PHYSICAL REVIEW A VOLUME 9, NUMBER 5 MAY 1974

Quadrupole shielding and antishielding factors for the excited *nd* states of the alkali-metal atoms*

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(Received 20 December 1973)

Extensive calculations have been carried out to obtain the quadrupole shielding or antishielding factors $R(nd)$ for the lowest excited nd states of the alkali-metal atoms. In all cases except for lithium, an appreciable net antishielding $[R(nd)<0]$ is found. For Li and Na, $R(nd)$ is approximately equal to the total ionic shielding or antishielding factor γ_∞, as a result of the fact that the nd wave function $v_0(nd)$ for these atoms is essentially hydrogenic, and hence the overlap between $v_0(nd)$ and the core wave functions $u_0(nl)$ and their perturbations $v_1(nl\rightarrow l')$ is very small. For Li, γ_∞ is positive, and accordingly $R\cong 0.25$, whereas for Na, γ_∞ is negative (antishielding), and correspondingly $R\cong -3.9$ to -4.8, in going from 3*d* to 5*d*. For the heavier alkali-metal atoms, namely, K, Rb, and Cs, $R(nd)$ is generally antishielding, but with much smaller absolute values than for Na. Thus $R(nd)$ lies generally in the range from -0.2 to -0.5. The values obtained for Rb are the most reliable, and range from -0.48 for Rb 4*d* to -0.20 for Rb 6*d*. For K and Cs, the values of $R(nd)$ obtained are less reliable, because of the sensitivity of the valence wave functions $v_0(nd)$ to the details of the effective one-electron potential $V_{\text{eff}}(r)$.

I. INTRODUCTION

Values of the atomic quadrupole shielding or antishielding factors[1] R have been obtained in several recent papers by the present author.[2-5] In these papers, a serious attempt was made to obtain reliable and accurate values, by using valence-electron wave functions which reproduce the experimental energy eigenvalues[6] (ionization potentials). The results of Refs. 2–5 refer to both atomic ground states and low-lying excited states. Reference 2 deals mainly with two excited states of the copper atom; Refs. 4 and 5 concern themselves with a number of atomic ground states, while the paper of Ref. 3 is devoted to a study of R for the first three excited *np* states of each of the five alkali atoms. With the exception of the lithium *np* states for which $R>0$, it was found that for the other alkali atoms, R is negative (antishielding), and of the order of -0.1 to -0.25, depending upon the atomic *np* state considered. The results for R are given in Table XI of Ref. 3, and they enabled us to obtain accurate values of the nuclear quadrupole moments Q of twelve alkali isotopes, using the experimental (uncorrected) values of Q, which have been compiled in the review article of Fischer.[7] The resulting corrected quadrupole moments of the alkali isotopes (together with those of Cu^{63} and Cu^{65})[2] are listed in Table XIV of Ref. 3.

About a year ago, it was pointed out to the author by Happer[8] that a calculation of R for the excited *nd* states of the alkali-metal atoms would be of interest, in view of the experiments on these excited states which he was then carrying out. Some of the results of Happer and co-workers have since been published,[9] and although the values of the quadrupole coupling constants B are not very accurate at present, there is the expectation that future experiments along similar lines will provide values which are sufficiently accurate to permit a check on the atomic theory of hyperfine structure (hfs) for excited *d* states, using the corrected Q values obtained from the hfs for *np* states as input data.

Following the suggestion of Happer, a systematic attempt was made to obtain the values of $R(nd)$ for a few of the lowest excited *d* states for each of the five alkali atoms. The purpose of the present paper is to give the results of this investigation. Some of the results were rather unexpected, and most of these features can be attributed to the very external nature of the *nd* states (with the exception of Rb 4*d*, Cs 5*d* and 6*d*), and the resulting small values of $\langle r^{-3}\rangle_{nd}$, which determines the uncorrected (valence) part of the quadrupole hfs.

In Sec. II, we present the method of calculation of $R(nd)$, and the resulting values of this parameter. Section III gives a summary and discussion of the results obtained here.

II. CALCULATIONS OF $R(nd)$

The formalism used to calculate $R(nd)$ is essentially the same as that employed in our earlier papers on this subject,[1-5] in particular, Refs. 2 and 3, in which R was determined for two excited states of copper, and for the excited np states of the alkali atoms. In particular, we could use the radial wave functions $v_1'(nl\to l')$ of the core electrons of the alkali atoms, which had been previously determined in Ref. 3. These wave functions are the solutions of the following inhomogeneous equation[1]:

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

where $u_0'(nl)$ is r times the radial part of the unperturbed (nl) core wave function. The effective values[10] of $V_0(r)-E_0$ (V_0 is the unperturbed potential; E_0 is the unperturbed energy eigenvalue) were obtained in the same manner as in Refs. 1 and 10:

$$V_0-E_0=\frac{1}{u_0'}\frac{d^2u_0'}{dr^2}-\frac{l(l+1)}{r^2} \ . \qquad (2)$$

The method of solution of Eq. (1) has been described in Ref. 2 (see the discussion on pp. 13–15). The core wave functions $u_0'(nl)$ are the Hartree-Fock wave functions of the corresponding alkali (positive) ions. Thus for Na^+ and K^+, we used the functions of Hartree and Hartree[11]; for Rb^+ and Cs^+, the wave functions of Watson and Freeman[12] were employed. For Li, the $1s$ function of James[13] was used.

The valence wave functions $v(nd)$ were obtained in essentially the same manner as the valence functions $v(np)$ of Ref. 3. Thus for the zero-order potentials V_0, we used the effective potentials V_{n_0s} which reproduce the ground-state eigenvalues, as given in the tables of Moore.[6] These effective potentials V_{n_0s} were previously used by the author in a calculation of the dipole and quadrupole polarizabilities α_d and α_q of the alkali atoms.[14] The effective potentials V_{n_0s} were obtained for Li, by Seitz[15]; for Na, by Prokofjew[16]; for Rb, by Callaway and Morgan[17]; and for K and Cs by Sternheimer.[14,18] The potentials $V_{n_0s}(r)$ should form a very good first approximation to the effective potentials for the excited nd states, which will be denoted by $V_{nd}(r)$. The fact that V_{n_0s} will not exactly reproduce the observed $E_0(nd)$ is presumably due to the slightly different effects of exchange and correlation for different valence states (n_0s and nd). For the purpose of obtaining the radial dependence (shape) of $\delta V\equiv V_{nd}-V_{n_0s}$, we have assumed that this radial dependence is given by the Slater exchange potential.[19] When this potential is multiplied by the factor $\frac{2}{3}$ introduced by Gáspár, and by Kohn and Sham,[20] it becomes

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

where ρ is the electron density in atomic units (number of electrons per a_H^3, where a_H is the Bohr radius). In terms of the core wave functions $u_0'(nl)$, which are normalized to 1,

$$\int_0^\infty [u_0'(nl)]^2\,dr=1 \ , \qquad (4)$$

$V_{\mathrm{exch}}(r)$ can be written as follows:

$$V_{\mathrm{exch}}(r)=-\left(\frac{12}{\pi^2}\right)^{1/3}\left(\sum_{nl}\frac{(2l+1)[u_0'(nl)]^2}{r^2}\right)^{1/3}\mathrm{Ry} \ , \qquad (5)$$

where the numerical factor $(12/\pi^2)^{1/3}=1.0673$.

The potentials[21] $V_{n_0s}(r)$ have been tabulated in Ref. 21, which pertains to the calculation of the alkali-atom dipole and quadrupole polarizabilities[14] α_d and α_q. With the experimental value[6] of $E_0(nd)$, we now write

$$V_{\mathrm{eff}}(nd)=V_{n_0s}+a|\,V_{\mathrm{exch}}\,| \ , \qquad (6)$$

where a is an adjustable parameter determined by the Schrödinger equation for $v(nd)$, namely,

$$\left(-\frac{d^2}{dr^2}+\frac{6}{r^2}+V_{n_0s}+a|\,V_{\mathrm{exch}}\,|-E_0(nd)\right)v(nd)=0 \ . \qquad (7)$$

Thus $|\,V_{\mathrm{exch}}\,|$ provides the shape of the small correction to the potential V_{n_0s}. Equation (7) is an eigenvalue equation for a, i.e., the constant a must be so chosen that $v(nd)$ will be well behaved at $r\to\infty$. The computer program, which integrates Eq. (7), tries a large number of a values, and by interpolating between two final functions (both of which diverge very slowly as $r\to\infty$, with different signs), one obtains a function which behaves properly, i.e., it is approximately proportional to $\exp[-|E_0(nd)|^{1/2}r]$ at large r. It may be noted that the total running time is 32 sec on a CDC-6600 computer, distributed into four calculations of 8 sec each. Between each two successive calculations, one narrows down the range of a values, which the computer investigates, by a factor of ~50. Thus initially a is allowed to range from -0.5 to $+0.5$ (interval equal to 1), and after the fourth (final) set of integrations, a is determined to better than 10^{-6}. We note that this very efficient computer program for solving for a was devised and written by Peierls. The values of a are quite small, as would be expected, since V_{n_0s} is a good approximation to the actual effective potential V_{nd}.

The method of calculation of R was the same as in Refs. 2 and 3. In particular, the values of the coefficients $C(nl\to l';n_ed;L)$ which appear in the exchange terms of $R(n_ed)$ were obtained from

Table II of Ref. 2. These values are as follows for the cases of interest in the present work:

$$C(ns\to d;\, n_e d;\, L=2)=4/5; \tag{8}$$

$$\begin{aligned} &C(np\to p;\, n_e d;\, L=1)=28/25,\\ &C(np\to p;\, n_e d;\, L=3)=36/175; \end{aligned} \tag{9}$$

$$\begin{aligned} &C(np\to f;\, n_e d;\, L=1)=12/25,\\ &C(np\to f;\, n_e d;\, L=3)=144/175; \end{aligned} \tag{10}$$

$$\begin{aligned} &C(nd\to d;\, n_e d;\, L=2)=-12/49,\\ &C(nd\to d;\, n_e d;\, L=4)=16/49; \end{aligned} \tag{11}$$

$$\begin{aligned} &C(nd\to g;\, n_e d;\, L=2)=144/245,\\ &C(nd\to g;\, n_e d;\, L=4)=40/49. \end{aligned} \tag{12}$$

Radial wave functions $v(nd)$ were obtained for the following states: Li $3d$; Na $3d$; K $3d$, $4d$, and $5d$; Rb $4d$, $5d$, and $6d$; Cs $5d$ and $6d$. The corresponding values of $\langle r^{-3}\rangle_{nd}$ are given in Table I. Of course, $\langle r^{-3}\rangle_{nd}$ is obtained from

$$\langle r^{-3}\rangle_{nd}=\int_0^\infty [v(nd)]^2 r^{-3}\, dr\ . \tag{13}$$

It should be noted that in several cases, we have actually obtained two wave functions for each nd state, which will be denoted by type a and type b. Type a wave functions are those calculated in the potential $V_{n_0 s}+a|V_{\text{exch}}|$ described above. They are thus based on the potential $V_{n_0 s}$ for each alkali atom [see Eq. (7)].

Type b wave functions are based on the effective potentials given by Herman and Skillman,[22] V_{HS}, which were derived from the Hartree-Fock-Slater method.[19] V_{HS} in Rydberg units is actually given by $-2ZU(r)/r$, where $U(r)$ is the function tabulated in Ref. 22. The potential V_b of type b is given by

$$V_b=V_{\text{HS}}+a'|V_{\text{exch}}|\ , \tag{14}$$

where a' is a constant similar to a, which is so adjusted that the corresponding wave equation

$$\left(-\frac{d^2}{dr^2}+\frac{6}{r^2}+V_{\text{HS}}+a'|V_{\text{exch}}|-E_0(nd)\right)v_b(nd)=0\ , \tag{15}$$

is satisfied by the function $v_b(nd)$, which is required to be well behaved at $r\to\infty$ with the experimental energy eigenvalue $E_0(nd)$, in the same manner as for Eq. (7) with $V_0=V_{n_0 s}$. In the same notation as for Eq. (15), $v(nd)$ in Eq. (7) should actually be written as $v_a(nd)$.

In Table I, n_0 is the principal quantum number of the lowest unoccupied d state. For greater ease of identification, we have actually noted the state involved in parentheses after the corresponding value of $\langle r^{-3}\rangle_{nd}$. The $3d$ functions for Li and Na, and the $4d$, $5d$, and $6d$ wave functions for Rb are of type a [potential of Eq. (7)]; the corresponding values of $\langle r^{-3}\rangle$ are listed in Table I. The functions $v_a(3d)$ for Na and $v_a(5d)$ for Rb are shown in Figs. 1 and 2, respectively. The reasons for considering wave functions of type b (as an alternative to type a) can be understood in terms of the behavior of $v(5d)$ for Rb, as shown in Fig. 2. We wish to point out the nearly flat region of $v_a(5d)$ between $r\cong 2.0a_H$ and $r\cong 4.5a_H$. This arises from the fact that the function to be defined as $Q(r)$, which appears in Eq. (7), is nearly zero over this range, and moreover the derivative $dv(nd)/dr$ is also very small. Here $Q(r)$ is the function of radius inside the large parentheses of Eq. (7):

$$Q(r)\equiv\frac{6}{r^2}+V_{n_0 s}+a|V_{\text{exch}}|-E_0(nd)\ . \tag{16}$$

$Q(r)$ is very small in the above-mentioned region of r, as a result of the almost complete cancellation of the (positive) centrifugal term $6/r^2$ and the (negative) potential term $V_{n_0 s}+a|V_{\text{exch}}|-E_0(nd)$. As a result, d^2v/dr^2 is essentially zero, and since dv/dr is also very small in this region, $v(r)$ is approximately constant over this interval of r. A similar behavior has been found for the other two heavy alkali atoms, i.e., K nd and Cs nd. However, the cancellation described above is ob-

TABLE I. Calculated values of $\langle r^{-3}\rangle_{nd}$ (in units a_H^{-3}) for the nd states of the alkali atoms. In the entry for (nd), n_0 is the principal quantum number of the lowest unoccupied d state of the atom. Actually, for easier identification, we have also listed the pertinent nd value in parentheses after each $\langle r^{-3}\rangle_{nd}$. In connection with the results for Li and Na, we note that for hydrogenic wave functions, $\langle r^{-3}\rangle_{3d}=1/15n^3=0.002\,469a_H^{-3}$. For K and Cs, the two results given for each nd were obtained by means of the wave functions a and b, respectively, described in the text.

(nd)	Li	Na	K	Rb	Cs
(n_0,d)	0.002 501 ($3d$)	0.002 802 ($3d$)	0.026; 0.074 ($3d$)	0.1896 ($4d$)	0.43; 0.79 ($5d$)
(n_0+1,d)	···	···	0.018; 0.044 ($4d$)	0.096 35 ($5d$)	0.156; 0.239 ($6d$)
(n_0+2,d)	···	···	0.010; 0.025 ($5d$)	0.04946 ($6d$)	···

viously a delicate phenomenon, and depending on the extent of the region of cancellation and the value of dv/dr in this region, a whole variety of shapes of $v(r)$ vs r can result. This in turn affects the value of $\langle r^{-3}\rangle_{nd}$.

For this reason, it was decided to recalculate $\langle r^{-3}\rangle$ in a few cases, using a second type of base potential, namely, V_{HS} (type b). For Na and Rb, the differences between $\langle r^{-3}\rangle_{nd}$ for type a and type b wave functions were very small, but this was not found to be the case for K and Cs. The results for K, which are listed in Table I, can be understood in terms of a phenomenon which is the $3d$ analog of the lanthanide contraction of the $4f$ wave function at the beginning of the rare-earth region.[23] First, we note that the smaller of the $\langle r^{-3}\rangle_{nd}$ values for K in Table I refers to the type a potential, while the larger $\langle r^{-3}\rangle_{nd}$ values refer to the type b potential. Although these values differ considerably in each nd case, they are always considerably larger than the values for Li and Na $3d$. These latter values are nearly hydrogenic. In this connection, we note that for a hydrogenic $3d$ wave function with effective charge $Z=1$, namely,

$$u_0(3d)_{\text{H}}=\frac{4r^3}{81(30)^{1/2}}\,e^{-r/3}\,, \tag{17}$$

the value of $\langle r^{-3}\rangle_{3d,H}$ is $1/15n^3=1/(15)(27)=2.469\times10^{-3}\,a_{\text{H}}^{-3}$. Thus for Li, we have

$$\frac{\langle r^{-3}\rangle_{3d,\text{Li}}}{\langle r^{-3}\rangle_{3d,\text{H}}}=\frac{2.501}{2.469}=1.013\,, \tag{18}$$

and for Na,

$$\frac{\langle r^{-3}\rangle_{3d,\text{Na}}}{\langle r^{-3}\rangle_{3d,\text{H}}}=\frac{2.802}{2.469}=1.135\,. \tag{19}$$

Considering the $3d$ wave function, we note that the values of $\langle r^{-3}\rangle_{3d}$ for K are $0.026/0.00247=10.5$ and $0.074/0.00247=30.0$ times larger than the hydrogenic values (for $Z_{\text{eff}}=1$) for type a and type b, respectively. We note that for Na, we have plotted the $3d$ hydrogenic wave function, alongside the Na $3d$ wave function in Fig. 1, showing that the two functions are almost indistinguishable. Actually beyond the maximum at $r=9a_H$, the differences are so small that they could not be shown in the figure. What is happening for K is that this element is in the region where the $3d$ wave function rapidly becomes more internal with increasing Z, in the same manner as the $4f$ wave function in the region of lanthanum ($Z=57$) and cerium ($Z=58$). Thus K has atomic number $Z=19$, and scandium, with $Z=21$, is the first element for which the $3d$ wave function is essentially internal; for Sc, we have[5] $\langle r^{-3}\rangle_{3d}=1.428a_H^{-3}$, as calculated in Ref. 5. Thus $\langle r^{-3}\rangle_{3d}$ varies very rapidly with Z near $Z=19$ (K), and this fact probably accounts for the disparity in the values of $\langle r^{-3}\rangle_{3d}$ obtained with wave functions of type a and b. The same argument applies to the values of $\langle r^{-3}\rangle_{4d}$ and $\langle r^{-3}\rangle_{5d}$ for $4d$ and $5d$, respectively, for the case of potassium. However, because of the high sensitivity of $\langle r^{-3}\rangle_{nd}$ to the details of the wave functions, we do not consider the resulting values of $R(nd)$ for K as very reliable. On the other hand, for Na $3d$, the two values of $\langle r^{-3}\rangle_{3d}$ obtained from type a and type b wave functions are 2.790×10^{-3} and $2.813\times10^{-3}a_H^{-3}$, respectively. The difference is less than 1%, and the

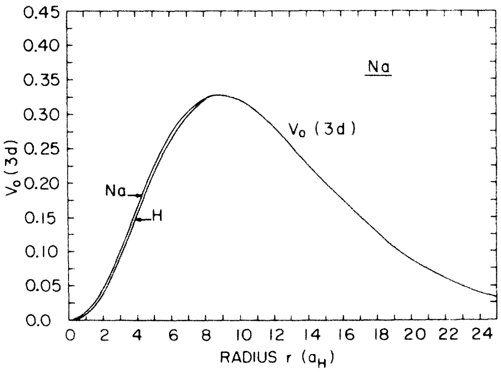

FIG. 1. Valence wave functions $v_0(3d)$ for Na and H, as a function of the distance r from the nucleus. Note that the radial wave functions are multiplied by r, and normalized to 1; $\int_0^\infty v_0^2\,dr=1$. For $r\gtrsim8a_H$, the wave functions $v_0(3d)$ for Na and H are essentially indistinguishable, and for this reason, a single curve has been shown in this region.

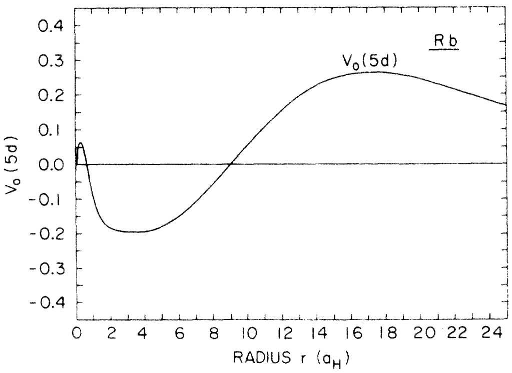

FIG. 2. Radial wave function $v_0(5d)$ for Rb, as a function of the distance r from the nucleus. The flat region of $v_0(5d)$ from $r\sim2a_H$ to $r\sim4.5a_H$ reflects the near-zero values of the differential coefficient $Q(r)$ [Eq. (16)], which results in d^2v_0/dr^2 being nearly zero in this region. For larger r ($r\gtrsim9a_H$), $v_0(5d)$ has an essentially normal third maximum, which is attained at $r\sim17a_H$.

value of $R(3d)$ is therefore believed to be very reliable.

For Rb $5d$, we have also carried out calculations for both type a and type b wave functions. The resulting values of $\langle r^{-3}\rangle_{5d}$ are $\langle r^{-3}\rangle_{5d,a} = 0.096\,35$ and $\langle r^{-3}\rangle_{5d,b} = 0.108\,97$, which differ by only ~13%. The wave functions a were used in the calculations of $R(nd)$, and based on the small discrepancy between the two values of $\langle r^{-3}\rangle_{5d}$, the results are believed to be quite accurate.

For the case of Cs $5d$ and Cs $6d$, the two values of $\langle r^{-3}\rangle_{nd,\alpha}$ $(\alpha = a,b)$ differ considerably, and as a result the values of $R(nd)$ obtained in the calculations are not very accurate. In the table listing the final results (Table VII), we have given the average of the results of two calculations pertaining to wave functions a and b, respectively, for both $5d$ and $6d$.

For the details of the calculations of R, in particular the direct term R_D and the exchange term R_E, we refer to the papers of Refs. 2 and 3. The programs to calculate the direct and exchange integrals for R were written by Peierls in connection with the work of Ref. 2.

The results for $R(nd)$ will now be presented and discussed. For Li $3d$, we find $R_D(3d) = +0.2469$, $R_E(3d) = -0.0015$, giving a total value $R(3d) = +0.2454$. We note that in this case, the exchange term is very small, due to the smallness of the overlap between the $3d$ function (see Fig. 1 for Na) and the internal $1s$ function. For the $1s$ wave function, we used the hydrogenic approximation of James,[13] with $Z_0 = Z - 0.31 = 2.69$. Thus,

$$u_0'(1s) = 2Z_0^{3/2} r e^{-Z_0 r} , \tag{20}$$

for which the perturbation $v_1'(1s \to d)$ is given by[24]

$$v_1'(1s \to d) = \tfrac{1}{3}Z_0^{3/2}(1 + \tfrac{1}{3}Z_0 r)e^{-Z_0 r}. \tag{21}$$

We note that the value of γ_∞ (ionic antishielding factor)[25] corresponding to the functions (20) and (21) is $\gamma_\infty = 2/3Z_0$, which for $Z_0 = 2.69$ becomes $\gamma_\infty = 0.2478$. Thus the direct term $R_D(3d) = 0.2469$ is very close to γ_∞, and since R_E is so small, as discussed above, the total $R = 0.2454$ is also approximately equal to γ_∞. These results can be readily explained by the fact that the $3d$ wave function is so external to $1s$, that the $3d$ electron acts virtually like an external charge, for which we expect that R approaches γ_∞.

For the case of Na $3d$, the results for R_D, R_E, and R_{tot} are presented in Table II. For comparison, the values of $\gamma_\infty(nl \to l')$ are listed in the last column of the table. Similar to the case of Li $3d$, the values of $R_D(nl \to l')$ are very close to $\gamma_\infty(nl \to l')$, especially for the angular modes $(l' = l+2)$, namely, $1s \to d$, $2s \to d$, and $2p \to f$. For the radial mode $(l' = l)$, $2p \to p$, the difference between the two quantities is somewhat larger, and as a result the total R_D is -4.446, as compared to $\gamma_\infty = -4.778$. We also note that the exchange terms are very small for the angular modes (combined effect $= -0.0115$), whereas they are somewhat larger $(+0.554$, i.e., 11%) for the single radial mode present in Na. In any case, the total correction factor R is -3.904, which is of the same sign and not much smaller in magnitude than $\gamma_\infty = -4.778$. Thus the situation for Na is very similar to that for Li.

TABLE II. Values of the direct terms R_D, the exchange terms R_E, and the total R for the Na $3d$ state. The values of the ionic antishielding factor $\gamma_\infty(nl \to l')$ are listed in the last column for comparison with the corresponding entries for R_{tot} .

$nl \to l'$	R_D	R_E	R_{tot}	γ_∞
$1s \to d$	0.064 05	−0.000 05	0.064 00	0.064 10
$2s \to d$	0.2234	−0.0046	0.2188	0.2286
$2p \to f$	0.3098	−0.0069	0.3029	0.3180
Total (ang)	+0.5973	−0.0115	+0.5857	+0.6107
$2p \to p$	−5.043	+0.554	−4.489	−5.389
Total	−4.446	+0.542	−3.904	−4.778

For the case of potassium, as discussed above, a very reliable value of R could not be obtained in the present work, on account of the sensitive dependence of $\langle r^{-3}\rangle_{nd}$ on the details of the radial wave functions. The final values of R calculated here exhibit a small antishielding $(R < 0)$; these values were obtained using the wave functions of type b for which $\langle r^{-3}\rangle_{nd}$ has the larger values. The values of $R(nd)$ are as follows $R(3d) = -0.32$, $R(4d) = -0.09$, and $R(5d) = -0.03$.

For the case of rubidium, the $5d$ wave function is not sensitive to the details of the potential, and the resulting values of $\langle r^{-3}\rangle_{5d}$ for type a and type

TABLE III. Values of the terms of R_{tot} (=direct+exchange) for the angular modes for Rb $4d$, $5d$, and $6d$. For convenience, each of the terms has been multiplied by 10^2.

$nl \to l'$	$10^2 R_{4d}$	$10^2 R_{5d}$	$10^2 R_{6d}$
$1s \to d$	1.711	1.709	1.709
$2s \to d$	1.722	1.701	1.693
$3s \to d$	1.657	1.579	1.553
$4s \to d$	1.715	1.478	1.402
$2p \to f$	2.997	2.972	2.965
$3p \to f$	2.641	2.522	2.482
$4p \to f$	2.733	2.334	2.206
$3d \to g$	3.327	3.185	3.137
$3d \to s$	0.809	0.741	0.718
Total (ang)	19.312	18.221	17.865

TABLE IV. Values of the terms of R_{tot} for the radial modes $nl \to l$ for Rb $4d$, $5d$, and $6d$. The last three rows of the table list the total radial contribution from all radial modes, the similar total for all angular modes (from Table III), and the grand total R for Rb $4d$, $5d$, and $6d$.

$nl \to l$	R_{4d}	R_{5d}	R_{6d}
$2p \to p$	−0.0516	−0.0482	−0.0470
$3p \to p$	−0.4453	−0.4159	−0.4061
$3d \to d$	−0.1197	−0.1097	−0.1062
$4p \to p$	−0.0584	+0.1354	+0.1788
Total (rad)	−0.6750	−0.4384	−0.3805
Total (ang)	+0.1931	+0.1822	+0.1787
Total	−0.4819	−0.2562	−0.2018

b wave functions differ by only 13%, as discussed above. It is therefore believed that the calculations of R are reliable and accurate in this case. We will present detailed results for R of Rb nd obtained with the type a wave functions based on V_{4s} [cf. Eq. (7)]. These results are presented in Tables III–VI. Table III gives the angular terms $R_{n_ed}(nl \to l')$ for the three states $n_ed = 4d$, $5d$, and $6d$. Note that these terms have been multiplied by 10^2 for convenience. The radial terms $R_{n_ed}(nl \to l)$ are listed in Table IV, which also gives the total angular contribution and the resulting total R_{4d}, R_{5d}, and R_{6d}. As pointed out above, the $5d$ wave function (of type a) for Rb is shown in Fig. 2, as an example of the n_ed wave functions for the heavier alkali atoms.

Tables V and VI give, separately, the direct and exchange terms in each case, i.e., for each $nl \to l'$ mode for Rb $5d$. We note that for the angular modes (Table V), R_E is generally much smaller than R_D, so that the resulting values of $R_{\text{tot}}(nl \to l')$ are positive in all cases. The notation $R_E(L_1)$ and $R_E(L_2)$ in the heading of these tables should be explained. As discussed in previous papers, in particular in Refs. 2 and 3, the exchange terms involve the angular momentum (multipolarity) L of the interaction, and there may be more than one L value for a given $nl \to l'$ interacting with n_ed (n_e is the principal quantum number of valence electron; n the principal quantum number of core electron). The L-type interaction energy involves the double integral:

$$K(nl \to l'; n_ed; L) = \int_0^\infty u_0' v'(n_ed) g_L \, dr \ , \tag{22}$$

where the function $g_L(r)$ is defined by

$$g_L(nl \to l'; n_ed) = \frac{1}{r^{L+1}} \int_0^r v_1'(nl \to l') \, v'(n_ed) r'^L \, dr' + r^L \int_r^\infty v_1'(nl \to l') v'(n_ed) r'^{-L-1} \, dr' \tag{23}$$

The term $R_E(nl \to l'; n_ed; L)$ is then given by

$$R_E(nl \to l'; n_ed; L) = \frac{\Gamma_E(nl \to l'; n_e d; L)}{\langle r^{-3} \rangle_{n_ed}} \ , \tag{24}$$

where $\Gamma_E(nl \to l'; n_ed; L)$ is defined by

$$\Gamma_E(nl \to l'; n_ed; L) = - C(nl \to l'; n_ed; L) \times K(nl \to l'; n_ed; L) \ , \tag{25}$$

and $C(nl \to l'; n_ed; L)$ is the coefficient given by Eqs. (8)–(12).

In Eq. (23), $v_1'(nl \to l')$ is the solution of the equation[1]

$$\left(- \frac{d^2}{dr^2} + \frac{l'(l'+1)}{r^2} + V_0 - E_0 \right) v_1'(nl \to l') = u_0'(nl) \left(\frac{1}{r^3} - \left\langle \frac{1}{r^3} \right\rangle_{nl} \delta_{ll'} \right) \ . \tag{26}$$

TABLE V. Values of the direct and exchange contributions for the angular modes $(l' \neq l)$ of Rb $5d$. For the exchange terms $R_E(L_i)$, L_i denotes the multipolarity of the exchange interaction between $nl \to l'$ and $5d$, as discussed in the text [Eqs. (22)–(25)]. The value of L_i is entered in parentheses after each value of $R_E(L_i)$.

$nl \to l'$	R_D	$R_E(L_1)$	$R_E(L_2)$	R_{tot}
$1s \to d$	0.017 87	−0.000 78 (2)		0.017 09
$2s \to d$	0.024 08	−0.007 07 (2)		0.017 01
$3s \to d$	0.016 49	−0.000 70 (2)		0.015 79
$4s \to d$	0.022 70	−0.007 92 (2)		0.014 78
$2p \to f$	0.038 76	−0.004 58 (1)	−0.004 46 (3)	0.029 72
$3p \to f$	0.026 84	−0.000 52 (1)	−0.001 10 (3)	0.025 22
$4p \to f$	0.034 99	−0.005 82 (1)	−0.005 83 (3)	0.023 34
$3d \to g$	0.035 21	−0.001 69 (2)	−0.001 67 (4)	0.031 85
$3d \to s$	0.007 71	−0.000 30 (2)		0.007 41
Total (ang)	0.224 65	−0.029 38	−0.013 06	0.182 21

TABLE VI. Values of the direct and exchange contributions for the radial modes ($l'=l$) of Rb 5d. For the exchange terms $R_E(L_i)$, L_i denotes the multipolarity of the exchange interaction between $nl\to l$ and 5d, as discussed in the text [Eqs. (22)–(25)]. The value of L_i is entered in parentheses after each value of $R_E(L_i)$.

$nl\to l$	R_D	$R_E(L_1)$	$R_E(L_2)$	R_{tot}
$2p\to p$	−0.1607	+0.1014 (1)	+0.0111 (3)	−0.0482
$3p\to p$	−0.3531	−0.0585 (1)	−0.0043 (3)	−0.4159
$4p\to p$	−0.8131	+0.8588 (1)	+0.0897 (3)	+0.1354
$3d\to d$	−0.1103	−0.0009 (2)	+0.0015 (4)	−0.1097
Total (rad)	−1.4372	+0.9008	+0.0980	−0.4384

We note that the direct term $R_D(nl\to l';n_ed)$ is given by

$$R_D(nl\to l';n_ed)=\frac{\Gamma_D(nl\to l';n_ed)}{\langle r^{-3}\rangle_{n_ed}}\,, \tag{27}$$

where the integral $\Gamma_D(nl\to l';n_ed)$ is defined by

$$\Gamma_D(nl\to l';n_ed)=\int_0^\infty \frac{\gamma(nl\to l';r)}{r^3}\,[v(n_ed)]^2dr\,, \tag{28}$$

and the function $\gamma(nl\to l';r)$ is given by

$$\gamma(nl\to l';r)=c(nl\to l')\left(\int_0^r u_0'(nl)v_1'(nl\to l')\,r'^2\,dr' + r^5\int_0^\infty u_0'(nl)v_1'(nl\to l')r'^{-3}\,dr'\right). \tag{29}$$

The angular coefficients $c(nl\to l')$ have the following values: 8/5 for $ns\to d$ and $nd\to s$; 48/25 for $np\to p$; 72/25 for $np\to f$; 16/7 for $nd\to d$; and 144/35 for $nd\to g$.

Referring again to Tables V and VI, the numbers in parentheses after each entry for $R_E(L_1)$ and $R_E(L_2)$ give the multipolarity L of the exchange interaction involved for $K(nl\to l';n_ed;L)$, as given by Eqs. (22) and (23). As an example, in Table VI, for Rb $2p\to p$; the $L_1=1$ term of R_E is +0.1014, and the $L_2=3$ term is +0.0111.

The entries of Table V show that for the angular modes ($l'=l+2$), the direct terms R_D are always shielding (i.e., positive), whereas the exchange terms R_E are negative (antishielding), and generally much smaller than R_D, so that the net effect for each mode is shielding (positive). The largest ratios of $|R_E|/R_D$ occur for $2s\to d$, $4s\to d$, and $4p\to f$, in which cases $|R_E|/R_D$ is of the order of $\frac{1}{3}$. The situation is quite different for the radial modes, $np\to p$ and $3d\to d$, as is shown by Table VI. For the modes $2p\to p$ and $4p\to p$ in this table, the exchange terms are of the same order as the direct terms, and since they have opposite sign, they actually reverse the sign of R_{tot} for the case of $4p\to p$, where $R_D=-0.8131$ and $R_{\text{tot}}=+0.1354$. The large magnitude of $R_D(4p\to p)$ and $R_E(4p\to p;\,L=1)=+0.8588$ can partially understood in terms of the smallness of the denominator $\langle r^{-3}\rangle_{5d}$ in Eqs. (24) and (27). Thus $\langle r^{-3}\rangle_{5d}$ is only $0.096\,35a_H^{-3}$ for the 5d state of Rb. The interaction energies $\Gamma_D(4p\to p;\,5d)$ and $C(4p\to p;\,5d;\,L=1)\Gamma_E(4p\to p;\,5d;\,L=1)$ are of the same order of magnitude as $\langle r^{-3}\rangle_{5d}$, because of the relatively large overlap of the $v_1'(4p\to p)$ perturbation with the valence wave function $v_0'(5d)$.

It is seen from Table VI that when the results from all four radial modes are added, the corresponding total R_{rad} is negative, i.e., −0.4384, and thus gives the antishielding effect which is generally expected for the radial modes. When this result is added to the shielding term $R_{\text{ang}}=0.1822$ (see Table V), there is a net total antishielding $R=-0.2562$. Table IV shows that this net antishielding effect exists for all three states, 4d, 5d, and 6d, although there is a large variation in going from 4d to 5d and 6d. This variation is obviously due to the wide variability of the radial term (see Table IV), which is in turn due to the near-cancellation of the direct and exchange terms, particularly for $4p\to p$ interacting with nd.

For the case of cesium, very extensive calculations were carried out for the states 5d and 6d, both with the wave functions of type a and type b. The situation with respect to the angular terms $R(nl\to l+2)$ is essentially the same as for Rb nd. These terms each give a shielding, with the direct term being appreciably larger than the (negative) exchange term in all cases. However, it may be noted that the total $R(\text{ang})$ is somewhat smaller than for Rb nd. Thus the values are

$$R(\text{ang};\,6d_a)=0.1293\,;\quad R(\text{ang};\,6d_b)=0.1257\,; \tag{30}$$

$$R(\text{ang};\,5d_a)=0.1399\,;\quad R(\text{ang};\,5d_b)=0.1305\,. \tag{31}$$

These results are ~30% smaller than the corresponding values for Rb, namely, $R(\text{ang};nd)\approx 0.18$, as given in Tables III and IV. We note that in Eqs. (30) and (31), the subscript (a or b) of nd denotes the type of valence wave function used in the calculations.

For the radial modes of Cs 5d and 6d, the situation is somewhat more complicated. For all modes except for $5p\to p$, the net value of $R(=R_D+R_E)$ is negative (antishielding), i.e., it has the same sign as the predominant direct term R_D. The largest term $R(nl \to l)$ among these modes is provided by $4p \to p$, for which the calculated values range from -0.3660 for $6d_b$ to -0.4522 for $5d_a$. On the other hand, for $5p \to p$, there is a net shielding in all cases (i.e., $5d_a$, $5d_b$, $6d_a$, and $6d_b$). This shielding ranges from $+0.2219$ for $5d_a$ to $+0.3249$ for $5d_b$. (The values for $6d_a$ and $6d_b$ are intermediate between these limits.) To see how these results are obtained, we consider, as an example, $5p \to p$ interacting with $6d_b$. We have

$$R_D(5p \to p;\, 6d_b) = -0.4125\;; \tag{32}$$

$$R_E(5p \to p;\, 6d_b;\, L=1) = +0.6360\;; \tag{33}$$

$$R_E(5p \to p;\, 6d_b;\, L=3) = +0.0679\;, \tag{34}$$

giving a total $R(5p \to p;\, 6d_b) = +0.2914$. It is obvious from Eqs. (32)–(34) that the $L=1$ exchange term is dominant, and together with the $L=3$ exchange term, it provides a substantial shielding which outweighs the antishielding produced by the direct term. The total values of $R_{\rm rad}$ (as obtained by combining all modes $nl \to l$) are negative (antishielding), but vary from -0.2697 for $5d_b$ to -0.4631 for $5d_a$. The resulting grand total $R = R_{\rm rad} + R_{\rm ang}$ is antishielding in all cases, with the following values: $R(6d_a) = -0.2552$; $R(6d_b) = -0.1610$; $R(5d_a) = -0.3232$; and $R(5d_b) = -0.1392$.

The average of the two results for wave functions a and b is $R(5d) = -0.23 \pm 0.09$ and $R(6d) = -0.21 \pm 0.05$, where we have included a probable error of such magnitude as to overlap the results found with wave functions a and b, separately. These values are listed in Table VII, together with the corresponding results for Li, Na, K, and Rb. As mentioned above, the values for K are only to be taken as indications, on account of the great sensitivity of $\langle r^{-3}\rangle$ to the type of wave function considered. For Li and Na, values for $3d$ were calculated and are appropriately given in Table VII. The values for $4d$ and $5d$ are estimated on the basis of $R(3d)$ and the limiting value for large n, for hydrogenic nd wave functions, namely, the ionic antishielding factor[25] γ_∞ for the corresponding positive ion. Thus $\gamma_\infty(\mathrm{Li}^+) = 0.2478$ and $\gamma_\infty(\mathrm{Na}^+) = -4.78$ (see Table II).

The results of Table VII exhibit a general antishielding (except for Li), as was expected from the previous results for the excited np states of the alkalis.[3] However, for the case of Na, the antishielding is much larger than the range of values $R \sim -0.1$ to -0.3 previously encountered for the alkali atom np states. As explained above, the reason is that for hydrogenic nd states (which exist up to atomic number $Z \sim 15$), $R(nd)$ approaches γ_∞ with increasing n, and this fact is borne out both for Li and for Na. The situation for Li $3d$ may be contrasted with that for Li np (see Ref. 3, Table V), where already the direct term R_D is appreciably less than $\gamma_\infty (R_D \approx 0.17)$, while the exchange term R_E is also appreciable ($R_E \approx -0.07$), owing to the extensive overlap of the np wave function with $u_0(1s)$. The resulting $R_{\rm tot}$ is of the order of 0.10, and thus much smaller than $\gamma_\infty = 0.248$. By contrast, for Li $3d$, we have $R_D(3d) = 0.2469$ ($\approx \gamma_\infty$), and $R_E(3d) = -0.0015$ is very small, indicating the smallness of the overlap of $3d$ with $1s$, as opposed to the overlap of $2p$ with $1s$.

The results for the heavy alkalis (K, Rb, and Cs) show a much smaller antishielding than γ_∞, as a result of the fact that the nd wave functions are much more contracted than the hydrogenic wave functions. This is, of course, also demonstrated by the values of $\langle r^{-3}\rangle_{nd}$ in Table I. For Rb and Cs, the antishielding $R(nd)$ is of the same order as $R(np)$ (see Ref. 3, Table XI), namely, $R(nd) \sim -0.20$ to -0.25, except for Rb $4d$, for which the calculated R is -0.48. However, in contrast to the situation for the np states (Ref. 3), we must emphasize that for nd states, there is potentially a large variability of R owing to the cancellation of large direct antishielding terms R_D with equally large exchange shielding terms R_E, both of order 0.6–0.8, for the outermost $np \to p$ excitations interacting with $n_e d$. This situation has been extensively described in connection with the results for Rb in Table VI, and in connec-

TABLE VII. Summary of the resulting values of $R(nd)$ for the lowest three excited nd states of the alkali atoms. As discussed in the text, the results for Li, Na, and Rb are believed to be essentially reliable. The values for K have considerable uncertainty, owing to the difficulty of obtaining a reliable value of $\langle r^{-3}\rangle_{nd}$ from the radial wave functions. The results for Cs represent the range of values obtained with valence nd wave functions a and b, respectively (e.g., -0.16 for the wave function $6d_b$, as compared to -0.26 for the wave function $6d_a$).

(nd)	Li	Na	K	Rb	Cs
(n_0, d)	$+0.245$ ($3d$)	-3.90 ($3d$)	-0.32 ($3d$)	-0.48 ($4d$)	-0.23 ± 0.09 ($5d$)
(n_0+1, d)	≈ 0.25 ($4d$)	~ -4.5 ($4d$)	-0.09 ($4d$)	-0.26 ($5d$)	-0.21 ± 0.05 ($6d$)
(n_0+2, d)	≈ 0.25 ($5d$)	~ -4.8 ($5d$)	-0.03 ($5d$)	-0.20 ($6d$)	⋯

tion with the similar results for Cs $5p \to p$ interacting with $6d$ [see Eqs. (32)-(34)]. Thus it is possible to have a rather wide variation in the total R with increasing nd, although the trend of all of the values for Rb and Cs is that the total net R is antishielding, and of order -0.2 to -0.5.

III. SUMMARY AND DISCUSSION

We have carried out extensive calculations of the quadrupole shielding or antishielding factors $R(nd)$ for the three lowest excited nd states of the alkali atoms. The results are essentially reliable for the cases of Li, Na, and Rb, while for the cases of K and Cs, there are appreciable uncertainties, which are connected with the difficulty in those cases in obtaining reliable valence nd wave functions. For the case of K, this difficulty has been attributed to the rapid change with Z of the nature of the nd wave function from an essentially hydrogenic function for $Z \lesssim 17$ to an internal wave function for $Z \gtrsim 21$ (case of scandium). This situation is analogous to the lanthanide contraction of the $4f$ wave function, which was first investigated by Mayer.[23]

In all cases, except for lithium, an appreciable net antishielding was found. The results are summarized in Table VII. For Li and Na, $R(nd)$ is approximately equal to the total ionic shielding or antishielding factor γ_∞. This results from the fact that the nd wave function for these atoms is essentially hydrogenic (with effective charge $Z_0 = 1$), and, as a result, the overlap between $v_0(nd)$ and the core wave functions $u_0(nl)$ and their perturbations $v_1(nl \to l')$ is very small. Of course, for Li, γ_∞ is positive, and accordingly $R \cong +0.25$, whereas for Na, γ_∞ is negative (antishielding), and correspondingly $R \cong -3.9$ to -4.8, in going from $3d$ to $5d$.

For the heavier alkalis, namely, K, Rb, and Cs, $R(nd)$ is generally antishielding, but with much smaller absolute values than for Na. Thus $R(nd)$ varies generally in the range from -0.2 to -0.5 (with the exception of K $4d$ and $5d$, for which no reliable values could be obtained, as discussed in Sec. II).

This situation differs somewhat from that encountered previously for the excited np states of the alkali atoms, as described in Ref. 3. In that case, $R(np)$ was $\sim +0.1$ for Li np, and in the range from -0.12 to -0.26 for all of the excited np states of the four other alkali atoms (see Table XI of Ref. 3). Also the expected uncertainties of the calculated $R(np)$ values were sufficiently small ($\sim \pm 0.03$), that is was possible to obtain corrected values of the nuclear quadrupole moments Q of twelve alkali isotopes (see Table XIV of Ref. 3).

In the present work (and also in the work of Refs. 1-5), we have used only the first order of the perturbation of the core by the nuclear moment Q, and also the first order of the electrostatic interaction between different electrons (e.g., the valence electron and a core electron). Recently, calculations which incorporate some of the higher-order diagrams in the interelectronic interaction have been carried out by Nesbet,[26] Hameed and Foley,[27] and Ray, Lee, and Das.[28] We note that these higher-order diagrammatic calculations are related to the earlier work of Kelly,[29] and of Chang, Pu, and Das.[30] The calculations of Ray *et al.*[28] utilize the linked-cluster many-body perturbation-theory (LCMBPT) procedure of Brueckner and Goldstone.[31] Without a detailed calculation for the nd states, it seems impossible to estimate the effect of the higher-order terms on the values of $R(nd)$, except for the general comment that the values of R for the more highly excited states are expected to be less affected by the higher-order terms than the values of R for the ground states or the first excited states (e.g., for lithium[26,27] and beryllium[28]).

The effect of the higher-order terms on the ionic antishielding factor γ_∞ has also been investigated by Ray *et al.* both for[32] Fe^{3+} and for the ions[33] Rb^+ and Cs^+. In both cases, the net effect of the higher-order terms is small, of the order of 10% for Fe^{3+}, and 1% for Rb^+ and Cs^+. Thus the first-order calculations of γ_∞ for these ions, which had been previously carried out by the present author[34] are reliable to at least 10%, which is the order of the inaccuracy introduced by uncertainties in the zero-order wave functions $u_0(nl)$. In this connection, we may note that extensive first-order calculations of γ_∞ have been recently carried out by Feiock and Johnson[35] (relativistic calculations) and by Gupta, Rao, and Sen.[36] The calculations of Gupta *et al.*[36] go beyond previous calculations,[34] in that the shielding or antishielding factor has been evaluated not only for the nuclear site (γ_∞ here denoted by λ_0), but also for various sites within the atom (denoted by λ_{nl} for the site at the nl shell).

In connection with the validity of the first-order calculations presented in this paper, we wish to point out that similar first-order calculations previously carried out using the same formalism have given very good agreement with experiment in several cases. Thus for two excited states of the copper atom,[37,38] namely, $3d^9 4s^2$ and $3d^{10} 4p$, the uncorrected values of the nuclear quadrupole moment Q differ by $42 \pm 4\%$. When the two different correction factors $C_{3d} = 1/(1 - R_{3d}) = 1/0.822 = 1.217$ and $C_{4p} = 1/(1 - R_{4p}) = 1/1.175 = 0.851$ calculated in Ref. 2 are applied, the resulting corrected values of $Q(\text{Cu}^{65})$ are in excellent agreement with each other. A similar situation exists for the configurations $4f^9 6s^2$ and $4f^8 5d6s^2$ of the terbium atom, i.e., for the quadrupole hyperfine structure of Tb^{159}, which has been investigated by Childs.[39] Again the two uncorrected Q values are brought into good agreement by applying the two (different) correction factors $C_{4f} \approx 1.1$ and $C_{5d} \approx 0.77$ (see the discussion in Ref. 3, p. 847).

Besides the striking evidence of considerably different shielding and antishielding effects for different atomic states of copper and terbium, there is additional evidence in favor of the values of R for excited states calculated by the present first-order theory. In particular, the extensive investigation of zu Putlitz and co-workers[40,41] has shown that when the quadrupole moments of Rb^{87} and Cs^{134} are obtained from different excited atomic np states, there is appreciably better agreement between the values of Q obtained from different states, when the correction factors $C_{nl} = 1/(1 - R_{nl})$ for each state are appropriately applied, than without these correction factors. As an example, Bucka, zu Putlitz, and Rabold[41] have shown that for the uncorrected "experimental" values Q_{expt} for Rb^{85} and Rb^{87},

$$Q_{5p,\text{expt}}/Q_{7p,\text{expt}}(\text{Rb}^{85}, \text{Rb}^{87}) = 1.07 \pm 0.03 \ , \qquad (35)$$

which can be compared with the calculated ratio $C_{7p}/C_{5p} = 0.840/0.796 = 1.055$. The improved agreement for several alkali isotopes, when the calculated values of C_{nl} are applied, is shown specifically in Table XIII of Ref. 3.

Summarizing the situation, there is extensive evidence from a number of excited atomic states that the first-order perturbation theory for R used in the present work gives good agreement with the experimental results on the quadrupole hyperfine structure.

ACKNOWLEDGMENTS

I wish to thank Professor W. Happer for suggesting an investigation of quadrupole shielding and antishielding factors for the excited nd states of the alkali atoms. I would also like to thank Dr. R. F. Peierls for the computer programs described in Ref. 2, without which the present calculations would not have been possible in the limited time available. I am also indebted to Professor H. M. Foley for helpful discussions.

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

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