3+})$.

In this connection, we believe that the present value of $\gamma_\infty(\text{Al}^{3+})$ [Eq. (15)] is more accurate than that of Das and Bersohn, since it is based on a numerical integration of the perturbation equations [Eq. (12)]. In particular, for $1s \to d$, the result of Ref. 22 (see Table III) is appreciably too small [0.031, as compared to our value 0.054, which is close to the hydrogenic result $\frac{2}{3}/Z_e = \frac{2}{3}/12.7 = 0.0525$]. In addition, for $2s \to d$, $\gamma_\infty$ of Ref. 22 is considerably too large (0.278 as compared to 0.175, see Table II) for the same reason as the similar discrepancy for Na$^+$, which was discussed by one of us (R. M. S.) in Ref. 23 (see p. 1205).

The only limitation of our calculation of $\gamma_\infty(\text{Al}^{3+})$ is that it was carried out using neutral-atom wave functions for aluminum, rather than wave functions for the trivalent ion. However, it is not expected that the tightly bound Al$^{3+}$ core will be much affected by the absence of the three valence electrons. In any case, this effect will be such as to reduce $|\gamma_\infty(\text{Al}^{3+})|$ slightly from the value calculated using neutral-atom wave functions. Thus our best estimate of $\gamma_\infty(\text{Al}^{3+})$, taking into account the slight additional binding, is $\gamma_\infty(\text{Al}^{3+}) \cong -2.4$.

## IV. SUMMARY AND DISCUSSION

In the present paper, we have given the results of calculations of the fine-structure splitting $\Delta\nu$ of 15 excited states of the alkali atoms, and also of the atomic quadrupole shielding (or antishielding) factors $R$ for the ground states of boron (B $2p$) and aluminum (Al $3p$). In addition, the ionic quadrupole antishielding factors $\gamma_\infty$ of the ions $B^+$, $Al^+$, and $Al^{3+}$ have also been obtained.

Concerning the calculated values of the fine-structure splittings $\Delta\nu$, we have found good agreement with the corresponding experimental values[2] for all of the alkalis except for lithium. For each alkali, $\Delta\nu$ was obtained for the three lowest excited $np$ states, e.g., Na $3p$, $4p$, and $5p$ for the case of sodium. For the case of lithium, it was previously shown by Blume, Freeman, and Watson[4,5] that the effect of exchange of the valence electron with the core electrons ($1s^2$) will reduce $\Delta\nu$ by a considerable factor, i.e., 3.00 for Li $1s^2 2p$ and 3.39 for Li $1s^2 3p$. When this reduction factor (due to exchange) is applied to our results, good agreement is also obtained with the experimental values $\Delta\nu_{\text{expt}}$ for the case of lithium.

In Sec. III of this paper, we have calculated the atomic and ionic quadrupole antishielding factors $R$ and $\gamma_\infty$ for the ground states of boron (B $2p$) and aluminum (Al $3p$). Hartree-Fock wave functions[11,15] were used for the core electrons in both cases. For the valence electron, we used a wave function obtained from a potential $V$ derived from the condition that it shall reproduce the experimental eigenvalue[2] [Eq. (11)]. $V$ is actually very close to the potential $V_0$ derived from the corresponding Hartree-Fock wave function (for B $2p$ or Al $3p$). The resulting contributions to $R$ and $\gamma_\infty$ are given in Tables II and III. The values of the total $R$ are $R(\text{B } 2p) = +0.048$ and $R(\text{Al } 3p) = -0.063$.

The value of $R(\text{B } 2p)$ is positive, indicating a small net shielding effect. The sign and magnitude of this shielding factor are corroborated by the work of Schaefer, Klemm, and Harris,[17] who found that an effective average $\langle r_q^{-3}\rangle$ defined by Eq. (25) is indeed smaller than the one-electron average $\langle r^{-3}\rangle$ leading to a value of $R = +0.041$. Moreover, the work of Larsson[19] yields values of $R_D$ and $R_E$ for B $2p$ which are very close to those of Table III, giving a total $R = +0.050$, in very good agreement with our value.

On the other hand, the value of $R(\text{Al } 3p)$ is negative, indicating a small antishielding effect, which is due to the predominant effect of the $2p \to p$ antishielding mode (see Table II). The correction factor $C = 1/(1-R)$ is therefore somewhat smaller than 1, namely $C = 0.941$. Upon applying this correction factor to the value of the nuclear quadrupole moment $Q(Al^{27})$ obtained by Lew and Wessel,[16] we find a corrected value $Q_{\text{corr}}(Al^{27}) = 0.140 \pm 0.002\,\text{b}$.

As concerns the ionic antishielding factor[14] $\gamma_\infty$, we have obtained values for $B^+$, $Al^+$, and $Al^{3+}$. The value for $B^+$ is $\gamma_\infty(B^+) = 0.773$, of which the contribution of the $1s$ electrons alone, namely 0.147, can be regarded as a good approximation to $\gamma_\infty$ for the $B^{3+}$ ion.

For the singly ionized $Al^+$ ion, the value of $\gamma_\infty$ obtained directly from Table II is $\gamma_\infty(Al^+) = -1.68$. This result contains a large contribution, namely $+0.78$, from the $3s \to d$ mode which is shielding. Thus for the trivalent $Al^{3+}$ ion, for which the $3s$ shell is unfilled, we obtain $\gamma_\infty(Al^{3+}) = -1.68 - 0.78 = -2.46$. This value is slightly too large numerically, because it was calculated using wave functions for the neutral aluminum atom rather than the trivalent ion. We thus have obtained a best estimate $\gamma_\infty(Al^{3+}) \cong -2.4$ for the antishielding factor of the $Al^{3+}$ ion.

## ACKNOWLEDGMENTS

We wish to thank Dr. M. Blume and Dr. R. E. Watson for helpful discussions.

---

[*] Work performed under the auspices of the U. S. Atomic Energy Commission.

[1] R. M. Sternheimer and R. F. Peierls, Phys. Rev. A 3, 837 (1971).

[2] C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Std. Circular No. 467 (U. S. GPO, Washington, D.C., 1949), Vol. I.

[3] R. M. Sternheimer, Phys. Rev. 80, 102 (1950); 84, 244 (1951); 95, 736 (1954); 105, 158 (1957); 164, 10 (1967).

[4] M. Blume and R. E. Watson, Proc. Roy. Soc. (London) A270, 127 (1962); A271, 565 (1963).

[5] M. Blume, A. J. Freeman, and R. E. Watson, Phys. Rev. 134, A320 (1964).

[6] R. M. Sternheimer, Phys. Rev. 164, 10 (1967); 146, 140 (1966).

[7] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge U.P., London, 1935), p. 120.

[8] Tables of the alkali atom valence wave functions $v_{np}$ and of the derivatives $dV/dr$ of the potentials are given in a supplementary paper (unpublished). This paper also contains tables of the perturbed wave functions $v_1'(nl \to l')$ and valence wave functions $v_{np}$ determined in the calculation of $R$ for Al $3p$ and B $2p$ (see Sec. III). For this supplementary paper, order NAPS Document No. 01584 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34 Street, New York, N. Y. 10001, remitting \$2.00 for microfilm or \$5.00 for photocopies.

[9] R. M. Sternheimer, Phys. Rev. 183, 112 (1969).

[10] P. G. H. Sandars, Phys. Letters 22, 290 (1966).

[11] R. E. Watson and A. J. Freeman, Phys. Rev. 123, 521 (1961).

[12] R. M. Sternheimer, Phys. Rev. 86, 316 (1952); 96,

951 (1954).

[13] J. C. Slater, Phys. Rev. 81, 385 (1951).

[14] R. M. Sternheimer, Phys. Rev. 84, 244 (1951); 146, 140 (1966); H. M. Foley, R. M. Sternheimer, and D. Tycko, *ibid.* 93, 734 (1954).

[15] I. I. Glembotskii, V. V. Kibartas, and A. P. Iutsis, Zh. Eksperim. i Teor. Fiz. 29, 617 (1955) [Sov. Phys. JETP 2, 476 (1956)].

[16] H. Lew and G. Wessel, Phys. Rev. 90, 1 (1953).

[17] H. F. Schaefer, III, R. A. Klemm, and F. E. Harris, Phys. Rev. 176, 49 (1968).

[18] R. K. Nesbet, Phys. Rev. A 2, 1208 (1970).

[19] S. Larsson, Phys. Rev. A 2, 1248 (1970).

[20] G. A. Sawatzky and J. Hupkes, Phys. Rev. Letters 25, 100 (1970).

[21] R. R. Sharma, Phys. Rev. Letters 25, 1622 (1970).

[22] T. P. Das and R. Bersohn, Phys. Rev. 102, 733 (1956).

[23] R. M. Sternheimer, Phys. Rev. 115, 1198 (1959).

---

PHYSICAL REVIEW A VOLUME 4, NUMBER 5 NOVEMBER 1971

# *L* X-Ray Transition Probabilities in Elements with $Z \geqslant 57$

S. I. Salem, R. T. Tsutsui, and B. A. Rabbani

*Department of Physics and Astronomy, California State College,*
*Long Beach, California* 90801

(Received 23 April 1971)

The $L\beta_3/L\beta_4$, $L\gamma_1/L\beta_1$, $L\alpha_2/L\alpha_1$, $L\beta_{2,15}/L\alpha_1$ and the $L\beta_{2,15}/L\alpha_2$ transition probabilities have been measured for some 27 elements ranging in atomic number from $_{57}$La to $_{92}$U. Other *L* transitions have also been measured for a smaller number of elements in the same range of atomic numbers. This has been accomplished by bombarding these elements with a constant energy electron beam and measuring their x-ray emission spectrum. The measured ratios are compared with the most recent calculation based on a relativistic Hartree-Fock-Slater (RHFS) potential, and screened Coulomb potential. In general, the form of the dependence of these ratios on atomic number predicted by calculations based on a RHFS potential is favored and the agreement between theory and experiment ranges from excellent for the $L\alpha_2/L\alpha_1$ ratio to a discrepancy of about 22% in the $L\beta_{2,15}/L\alpha_1$ ratio for elements of large atomic number.

## INTRODUCTION

Recent interest in measuring relative x-ray transition probabilities has been confined to the relatively simple *K* series. The *L* x-ray transition probabilities of elements with atomic number $57 \leqslant Z \leqslant 72$ have never been measured before, and work in this region proved to be very informative in terms of testing the different theoretical models used in calculating the relative probability of these transitions.

Early measurements of transition probability of the *L* x-ray group comprise the work of Jönsson,[1] Allison,[2] Hicks,[3] and Andrew.[4] Their results have been tabulated by Compton and Allison.[5] More recent measurements include the work of Wyckoff and Davidson,[6] Victor,[7] Goldberg,[8] and Rao *et al.*[9] None of the measurements cover a large enough number of elements to establish reasonable correlation with theoretical calculations, and in many instances the discrepancies between these results are of large magnitude.

Relativistic calculations of x-ray transition probabilities were carried out by Massey and Burhop,[10] Laskar,[11] Payne and Levinger,[12] Asaad,[13] Taylor and Payne,[14] and more recently by Babushkin,[15] Scofield,[16] and Rosner and Bhalla.[17] All these calculations except those of Asaad, Scofield, and Rosner and Bhalla are based on a Coulomb potential. Babushkin carried out his calculations using a Coulomb potential with and without allowance for screening; he took into account the electron screening effect as prescribed by Slater[18] and by Burns.[19] Of Babushkin's calculations, those based on a potential screened by Burns's prescription show better agreement with experimental values,[20,21] and these are later compared with the results of this paper. Babushkin's numerical values are given as intensity ratios rather than relative transition probabilities and were transformed to transition probabilities by the relation

$$P_i = I_i/\hbar\omega_i \,, \tag{1}$$

where the subscript $i$ indicates a given transition of energy $\hbar\omega_i$.

Scofield, and Rosner and Bhalla assumed that the orbital electrons are in a relativistic Hartree-Fock-Slater potential[22] (RHFS):

$$V(r) = -Ze^2/r + (e^2/r)\int_0^r 4\pi r'^2\rho(r')\,dr' + e^2\int_r^\infty 4\pi r'\rho(r')\,dr' - e^2[(81/8\pi)\rho(r)]^{1/3}\,. \tag{2}$$

The effect of the finite size of the nucleus was neglected by Scofield, and was calculated and ne-