

Effect of the Atomic Core on the Nuclear Quadrupole Coupling*†

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The effect of the atomic core on the nuclear quadrupole coupling has been evaluated for several atomic ground states and excited states. It has been shown that for the excited states of the alkalis, as the principal quantum number n is increased, the ratio R of the induced effect to the direct interaction with the valence electron tends toward a constant asymptotic value which is of the same order as for the first excited state (~ -0.1 to -0.3). The sensitivity of R to inaccuracies in the zero-order core wave functions and valence wave functions has been investigated. Equations have been derived for the exchange terms in the quadrupole coupling due to the perturbation of the valence wave function by the nuclear quadrupole moment. The present calculations indicate that the exchange terms do not affect significantly the net antishielding obtained for the excited states of the alkalis.

I. INTRODUCTION

THE effect of the atomic core on the nuclear quadrupole coupling in atoms and molecules has been previously discussed and evaluated in several papers.^{1,2} The purpose of the present work is to extend the calculations to several atomic states not considered previously, and to examine in detail the exchange terms due to the perturbation of the valence wave function by the nuclear quadrupole moment Q . The results of this investigation show that the exchange terms have only a minor influence on the correction factor for Q for the excited states of the alkalis.

The main new result of the present calculations concerns the behavior of the core correction for the excited p states of the alkalis as the principal quantum number n is increased. For the Na $3p$, Rb $5p$, and Cs $6p$ first excited states, it was shown in III that the net effect of the core is antishielding, i.e., the ratio R which determines the core correction $C=1/(1-R)$ is negative. Here R is defined as minus the interaction energy due to the core divided by the direct interaction of Q with the valence electron. In the present work, R has also been obtained for Rb $6p$, Rb $7p$, and Cs $7p$. It was found that the values of R for the higher excited states are approximately the same as for the corresponding first excited states, and probably approach a constant value as $n \rightarrow \infty$. Thus the values of R for all of the excited states covered in the present work are of order -0.1 to -0.3 .

In Sec. II, we give the results of calculations of R for 11 atomic ground states and excited states. The behavior of R as n is increased will be discussed in

detail. We have also obtained results concerning the sensitivity of R to the core and valence wave functions used in the calculations.

In Sec. III, we present a derivation of the exchange terms due to the perturbation of the valence wave function by the potential due to the nuclear Q . It will be shown that the same terms also occur in the expression for the hfs interval a due to the nuclear magnetic moment, as a result of the exchange electrostatic interaction between the valence electron and the core. Hence these terms will cancel approximately in the ratio b/a from which the experimental values of Q are generally determined; here b is the hfs interval due to the quadrupole moment. Section III also gives the results of calculations of the other type of exchange terms, previously discussed in I, II, and III, which arise from the perturbation of the core wave functions by the nuclear Q . Similarly to the conclusions obtained in III, it is found that, although important for the atomic ground states, these terms are in general appreciably smaller than the direct Coulomb terms for the excited states and hence do not affect significantly the values of R for these states.

II. CORE CORRECTION FOR ATOMIC GROUND STATES AND EXCITED STATES

The calculations of the core correction R were carried out in the same manner as in III. R is given by

$$R = \langle \gamma r^{-3} \rangle / \langle r^{-3} \rangle, \quad (1)$$

where

$$\langle \gamma r^{-3} \rangle = \langle \gamma_{\text{ang}} r^{-3} \rangle + \langle \gamma_{\text{rad}} r^{-3} \rangle. \quad (2)$$

The notation $\langle \rangle$ represents an average over the valence wave function, whose radial part times r will be denoted by v_0' . The normalization of v_0' is: $\int_0^\infty v_0'^2 dr = 1$. γ/r^3 gives the radial dependence of the potential due to the induced quadrupole moment. $\gamma_{\text{ang}}(r)$ and $\gamma_{\text{rad}}(r)$ are the parts of $\gamma(r)$ due to the angular ($l' \neq l$) and radial ($l' = l$) modes of excitation of the core, respectively; here l' is the azimuthal quantum number of the perturbation, while l is the corresponding quan-

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¹ R. M. Sternheimer, Phys. Rev. **84**, 244 (1951); **86**, 316 (1952); **95**, 736 (1954). These papers will be referred to as I, II, and III, respectively.

² Foley, Sternheimer, and Tycko, Phys. Rev. **93**, 734 (1954); R. M. Sternheimer and H. M. Foley, Phys. Rev. **102**, 731 (1956). These papers will be referred to as IV and V, respectively.

tum number of the unperturbed closed shell. We have

$$\langle \gamma_{\text{ang}} r^{-3} \rangle = \int_0^\infty \gamma_{\text{ang}} v_0'^2 r^{-3} dr, \quad (3)$$

$$\langle \gamma_{\text{rad}} r^{-3} \rangle = \int_0^\infty \gamma_{\text{rad}} v_0'^2 r^{-3} dr, \quad (4)$$

$$\langle r^{-3} \rangle = \int_0^\infty v_0'^2 r^{-3} dr. \quad (5)$$

$\gamma_{\text{ang}}(r)$ and $\gamma_{\text{rad}}(r)$ are determined by the density of induced moment $Q_{i,\text{ang}}(r)$ and $Q_{i,\text{rad}}(r)$ due to the nuclear Q . Thus

$$\gamma_{\text{ang}}(r) = (1/Q) \left[\int_0^r Q_{i,\text{ang}} dr' + r^5 \int_0^\infty Q_{i,\text{ang}} r'^{-5} dr' \right], \quad (6)$$

and a similar equation gives $\gamma_{\text{rad}}(r)$ in terms of $Q_{i,\text{rad}}$. As shown in III, $Q_{i,\text{ang}}$ and $Q_{i,\text{rad}}$ are given by

$$Q_{i,\text{ang}}(r) = Qr^2 \left[\frac{8}{5} \sum_n (u_0' u'_{1,0 \rightarrow 2})_{ns} + \frac{72}{25} \sum_n (u_0' u'_{1,1 \rightarrow 3})_{np} + \frac{8}{5} \sum_n (u_0' u'_{1,2 \rightarrow 0})_{nd} + \frac{144}{35} \sum_n (u_0' u'_{1,2 \rightarrow 4})_{nd} \right], \quad (7)$$

$$Q_{i,\text{rad}}(r) = Qr^2 \left[\frac{48}{25} \sum_n (u_0' u'_{1,1 \rightarrow 1})_{np} + \frac{16}{7} \sum_n (u_0' u'_{1,2 \rightarrow 2})_{nd} \right], \quad (8)$$

where the sums extend over the occupied s , p , and d shells of the core. In Eqs. (7) and (8), u_0' is r times the radial unperturbed core wave function, normalized according to: $\int_0^\infty u_0'^2 dr = 1$; $u'_{1,l \rightarrow l'}$ is the radial part of the perturbed wave function and is determined by

$$\left[-\frac{d^2}{dr^2} + \frac{l'(l'+1)}{r^2} + V_0 - E_0 \right] u'_{1,l \rightarrow l'} = u_0' \left[\frac{1}{r^3} - \left\langle \frac{1}{r^3} \right\rangle_{nl} \right] \delta_{ll'}, \quad (9)$$

where V_0 is the spherical potential, E_0 is the unperturbed energy, and $\langle 1/r^3 \rangle_{nl}$ is the average of $1/r^3$ over the core wave function u_0' . For $l'=l$, that solution of (9) must be chosen which is orthogonal to u_0' . The potential V_0 is obtained from the requirement that it should reproduce the tabulated Hartree or Hartree-Fock function [see Eq. (9) or III]. Thus V_0 is given by

$$V_0 = \frac{1}{u_0'} \frac{d^2 u_0'}{dr^2} - \frac{l(l+1)}{r^2} + E_0. \quad (9a)$$

The results of the calculations are given in Table I. For B, the wave functions of Brown, Bartlett, and

TABLE I. Values of the core correction terms for several atomic ground states and excited states. The values of $\langle \gamma/r^3 \rangle$ and R do not include the exchange terms. $\langle \gamma/r^3 \rangle$ and $\langle 1/r^3 \rangle$ are in units a_H^{-3} . The results for K, Rb, and Cs were obtained with two different choices of the valence (np) wave function, as indicated by the superscript a or b . The wave functions a and b are described in the text.

Element State	$\langle \gamma_{\text{ang}}/r^3 \rangle$	$\langle \gamma_{\text{rad}}/r^3 \rangle$	$\langle \gamma/r^3 \rangle$	$\langle 1/r^3 \rangle$	R	$1/(1-R)$
B $2p$	0.0767	0	0.0767	0.535	0.143	1.17
Na $3p$	0.0151	-0.0504	-0.0353	0.145	-0.243	0.805
Cl $3p^5$	0.344	0.30	0.644	5.73	0.112	1.13
K $4p^a$	0.0271	-0.1135	-0.0864	0.460	-0.188	0.842
K $5p^a$	0.0085	-0.0301	-0.0216	0.152	-0.142	0.876
K $4p^b$	0.0347	-0.0406	-0.0059	0.669	-0.009	0.991
K $5p^b$	0.0120	-0.0128	-0.0008	0.234	-0.003	0.997
Cu $3d^9 4s^2$	2.02	-0.12	1.90	7.52	0.253	1.34
Rb $5p^a$	0.0443	-0.264	-0.220	0.813	-0.271	0.787
Rb $6p^a$	0.0155	-0.0772	-0.0617	0.295	-0.209	0.827
Rb $5p^b$	0.051	-0.189	-0.138	0.976	-0.141	0.876
Rb $6p^b$	0.0173	-0.0580	-0.0407	0.340	-0.120	0.893
Rb $7p^b$	0.0080	-0.0254	-0.0174	0.158	-0.110	0.901
Cs $6p^a$	0.0306	-0.366	-0.335	1.01	-0.332	0.751
Cs $7p^a$	0.0106	-0.111	-0.100	0.364	-0.275	0.784
Cs $6p^b$	0.036	-0.294	-0.258	1.26	-0.204	0.831
Cs $7p^b$	0.0127	-0.0946	-0.0819	0.459	-0.178	0.849

Dunn³ were used. The B results are essentially the same as obtained previously (Table I of III). The core excitations are $1s \rightarrow d$ and $2s \rightarrow d$, and were determined from (9).

For Na, the core ($1s, 2s, 2p$) and the $3p$ valence function of Fock and Petrashen⁴ were employed. Equation (9) was used to obtain all of the excitations. The value of $\langle \gamma_{\text{ang}}/r^3 \rangle$ is the same as obtained previously in III. It should be noted that for some of the cases, instead of calculating $\langle \gamma/r^3 \rangle$ from $u'_{1,l \rightarrow l'}$, we have obtained the terms of $\langle \gamma/r^3 \rangle$ from the perturbation $\bar{u}'_{1,l \rightarrow l'}$ of the core wave functions by the asymmetric part of the potential due to the valence electron. As has been shown previously,⁵ we have

$$\int_0^\infty \left[r^{-3} \int_0^r u_0' u'_{1,l \rightarrow l'} r'^2 dr' + r^2 \int_r^\infty u_0' u'_{1,l \rightarrow l'} r'^{-3} dr' \right] v_0'^2 dr = \int_0^\infty u_0' \bar{u}'_{1,l \rightarrow l'} r^{-3} dr, \quad (10)$$

where $\bar{u}'_{1,l \rightarrow l'}$ is the radial part of the perturbation of u_0' due to the P_2 term of the potential of the valence electron ($P_l =$ Legendre polynomial); $\bar{u}'_{1,l \rightarrow l'}$ is determined by

$$\left[-\frac{d^2}{dr^2} + \frac{l'(l'+1)}{r^2} + V_0 - E_0 \right] \bar{u}'_{1,l \rightarrow l'} = u_0' (\eta - \langle \eta \rangle \delta_{ll'}), \quad (11)$$

where

$$\eta(r) = r^{-3} \int_0^r v_0'^2 r'^2 dr' + r^2 \int_r^\infty v_0'^2 r'^{-3} dr', \quad (12)$$

$$\langle \eta \rangle = \int_0^\infty \eta u_0'^2 dr, \quad (13)$$

³ Brown, Bartlett, and Dunn, Phys. Rev. **44**, 296 (1933).

⁴ V. Fock and M. Petrashen, Physik. Z. Sowjetunion **6**, 368 (1934).

⁵ R. M. Sternheimer and H. M. Foley, Phys. Rev. **92**, 1460 (1953).

and for $l'=l$, we must choose that solution of (11) which is orthogonal to u_0' . Thus $\langle\gamma/r^3\rangle$ is given by

$$\langle\gamma/r^3\rangle = \sum_{nl'} c_{l \rightarrow l'} \left(\int_0^\infty u_0' \bar{u}'_{1, l \rightarrow l'} r^{-3} dr \right)_{nl}, \quad (14)$$

where the $c_{l \rightarrow l'}$ are the coefficients in (7) and (8), and the sum extends over the occupied (nl) shells of the core and over the possible excitations $l'=l \pm 2$ (angular) and $l'=l$ (radial).

For Na, the present value of $\langle\gamma_{\text{rad}}/r^3\rangle$ is appreciably larger than the result given in III. This difference is due to the fact that in the present calculation we used the perturbed wave function $u'_{1, l \rightarrow l}$ for $2p \rightarrow p$ which was obtained in V. In this connection, we note that in V, the perturbed wave functions $u'_{1, l \rightarrow l}$ for the radial modes of excitation for Na^+ , Cl^- , Cu^+ , Rb^+ , and Cs^+ have been recalculated. These new functions are more accurate than those previously obtained by Foley, Sternheimer, and Tycko in IV, and were used throughout the present work in the calculation of $\langle\gamma_{\text{rad}}/r^3\rangle$.

For Cl $3p^5$, we used the Hartree-Fock wave functions obtained by Hartree.⁶ While the present value of $\langle\gamma_{\text{ang}}/r^3\rangle$ is essentially the same as that given in III, the result for $\langle\gamma_{\text{rad}}/r^3\rangle$ is appreciably larger than that previously obtained ($0.30a_{\text{H}}^{-3}$ as compared to $0.104a_{\text{H}}^{-3}$). We note that $\langle\gamma_{\text{rad}}/r^3\rangle$ for Cl is the result of a partial cancellation of the shielding produced by $3p \rightarrow p$ and the antishielding due to $2p \rightarrow p$, as has been pointed out in I. Thus the $3p \rightarrow p$ term is $+0.59a_{\text{H}}^{-3}$, while the $2p \rightarrow p$ term is $-0.29a_{\text{H}}^{-3}$. The change from 0.104 to $0.30a_{\text{H}}^{-3}$ is due mainly to an increase of the $3p \rightarrow p$ term (from ~ 0.4 to $0.59a_{\text{H}}^{-3}$), while the $2p \rightarrow p$ contribution has been essentially unchanged.

Values of R for K $4p$ and $5p$ have not been given previously in III. In Table I, two results are given for these states, which correspond to two types of valence wave functions denoted by $4p^a$ and $4p^b$, $5p^a$, and $5p^b$. The choice of these wave functions will be described below. In the calculations, we used the Hartree-Fock functions for K^+ obtained by Hartree.⁷ In order to obtain $\langle\gamma_{\text{ang}}/r^3\rangle$, the angular modes of excitation of the core ($1s \rightarrow d$, $2s \rightarrow d$, $2p \rightarrow f$, $3s \rightarrow d$, and $3p \rightarrow f$) were determined by means of Eq. (9). The radial modes ($2p \rightarrow p$ and $3p \rightarrow p$) were also obtained from (9), using the techniques of numerical integration described in V. The valence wave functions a and b were obtained as follows. (1) In order to obtain the $4p$ (or $5p$) wave function a , the Schrödinger equation was integrated using for V_0 the effective potential which reproduces the Hartree-Fock $3p$ function $u_0'(3p)$ [see Eq. (9a)]. This potential V_0^a is given by

$$V_0^a = \frac{1}{u_0'(3p)} \frac{d^2 u_0'(3p)}{dr^2} - \frac{2}{r^2} + E_0(3p), \quad (15)$$

⁶ D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A156**, 45 (1936).

⁷ D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A166**, 450 (1938).

where $E_0(3p)$ is the energy for $3p$. The motivation for using V_0^a is that it gives valence functions v_0' for $4p$ and $5p$ which are orthogonal to $u_0'(3p)$. Actually in the calculations, the function v_0' obtained with V_0^a was also made orthogonal to the $2p$ wave function $u_0'(2p)$ by adding a suitable (small) multiple of $u_0'(2p)$. An important reason for using an orthogonal wave function for K is that the core wave functions⁷ have been obtained from the Hartree-Fock equations, so that they are orthogonal on one another. Hence it seems reasonable to use a valence wave function which is also orthogonal to the core wave functions. (2) The wave functions of type b were obtained from the Schrödinger equation using the potential V_0^b due to the charge distribution of the K^+ ion, i.e., the function $2Z_p/r$ tabulated by Hartree.⁷ It may be noted that the resulting wave function $v_0^b(4p)$ is not orthogonal to $u_0'(3p)$, contrary to $v_0^a(4p)$. The function $v_0^b(4p)$ is appreciably more internal than $v_0^a(4p)$, and correspondingly gives a smaller antishielding. Thus $\gamma_{\text{rad}}(r)$ for K becomes negative only for $r > 1.5a_{\text{H}}$. Hence the value of $\int_0^\infty \gamma_{\text{rad}} r^{-3} v_0'^2 dr$ depends sensitively on the radial distribution of v_0' . The negative value of the integral increases if the wave function is made more external. The extent to which $v_0^a(4p)$ is more external than $v_0^b(4p)$ is indicated by the values of $\langle r^{-3} \rangle$ for these wave functions which are 0.460 and $0.669a_{\text{H}}^{-3}$, respectively. As shown by Table I, $v_0^a(4p)$ and $v_0^a(5p)$ give a negative R (net antishielding) of the same order as for the excited states of the other alkalis, whereas for $v_0^b(4p)$ and $v_0^b(5p)$, $|\langle\gamma_{\text{rad}}/r^3\rangle|$ barely exceeds $\langle\gamma_{\text{ang}}/r^3\rangle$, so that R is close to zero. It is, of course, difficult to make a choice between the results given by wave functions a and b . We believe, however, that a gives the more reliable result, both because this function is more consistent with the Hartree-Fock wave functions of the core as regards the orthogonality, and because the value of R falls more closely in line with the results for the other alkalis, in contrast to the wave function b . Nevertheless, these arguments are not completely conclusive, and it appears, therefore, that there is an uncertainty of the order of 0.15 in R because of our inaccurate knowledge of the valence wave functions. The same conclusion is obtained below from the calculations for Rb and Cs.

The value of $\langle\gamma_{\text{ang}}/r^3\rangle$ for Cu of Table I is essentially the same as that previously given in III. These values were obtained by using the Thomas-Fermi expression for the distribution of induced moment due to the angular modes.⁸ Thus $Q_{i, \text{ang}}$ was determined from

$$Q_{i, \text{ang}} = (3/10) Q(\chi x)^{\frac{1}{2}}(x/r), \quad (16)$$

where χ and x are the Thomas-Fermi function and variable, respectively. At large r , Eq. (16) was replaced by an exponential so adjusted as to give the correct total induced moment $Q_{i, \text{ang}} \cong 2.0Q$. This modification

⁸ R. M. Sternheimer, Phys. Rev. **80**, 102 (1950).

of the Thomas-Fermi expression is the same as was used in III and IV.

The value of $\langle \gamma_{\text{rad}}/r^3 \rangle = -0.12a_H^{-3}$ of Table I was obtained by means of the perturbed wave functions $u'_{1,l \rightarrow i}$ for $2p \rightarrow p$, $3p \rightarrow p$, and $3d \rightarrow d$ which were previously determined in V. In these calculations, the Hartree-Fock functions⁹ for Cu^+ were used. We note that $\langle \gamma_{\text{rad}}/r^3 \rangle$ is the result of an almost complete cancellation of the terms due to the three radial modes. These terms have the following values: $-1.99a_H^{-3}$ for $2p \rightarrow p$, $+1.18a_H^{-3}$ for $3p \rightarrow p$, and $+0.69a_H^{-3}$ for $3d \rightarrow d$. Each of the three terms was obtained by the two independent methods discussed above, i.e., both from the perturbation $u'_{1,l \rightarrow i}$ and from $\bar{u}'_{1,l \rightarrow i}$ [see Eq. (14)]. The maximum difference between the two results was 6%.

The values of R obtained for Rb and Cs will now be discussed. In these cases, we have also used two types of valence wave functions, defined in the same manner as for K. (1) Valence function a was obtained from the potential V_0^a which reproduces the wave function for the highest occupied p shell of the core (Rb $4p$ or Cs $5p$). The resulting wave function $v_0^a(5p)$ for Rb is orthogonal to the core wave function $u_0(4p)$, and similarly $v_0^a(6p)$ for Cs is orthogonal to the corresponding $u_0(5p)$. (2) The valence functions b were determined from the Schrödinger equation using the potential $V_0^b (=2Z_p/r)$ due to the Rb^+ or Cs^+ core. For Rb^+ and Cs^+ , Hartree-Fock wave functions (including exchange) are not available. For the calculations of the radial modes of excitation² which enter into $\langle \gamma_{\text{rad}}/r^3 \rangle$, we used the Hartree functions obtained by Hartree.^{10,11} Since these wave functions are not exactly orthogonal to one another (for states of the same l), it is not clear whether a valence wave function such as v_0^a which is approximately orthogonal to the core wave functions will give a better value for R than v_0^b which is not orthogonal. Fortunately the difference between the values of R obtained with v_0^a and v_0^b is not as pronounced as for the K wave functions. Thus both types of wave functions give a definite antishielding ($R < 0$), although v_0^a is again more external than v_0^b , as for K, and gives an appreciably larger $|R|$. The difference of ~ 0.13 between the values of R from v_0^a and v_0^b for Rb $5p$ and Cs $6p$ is probably a good measure of the uncertainty in R due to our incomplete knowledge of the valence wave function. We note that this difference is somewhat smaller (~ 0.10) for the second excited states Rb $6p$ and Cs $7p$.

In obtaining $\langle \gamma_{\text{ang}}/r^3 \rangle$ for Rb and Cs, we used the same procedure as for Cu. $Q_{i,\text{ang}}(r)$ was calculated from the Thomas-Fermi expression⁸ [Eq. (16)], modified at large r so as to agree with the total induced moment,² $Q_{iT,\text{ang}} = 2.2Q$ for Rb^+ and $2.9Q$ for Cs^+ .

Table I shows that the values of R for a given atom change very slowly as the principal quantum number n is increased.¹² As an example, for Rb from the wave functions b , one finds $R = -0.141, -0.120, -0.110$ for $5p, 6p,$ and $7p$, respectively. Contrary to this result, it might have been anticipated that $|R|$ would increase very rapidly with n and give a progressively larger antishielding, for the following reason. It has been previously shown by Foley, Sternheimer, and Tycko² that for a completely external charge, the effect of the core is to produce a large antishielding, since the total induced quadrupole moment of the core, Q_{iT} , is added to the nuclear moment Q . The ratio Q_{iT}/Q has been denoted by γ_∞ ; revised values of γ_∞ have been given in V. These values¹³ are very large; they range from -4.0 for Na^+ to -71 for Rb^+ and -144 for Cs^+ , where the minus sign indicates a net antishielding. For a highly excited state for which the wave function v_0 is concentrated at large distances from the nucleus, it might be expected that R would be of the same order as γ_∞ , and thus $|R| \gg 1$. In order to explain the small values of R of Table I, we will take the case of Rb as an example. It is convenient to use $5p, 6p,$ and $7p$ radial wave functions which have the same values near $r=0$ (i.e., the same power expansions). These functions will, of course, have very different normalization constants $N \equiv \int_0^\infty v_0^2 dr$. The parts of R due to the radial and angular modes of excitation, to be denoted by R_{rad} and R_{ang} , are given by

$$R_{\text{rad}} = \int_0^\infty (\gamma_{\text{rad}} r^{-3}) v_0^2 dr / \int_0^\infty v_0^2 r^{-3} dr, \quad (17)$$

$$R_{\text{ang}} = \int_0^\infty (\gamma_{\text{ang}} r^{-3}) v_0^2 dr / \int_0^\infty v_0^2 r^{-3} dr. \quad (18)$$

Figure 1 shows $v_0^2(5p), v_0^2(6p),$ and $v_0^2(7p)$, together with the functions $\gamma_{\text{rad}} r^{-3}$ and $\gamma_{\text{ang}} r^{-3}$ for the Rb^+ ion.

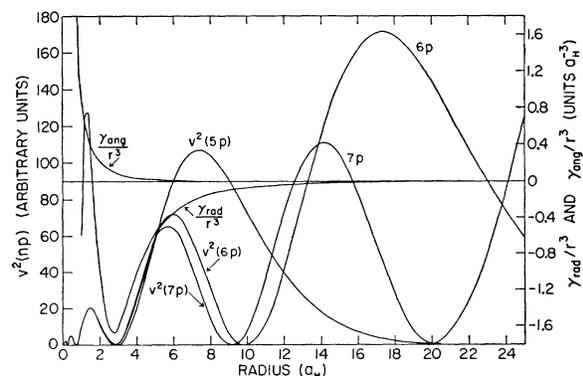


FIG. 1. Radial probability density v^2 for Rb $5p, 6p,$ and $7p$, and the functions γ_{ang}/r^3 and γ_{rad}/r^3 for the Rb^+ ion.

⁹ D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A157**, 490 (1936).

¹⁰ D. R. Hartree, Proc. Roy. Soc. (London) **A151**, 96 (1935).

¹¹ D. R. Hartree, Proc. Roy. Soc. (London) **A143**, 506 (1934).

¹² I would like to thank Professor H. M. Foley for suggesting to me this investigation of the values of R for excited states.

¹³ See also T. P. Das and R. Bersohn, Phys. Rev. **102**, 733 (1956).

TABLE II. Contribution of various regions of r to $\int_0^\infty (\gamma_{\text{rad}} v_0^2 / r^3) dr$ for the $5p$, $6p$, and $7p$ states of Rb. The radial functions $v(np)$ have the same values near $r=0$. The values of $\int_0^\infty (v_0^2 / r^3) dr$ and $R_{\text{rad}} = \langle \gamma_{\text{rad}} r^{-3} \rangle / \langle r^{-3} \rangle$ are listed below $\int_0^\infty (\gamma_{\text{rad}} v_0^2 / r^3) dr$. The normalization constant $\int_0^\infty v_0^2 dr$ (not needed to evaluate R_{rad}) and the values of $\langle \gamma_{\text{rad}} r^{-3} \rangle$ and $\langle r^{-3} \rangle$ (in units a_{H}^{-3}) are given in the last three rows of the table.

r/a_{H}	$5p$	$6p$	$7p$
0-0.3	6.91	6.91	6.91
0.3-0.8	4.06	4.05	4.05
0.8-1.6	3.06	2.98	2.95
1.6-4	-17.67	-20.32	-21.43
4-10	-126.77	-91.33	-82.81
10-20	-8.89	-20.91	-16.56
20- ∞	~ 0	-4.11	-8.60
$\int_0^\infty (\gamma_{\text{rad}} v_0^2 / r^3) dr$	-139.30	-122.73	-115.49
$\int_0^\infty (v_0^2 / r^3) dr$	719.55	719.19	719.04
$\langle \gamma_{\text{rad}} r^{-3} \rangle / \langle r^{-3} \rangle$	-0.194	-0.171	-0.161
$\int_0^\infty v_0^2 dr$	737.55	2114.8	4550.0
$\langle \gamma_{\text{rad}} r^{-3} \rangle$	-0.189	-0.0580	-0.0254
$\langle r^{-3} \rangle$	0.976	0.340	0.158

With the present normalization, the denominator $\int_0^\infty v_0^2 r^{-3} dr$ of (17) and (18) is practically the same for $5p$, $6p$, and $7p$, since the values of this integral depend only on the region close to the nucleus, where v_0 is essentially independent of n . Thus the values of $\int_0^\infty v_0^2 r^{-3} dr$ are 719.55, 719.19, and 719.04 for $5p$, $6p$, and $7p$, respectively. More than 94% of these integrals is due to the region from $r=0$ to $0.14a_{\text{H}}$. It is evident from Fig. 1 that the values of $v_0^2(5p)$, $v_0^2(6p)$, and $v_0^2(7p)$ differ appreciably only for $r \gtrsim 5a_{\text{H}}$.

We will now consider the behavior of the integral $\int_0^\infty (\gamma_{\text{rad}} r^{-3}) v_0^2 dr$ with increasing n . In the following, this integral will be denoted by Γ_{rad} . In Table II, we have listed the contributions to Γ_{rad} from the different regions of r , for $5p$, $6p$, and $7p$. These results were obtained from the wave functions of type b , calculated by means of the potential $2Z_p/r$ of Hartree. Table II shows that the region of r between 4 and $10a_{\text{H}}$ gives the largest contribution to Γ_{rad} . Hence the dependence of Γ_{rad} on n will be governed mainly by the values of v_0^2 in this region. As is shown by Fig. 1, the maximum of $v_0^2(6p)$ at $r=6a_{\text{H}}$ is appreciably smaller than that of $v_0^2(5p)$. This accounts for the decrease of the corresponding term in Γ_{rad} , which is -126.8 for $5p$ and -91.3 for $6p$ (see Table II). The terms due to the region of $r > 10a_{\text{H}}$ are somewhat larger for $6p$ than for $5p$, because of the contribution of the principal maximum of $6p$ at $r=17a_{\text{H}}$. However, the complete integral Γ_{rad} is smaller for $6p$ than the $5p$, showing that the behavior of the term due to $4 < r < 10a_{\text{H}}$ predominates. Similarly, the integral for $7p$ is somewhat smaller than that for $6p$, but the difference is less than half as large as the corresponding $5p-6p$ difference. It thus appears from the present calculations that R will attain a constant value for very large n , of the order of -0.15.

A crude estimate can be made which shows why R_{rad} is considerably smaller than the value $\gamma_{\text{rad}}(\infty)$ which would be expected for a completely external charge. We consider the Rb $5p$ state and assume that all of

the charge of the valence electron is concentrated at the position of the principal maximum of v_0 at $r=7.3a_{\text{H}}$. From Table I of V, it is seen that $\gamma_{\text{rad}}(\infty) = -72.9$; $\gamma_{\text{rad}}(\infty)$ is the sum of the $\gamma_{\text{ang}}(nl \rightarrow l')$ for all of the radial modes. With the present assumption, one obtains

$$\int_0^\infty \gamma_{\text{rad}} r^{-3} v_0^2 dr = -72.9 / (7.3)^3 = -0.187 a_{\text{H}}^{-3}. \quad (19)$$

Since $\langle r^{-3} \rangle$ for Rb $5p$ is $0.976 a_{\text{H}}^{-3}$, one finds $R_{\text{rad}} = -0.187 / 0.976 = -0.192$. The close agreement of this result with the actual calculated value of -0.194 (see Table II) is probably fortuitous to some extent. In any case, this estimate shows that the smallness of R_{rad} arises essentially because $\int_0^\infty \gamma_{\text{rad}} v_0^2 r^{-3} dr$ is compared with $\int_0^\infty v_0^2 r^{-3} dr$, which is quite large since the valence p electron can come relatively close to the nucleus.

The behavior of R_{ang} is quite similar to that of R_{rad} . Thus R_{ang} is almost constant with increasing n . The values for Rb $5p$, $6p$, and $7p$ are 0.0523, 0.0509, and 0.0506, respectively. In comparison with R_{rad} , the main contributions to $\int_0^\infty \gamma_{\text{ang}} v_0^2 r^{-3} dr$ [Eq. (18)] come from regions of smaller radius than for Γ_{rad} . Thus for Rb $6p$, 47% of the integral is due to the region from $r=0$ to $0.30a_{\text{H}}$. The values of r up to $4a_{\text{H}}$ contribute 90%. Similarly to the dependence of R_{rad} on n , the slight decrease of the above values of R_{ang} is due to the behavior of $v_0(np)$ for large r . However, since this region is not important for the integral, R_{ang} approaches rapidly an asymptotic value with increasing n . Thus the small decrease with n of the total R is essentially due to the decrease of R_{rad} .

In connection with the values of $\langle \gamma_{\text{ang}} / r^3 \rangle$, $\langle \gamma_{\text{rad}} / r^3 \rangle$, and R given in Table I, it seemed of interest to investigate whether these results are sensitive to the zero-order core wave functions used in the calculations. For Cl^- , both Hartree-Fock wave functions⁶ and Hartree functions¹⁴ (without exchange) are available. Since these two types of wave functions are considerably different [especially for $u_0(3p)$], it appeared that a good test could be made by calculating R from the Hartree wave functions and comparing the result with that obtained previously from the Hartree-Fock functions. Table III gives a comparison of the terms of $\langle \gamma_{\text{ang}} / r^3 \rangle$ and $\langle \gamma_{\text{rad}} / r^3 \rangle$ due to the various modes of excitation. These terms are denoted by $\Gamma(nl \rightarrow l')$. It is seen that for the angular modes, the individual Γ 's as well as the complete $\langle \gamma_{\text{ang}} / r^3 \rangle$ are not very different for the Hartree and Hartree-Fock wave functions. The discrepancy of the Γ values is very small for the $1s \rightarrow d$ excitation and is relatively largest for $3s \rightarrow d$ and $3p \rightarrow f$. The resulting values of $\langle \gamma_{\text{ang}} / r^3 \rangle$ differ by only 11%. By contrast, for the radial modes, the values of Γ differ appreciably for the two types of wave functions, particularly for $3p \rightarrow p$. These discrepancies tend to be magnified in the values of the total $\langle \gamma_{\text{rad}} / r^3 \rangle$, as a result of the partial cancellation of the $2p \rightarrow p$ and $3p \rightarrow p$ terms.

¹⁴ D. R. Hartree, Proc. Roy. Soc. (London) A141, 281 (1933).

The resulting R from the Hartree functions is 0.191, as compared to the Hartree-Fock value of 0.112.

A similar comparison was made for R_{rad} of K $4p$. Similarly to the Cl calculations, we used the Hartree functions¹¹ for the K^+ core. The $2p \rightarrow p$ and $3p \rightarrow p$ perturbations were calculated for these functions. The resulting values of R_{rad} are as follows: (1) for the $4p$ valence function a ($4p^a$) the Hartree functions give $R_{\text{rad}} = -0.362$, as compared to: $-0.1135/0.460 = -0.247$ (see Table I) from the Hartree-Fock functions; (2) for the $4p^b$ function, the Hartree result is: -0.075 , as compared to the Hartree-Fock value -0.061 . These discrepancies for the radial modes are of the same order as those obtained for Cl. It may be noted that a rough calculation of some of the angular terms $\Gamma(nl \rightarrow l')$ showed that the differences for these terms are quite small, in agreement with the corresponding result for Cl.

It can be concluded that the inaccuracy of the zero-order core wave functions introduces only a small uncertainty in the values of $\langle \gamma_{\text{ang}}/r^3 \rangle$ ($\sim 10\%$), but

may result in an appreciable error of the radial term $\langle \gamma_{\text{rad}}/r^3 \rangle$. For the $4p^a$ function of K, the difference between the Hartree and Hartree-Fock results for R_{rad} is 0.12, which is of the same order as the uncertainty in R due to the choice of the valence wave function. It is evident that whenever the Hartree-Fock wave functions are used, we avoid the errors considered in this discussion. However, it is possible that the actual atomic wave functions taking into account configuration interaction differ from the Hartree-Fock functions by an amount comparable to the difference between Hartree and Hartree-Fock functions. In this case, the Hartree-Fock results would still be subject to an uncertainty of the same order as that determined above.

III. EXCHANGE TERMS

In order to discuss the exchange terms due to the induced quadrupole moment, we consider the total wave function Ψ for the electrons of spin parallel to the spin of the valence electron. Ψ is given by

$$\Psi = (n!)^{-\frac{1}{2}} \begin{vmatrix} (\psi_{1,0} + \psi_{1,1})(1) & (\psi_{2,0} + \psi_{2,1})(1) & \cdots & (\psi_{n,0} + \psi_{n,1})(1) \\ (\psi_{1,0} + \psi_{1,1})(2) & (\psi_{2,0} + \psi_{2,1})(2) & \cdots & (\psi_{n,0} + \psi_{n,1})(2) \\ \vdots & \vdots & \ddots & \vdots \\ (\psi_{1,0} + \psi_{1,1})(n) & (\psi_{2,0} + \psi_{2,1})(n) & \cdots & (\psi_{n,0} + \psi_{n,1})(n) \end{vmatrix}, \quad (20)$$

where $\psi_{1,0}, \psi_{2,0}, \dots, \psi_{n-1,0}$ are the unperturbed wave functions of the core, $\psi_{n,0}$ is the unperturbed valence wave function; $\psi_{1,1}, \psi_{2,1}, \dots, \psi_{n,1}$ are the perturbations of these wave functions due to the nuclear Q . The parentheses (1), (2), \dots (n) label the different electrons. In the following, it will be assumed that the valence electron is in a p state. The zero-order wave functions $\psi_{i,0}$ are normalized in the usual manner:

$$2\pi \int_0^\infty \int_0^\pi |\psi_{i,0}|^2 r^2 dr \sin\theta d\theta = 1, \quad (21)$$

where θ is the polar angle of the electron with respect

TABLE III. Values of $\langle \gamma_{\text{ang}}/r^3 \rangle$ and $\langle \gamma_{\text{rad}}/r^3 \rangle$ for the ground state of Cl, as calculated from the Hartree and Hartree-Fock wave functions. The term of $\langle \gamma/r^3 \rangle$ due to the $nl \rightarrow l'$ excitation is denoted by $\Gamma(nl \rightarrow l')$. The Γ 's, $\langle \gamma/r^3 \rangle$, and $\langle 1/r^3 \rangle$ are in units a_H^{-3} .

Excitation	Hartree	Hartree-Fock
$\Gamma(1s \rightarrow d)$	0.126	0.130
$\Gamma(2s \rightarrow d)$	0.045	0.050
$\Gamma(2p \rightarrow f)$	0.078	0.086
$\Gamma(3s \rightarrow d)$	0.027	0.036
$\Gamma(3p \rightarrow f)$	0.032	0.042
$\langle \gamma_{\text{ang}}/r^3 \rangle$	0.308	0.344
$\Gamma(2p \rightarrow p)$	-0.22	-0.29
$\Gamma(3p \rightarrow p)$	0.96	0.59
$\langle \gamma_{\text{rad}}/r^3 \rangle$	0.74	0.30
$\langle \gamma/r^3 \rangle$	1.048	0.644
$\langle 1/r^3 \rangle$	5.50	5.73
R	0.191	0.112

to the axis of Q . It is assumed that the different $\psi_{i,0}$ are orthogonal to each other.

Before proceeding to a discussion of the exchange terms, we will show that the complete perturbed functions $\psi_{i,0} + \psi_{i,1}$ are also orthogonal, to terms of order Q^2 . We have

$$\int (\psi_{i,0}^* + \psi_{i,1}^*) (\psi_{j,0} + \psi_{j,1}) d\mathbf{r} = \delta_{ij} + \int (\psi_{i,1}^* \psi_{j,0} + \psi_{i,0}^* \psi_{j,1}) d\mathbf{r}, \quad (22)$$

where a second-order term involving $\psi_{i,1}^* \psi_{j,1}$ has been omitted. For $i=j$, the integral on the right-hand side is automatically zero, since the perturbed wave function $\psi_{i,1}$ is orthogonal to $\psi_{i,0}$. We now consider the case $i \neq j$. From perturbation theory, $\psi_{i,1}$ is given by

$$\psi_{i,1} = \sum_{k \neq i} \frac{\int \psi_{k,0}^* H_1 \psi_{i,0} d\mathbf{r}}{E_i - E_k} \psi_{k,0}, \quad (23)$$

where H_1 is the perturbation due to the nuclear Q :

$$H_1 = -Q(3 \cos^2\theta - 1)/(2r^3). \quad (24)$$

E_i and E_k are the unperturbed energies pertaining to $\psi_{i,0}$ and $\psi_{k,0}$. It is assumed that the different functions $\psi_{k,0}$ are the solutions of a single Schrödinger equation with the same potential V_0 . The sum in (23) extends

over all of the bound states (except $k=i$) and over the continuum states. Similarly to (23), $\psi_{j,1}$ is given by

$$\psi_{j,1} = \sum_{k \neq j} \frac{\int \psi_{k,0}^* H_1 \psi_{j,0} d\mathbf{r}}{E_j - E_k} \psi_{k,0}. \quad (25)$$

From (23) and (25), one obtains

$$\int \psi_{i,1}^* \psi_{j,0} d\mathbf{r} = - \int \psi_{i,0}^* \psi_{j,1} d\mathbf{r} = \frac{\int \psi_{i,0}^* H_1 \psi_{j,0} d\mathbf{r}}{E_i - E_j}, \quad (26)$$

so that the integral in (22) is zero for $i \neq j$. This result is, of course, very reasonable, since it states that the $nl \rightarrow n'l'$ excitation just cancels the $n'l' \rightarrow nl$ term, as was expected because the nl and $n'l'$ shells are already filled in the unperturbed state. We note that the orthogonality and normalization of the $(\psi_{i,0} + \psi_{i,1})$ implies that the perturbed Ψ [Eq. (20)] is normalized to 1, to terms of order Q^2 .

In Sec. II, we have considered the direct Coulomb terms due to the induced moment. The complete quadrupole coupling including these terms is obtained by replacing $\langle r^{-3} \rangle$ by $\langle r^{-3} \rangle (1-R)$ in the expression for the quadrupole hfs splitting. Thus for the valence electron in the $m=0$ state, the total energy of interaction with the nuclear Q is given by

$$E_Q = -(2/5)Q \langle r^{-3} \rangle (1-R), \quad (27)$$

where E_Q is in Rydberg units and lengths are in units a_H . Hence if Q_0 is the value of the nuclear moment obtained from the observed E_Q by disregarding the core effects, the actual Q is given by

$$Q = Q_0 [1/(1-R)]. \quad (28)$$

We will now discuss the exchange terms due to the induced moment. These exchange terms are of two types: (A) those due to the perturbation of the core wave functions; (B) those due to the perturbation of the (p) valence wave function¹⁵ by the nuclear Q . The terms (A) have been evaluated in I-III for some typical cases. The terms (B) have not been previously considered. It will be shown below that they make only a very small contribution to the quadrupole correction factor for excited states.

The correction to R due to the terms (A) has been previously denoted by δR_e and is given by [see Eq. (14) of III]:

$$\delta R_e = - \frac{1}{\langle r^{-3} \rangle_n} \left\{ \sum_n [(4/3)K(ns \rightarrow d, P_1)]_{ns} + \sum_n [4K(np \rightarrow p, P_0) + (4/25)K(np \rightarrow p, P_2) + (36/25)K(np \rightarrow f, P_2)]_{np} \right\}, \quad (29)$$

¹⁵ I am very much indebted to Professor H. M. Foley for calling my attention to the terms due to the perturbation of the valence wave function.

where the sums extend over the occupied s and p shells of the core. K is defined by

$$K(nl \rightarrow l', P_L) \equiv \int_0^\infty u_0' v_0' f_L d\mathbf{r}, \quad (30)$$

where u_0' is the unperturbed core wave function and f_L is given by

$$f_L(\mathbf{r}) \equiv r^{-L-1} \int_0^r u'_{1,l \rightarrow l'} v_0' r'^L dr' + r^L \int_r^\infty u'_{1,l \rightarrow l'} v_0' r'^{-L-1} dr', \quad (31)$$

in which $u'_{1,l \rightarrow l'}$ is the core perturbation.

As has been discussed in III, the term $-\langle r^{-3} \rangle^{-1} \times \sum_n 4K(np \rightarrow p, P_0)$ in (29) (denoted by $\delta R_{e,0}$) plays a somewhat different role than the remaining terms of δR_e . In the experimental determination of Q , the value of $\langle r^{-3} \rangle$ [Eq. (27)] is generally deduced from the ratio a/μ of the magnetic hfs splitting a to the nuclear magnetic moment μ as obtained from nuclear induction experiments. Thus a is given by

$$a = 2l(l+1)\mu_0 \mu F(j) \langle r^{-3} \rangle (1 - \delta R_m) / [Ij(j+1)h], \quad (32)$$

where μ_0 = Bohr magneton, I is the nuclear spin, l and j are the orbital and total angular momentum of the atomic state, $F(j)$ is a relativistic correction, and δR_m is a core correction for the magnetic hfs¹ which is similar to δR_e for the quadrupole coupling. It has been shown previously that δR_m contains a term equal to $\delta R_{e,0}$, besides other terms which will be discussed below. If $\langle r^{-3} \rangle$ is obtained from a/μ , then it is easily seen from (28) and (32) that Q is proportional to

$$Q \propto \frac{1}{(1-R-\delta R_e) \langle r^{-3} \rangle} \propto \frac{\mu(1-\delta R_m)}{a(1-R-\delta R_e)}. \quad (33)$$

Thus the effective correction factor is given by

$$C = (1-\delta R_m)/(1-R-\delta R_e). \quad (34)$$

In taking this ratio, the common term in δR_m and δR_e cancels out to a large extent. This can be shown by writing for δR_e and δR_m :

$$\delta R_e = \delta R_{e,0} + \delta R_e', \quad (35)$$

$$\delta R_m = \delta R_{e,0} + \delta R_m', \quad (35a)$$

where $\delta R_e'$, $\delta R_m'$ are the remaining terms of δR_e and δR_m , respectively. Thus C becomes

$$C = \left[1 - \frac{\delta R_m'}{1-\delta R_{e,0}} \right] / \left[1 - \frac{R+\delta R_e'}{1-\delta R_{e,0}} \right]. \quad (36)$$

Hence the effect of $\delta R_{e,0}$ is merely to multiply the corrections $\delta R_m'$ and $R+\delta R_e'$ by a common factor $(1-\delta R_{e,0})^{-1}$. Numerical values of $\delta R_{e,0}$ and $\delta R_e'$ will be given below.

We will now discuss the exchange terms (B) which arise from the excitation of the valence electron. The valence electron is in a p state, so that there will be two types of perturbation involving excitation to higher p states and to f states. The perturbed functions are obtained by the same procedure as in Eqs. (15) to (20) of I. One thus finds for the p and f wave parts of the perturbation v_1 :

$$v_{1,p} = \frac{2}{5} \left(\frac{3}{2}\right)^{\frac{1}{2}} Q v'_{1,1 \rightarrow 1} \cos\theta, \quad (37)$$

$$v_{1,f} = \frac{1}{2} \left(\frac{3}{2}\right)^{\frac{1}{2}} Q v'_{1,1 \rightarrow 3} [3 \cos^3\theta - (9/5) \cos\theta], \quad (38)$$

where the radial functions $v'_{1,l \rightarrow l'}$ are determined by

$$\left[-\frac{d^2}{dr^2} + \frac{l'(l'+1)}{r^2} + V_0 - E_0 \right] v'_{1,l \rightarrow l'} = v_0' \left[\frac{1}{r^3} - \left\langle \frac{1}{r^3} \right\rangle \delta_{ll'} \right], \quad (39)$$

where $\langle 1/r^3 \rangle$ is the average of $1/r^3$ over the unperturbed valence function v_0' . For $l'=l$, we must choose that solution of (39) which is orthogonal to v_0' .

We will first consider the exchange terms due to s states of the core. The p wave $v_{1,p}$ gives rise to the following overlap density with the s -wave function $u_0 = 2^{-\frac{1}{2}} u_0'$:

$$\rho_v = -2u_0 v_{1,p} = -(2\sqrt{3}/5) Q u_0' v'_{1,1 \rightarrow 1} \cos\theta. \quad (40)$$

Here the minus sign arises from the exchange, and the factor of 2 is due to the presence of two equivalent terms in Ψ^2 . The potential due to ρ_v is

$$V_v = -(8/5\sqrt{3}) Q g_1 \cos\theta, \quad (41)$$

where V_v is in Rydberg units, and $g_1(r)$ is defined by

$$g_L(r) \equiv r^{-L-1} \int_0^r u_0' v'_{1,l \rightarrow l'} r'^L dr' + r^L \int_r^\infty u_0' v'_{1,l \rightarrow l'} r'^{-L-1} dr'. \quad (42)$$

The exchange energy is given by

$$\Delta E_v = \int_0^\infty \int_0^\pi V_v u_0 v_0 dr \sin\theta d\theta = -(8/15) Q M(ns, P_1), \quad (43)$$

where M is obtained from

$$M(nl, P_L) \equiv \int_0^\infty u_0' v_0' g_L dr. \quad (44)$$

Finally, the term in R is defined as $-\Delta E_v$ divided by the direct interaction of Q with the valence electron [Eq. (27)]. Thus the correction to R is given by

$$\delta R_v(ns) = -(4/3) M(ns, P_1) / \langle r^{-3} \rangle. \quad (45)$$

It may be noted that the f wave $v_{1,f}$ does not contribute any exchange term with ns , since the corre-

sponding ρ_v and V_v have the angular dependence Θ_3^0 which is orthogonal to $u_0 v_0$ ($\propto \Theta_1^0$).

We now obtain the exchange of $v_{1,p}$ with a closed p shell of the core. The electron of parallel spin with magnetic quantum number $m_u=0$ will be considered first. Its wave function is

$$u_0 = (3/2)^{\frac{1}{2}} u_0' \cos\theta. \quad (46)$$

The exchange density ρ_v is given by

$$\rho_v = -2u_0 v_{1,p} = -(2/5) Q u_0' v'_{1,1 \rightarrow 1} [(3 \cos^2\theta - 1) + 1], \quad (47)$$

in which the square bracket is the sum of a P_2 and a P_0 function. The potential due to the P_0 part is

$$V_{v,0} = -(8/5) Q g_0, \quad (48)$$

where g_0 is obtained from (42). The corresponding exchange energy is given by

$$\Delta E_{v,0} = \int_0^\infty \int_0^\pi V_{v,0} u_0 v_0 dr \sin\theta d\theta = -(8/5) Q M(np, P_0), \quad (49)$$

where M is defined by Eq. (44). There is no similar P_0 term in the interaction with the $m_u = \pm 1$ electrons. Hence the correction to R due to $M(np, P_0)$ is

$$\delta R_v(np, P_0) = -4M(np, P_0) / \langle r^{-3} \rangle. \quad (50)$$

The potential due to the P_2 part of (47) is

$$V_{v,2} = -(16/25) Q g_2 P_2, \quad (51)$$

with g_2 obtained from (42). The resulting exchange energy is given by

$$\Delta E_{v,2}^{(0)} = \int_0^\infty \int_0^\pi V_{v,2} u_0 v_0 dr \sin\theta d\theta = -(32/125) Q M(np, P_2). \quad (52)$$

For the two np electrons with $m_u = \pm 1$, one obtains the following energy term:

$$\Delta E_{v,2}^{(\pm 1)} = -(48/125) Q M(np, P_2). \quad (53)$$

Hence the complete P_2 contribution of the np shell is

$$\Delta E_{v,2} = -(16/25) Q M(np, P_2), \quad (54)$$

giving

$$\delta R_v(np, P_2) = -(8/5) M(np, P_2) / \langle r^{-3} \rangle. \quad (55)$$

For the f -wave perturbation of the valence function, $v_{1,f}$, one finds that the contribution of the $m_u=0$ electron [$\Delta E_v = -(216/875) Q M$] is exactly canceled by the term due to $m_u = \pm 1$. Hence the net term due to $v_{1,f}$ is zero. Thus the complete correction δR_v is given by

$$\delta R_v = -\frac{1}{\langle r^{-3} \rangle} \left\{ \sum_n [(4/3) M(ns, P_1)]_{ns} + \sum_n [4M(np, P_0) + (8/5) M(np, P_2)]_{np} \right\}, \quad (56)$$

where the sums extend over the occupied s and p shells of the core.

It will now be shown that a term equal to δR_v also occurs in the complete core correction δR_m for the magnetic hfs and in the fine structure. We will consider first the exchange of the valence p electron with the p shells of the core. The procedure of the derivation is similar to that given in II for the terms due to the perturbation of the core wave functions. We assume for definiteness that the valence electron is in the $3p$ state with $m=1$ and spin up, and consider the interaction with the closed $2p$ shell. The unperturbed wave function is given by

$$\Psi = 6^{-3} [\psi_{2p,1}(1)\psi_{u,-1} - \psi_{2p,0}(1)\psi_{u,0} + \psi_{2p,-1}(1)\psi_{u,1}] \times \psi_{3p,1}(7) [a(1)b(u) - b(1)a(u)] a(7), \quad (57)$$

where $\psi_{2p,m_1}(1)$ is the $2p$ function with magnetic quantum number m_1 for electron 1, $\psi_{u,m}$ is the combined wave function of the other 5 electrons in the $2p$ shell with total magnetic quantum number m ; ψ_{3p,m_2} is the $3p$ function with magnetic quantum number m_2 ; a and b are eigenfunctions for spin up and spin down, respectively; in particular, $a(u)$ and $b(u)$ are the spin functions for the five $2p$ electrons labeled 2, \dots 6.

We are interested in the perturbation of Ψ due to the excitation of the valence wave function $\psi_{3p,1}$ by the exchange with $2p$. The space part of the perturbation, to be denoted by χ_M (M =total magnetic quantum number of system) is obtained from the Schrödinger equation:

$$\sum_i [-\nabla_i^2 + V_0(r_i)] \chi_M - E_0 \chi_M = - \sum_{i>j} \frac{2}{r_{ij}} \psi_0 + E_1 \psi_0, \quad (58)$$

where ψ_0 is the space part of the unperturbed function, $V_0(r_i)$ is the central potential acting on the i th electron (with radial coordinate r_i), r_{ij} is the distance between electrons i and j , E_1 is the perturbation of the energy due to exchange. In the term $-\sum_{i>j} (2/r_{ij})\psi_0$ of (58) we must include only the exchange part of the interaction, since the direct Coulomb term does not produce a net magnetic field at the nucleus.

Upon using the same procedure as in II, one finds that the perturbation of the term $\psi_{2p,m_1}(1)\psi_{3p,m_2}(7)$ of Ψ is given by

$$\chi_{M(m_1 m_2)} = \sum_{mm'} A_{mm'}^{(0)} \psi_{2p,m}(7) \psi_{p,m'}^{(0)}(1) + \sum_{mm'} A_{mm'}^{(2)} \psi_{2p,m}(7) \psi_{p,m'}^{(2)}(1), \quad (59)$$

where $\psi_{p,m'}^{(0)}$ and $\psi_{p,m'}^{(2)}$ are perturbed p -wave functions, and the coefficients $A_{mm'}^{(L)}$ are obtained from

$$A_{mm'}^{(L)} = -2 \int_0^\pi \Theta_1^{m'} P_L^{m'-m_1} \Theta_1^{m_1} \sin\theta_1 d\theta_1 \times \int_0^\pi \Theta_1^{m*} P_L^{m_1-m'} \Theta_1^{m_2} \sin\theta_7 d\theta_7. \quad (60)$$

Here the spherical harmonics Θ_l^m are normalized according to

$$\int_0^\pi |\Theta_l^m|^2 \sin\theta d\theta = 1. \quad (60a)$$

For $L=0$, $A_{mm'}^{(0)}$ is zero unless $m'=m_1$, $m=m_2$, so that the sum of (59) reduces to a single term with $A_{mm'}^{(0)} = -2$.

The perturbed one-electron functions $\psi_{p,m'}^{(L)}$ are given by

$$\psi_{p,m'}^{(L)} = (w_{1,L}/r) \Theta_1^{m'}, \quad (L=0,2) \quad (61)$$

where $w_{1,L}$ is that solution of

$$\left(-\frac{d^2}{dr^2} + \frac{2}{r^2} + V_0 - E_0 \right) w_{1,L} = h_L u_0', \quad (62)$$

which is orthogonal to the $3p$ function v_0' . In (62), u_0' denotes the radial $2p$ function, and $h_L(r)$ is defined by

$$h_L(r) \equiv r^{-L-1} \int_0^r u_0' v_0' r'^L dr' + r^L \int_r^\infty u_0' v_0' r'^{-L-1} dr'. \quad (63)$$

Upon using (59) for each term $\psi_{2p,m_1}\psi_{3p,1}$ of the space part of Ψ [Eq. (57)] one obtains the perturbation χ_1 :

$$\chi_1 = - (2/\sqrt{3}) [\psi_{p,1}^{(0)}\psi_{u,-1} - \psi_{p,0}^{(0)}\psi_{u,0} + \psi_{p,-1}^{(0)}\psi_{u,1}] \psi_{2p,1} - (2/25\sqrt{3}) \{ \psi_{u,-1} \psi_{2p,1} \psi_{p,1}^{(2)} - \psi_{u,0} [3\psi_{2p,0} \psi_{p,1}^{(2)} - 2\psi_{2p,1} \psi_{p,0}^{(2)}] + \psi_{u,1} [6\psi_{2p,-1} \psi_{p,1}^{(2)} - 3\psi_{2p,0} \psi_{p,0}^{(2)} + \psi_{2p,1} \psi_{p,-1}^{(2)}] \}, \quad (64)$$

in which the coordinates of $\psi_{p,m'}^{(L)}$ are \mathbf{r}_1 , while those of $\psi_{2p,m}$ are \mathbf{r}_7 .

In the same manner, one finds for the perturbation of the wave function with $M=0$:

$$\chi_0 = - (2/\sqrt{3}) [\psi_{p,1}^{(0)}\psi_{u,-1} - \psi_{p,0}^{(0)}\psi_{u,0} + \psi_{p,-1}^{(0)}\psi_{u,1}] \psi_{2p,0} + (2/25\sqrt{3}) \{ \psi_{u,-1} [2\psi_{2p,0} \psi_{p,1}^{(2)} - 3\psi_{2p,1} \psi_{p,0}^{(2)}] - \psi_{u,0} [3\psi_{2p,1} \psi_{p,-1}^{(2)} - 4\psi_{2p,0} \psi_{p,0}^{(2)} + 3\psi_{2p,-1} \psi_{p,1}^{(2)}] + \psi_{u,1} [2\psi_{2p,0} \psi_{p,-1}^{(2)} - 3\psi_{2p,-1} \psi_{p,0}^{(2)}] \}. \quad (65)$$

The magnetic field at the nucleus $\mathbf{H}(0)$, which determines the hfs splitting, is given by

$$\mathbf{H}(0) \cdot \mathbf{j} = -2\mu_0 \left\langle \sum_i \left[\frac{\mathbf{l}_i \cdot \mathbf{j}}{r_i^3} + \frac{3(\mathbf{s}_i \cdot \mathbf{r}_i)(\mathbf{r}_i \cdot \mathbf{j})}{r_i^5} - \frac{\mathbf{s}_i \cdot \mathbf{j}}{r_i^3} \right] \right\rangle, \quad (66)$$

where \mathbf{j} is the total angular momentum of the atom, \mathbf{l}_i and \mathbf{s}_i are the orbital angular momentum and the spin of the i th electron. For the magnetic field $\mathbf{H}_0(0)$ in the unperturbed case, one finds

$$\mathbf{H}_0(0) \cdot \mathbf{j} = -4\mu_0 \langle r^{-3} \rangle_{3p}, \quad (67)$$

both for the ${}^2P_{3/2}$ and ${}^2P_{1/2}$ states. In order to obtain the additional magnetic field $\mathbf{H}_1(0)$ due to the perturbation χ_M , one must combine the χ_M and the spin functions,

using the appropriate coefficients for ${}^2P_{3/2}$ or ${}^2P_{3/2}$. $\mathbf{H}_1(0) \cdot \mathbf{j}$ can then be obtained from (66). The resulting expressions contain the integrals $\int_0^\infty v_0' w_{1,L} r^{-3} dr$. In the same manner as in II [Eqs. (14) to (14c)], it can be shown that

$$\int_0^\infty v_0' w_{1,L} r^{-3} dr = M(2p, P_L), \quad (68)$$

where $M(2p, P_L)$ is the integral over $v'_{1,L}$ as defined by Eqs. (42) and (44). One thus obtains

$$\mathbf{H}_1(0) \cdot \mathbf{j} = -16\mu_0 M(2p, P_0) - (32/5)\mu_0 M(2p, P_2). \quad (69)$$

Equation (69) holds both for ${}^2P_{3/2}$ and ${}^2P_{3/2}$.

The exchange of $3p$ with the $2p$ shell also produces an excitation of $3p$ to f states. The resulting perturbation of Ψ is a sum of terms of the form $\psi_{2p,m} \psi_{u,m'} \psi_{f,m'}$, where $\psi_{f,m'}$ is the perturbation of $3p$. However, it is found (both for ${}^2P_{3/2}$ and ${}^2P_{3/2}$) that the $3p \rightarrow f$ excitation does not give rise to a net magnetic field at the nucleus. This result is similar to that obtained for the perturbation $v'_{1,1 \rightarrow 3}$ due to Q which also does not contribute to the hfs.

The exchange of $3p$ with the $1s$ shell of the core will now be discussed. The exchange of $3p$ with the $1s$ electron of parallel spin produces an additional excitation of $3p$ into higher p states. Thus for the unperturbed function $\psi_{1s}(1)\psi_{3p,m_2}(2)$, the exchange perturbation is given by

$$\chi_{m_2'} = \sum_{m'} B_{m'} \zeta_{p,m'}(1) \psi_{1s}(2), \quad (70)$$

where $\zeta_{p,m'}$ is the perturbed p function and the coefficient $B_{m'}$ is obtained from

$$B_{m'} = -2 \int_0^\pi \Theta_1^{m'} P_1^{m'} \Theta_0^0 \sin\theta_1 d\theta_1 \times \int_0^\pi \Theta_0^{0*} P_1^{-m'} \Theta_1^{m_2} \sin\theta_2 d\theta_2. \quad (71)$$

It is seen that $B_{m'}$ is zero, unless $m' = m_2$. Hence the sum of (70) reduces to a single term with $B_{m_2} = -\frac{2}{3}$. $\zeta_{p,m'}$ is given by

$$\zeta_{p,m'} = (w_2/r) \Theta_1^{m'}, \quad (72)$$

where w_2 is the solution (orthogonal to v_0') of the equation

$$\left[-\frac{d^2}{dr^2} + \frac{2}{r^2} + V_0 - E_0 \right] w_2 = h_1 u_0', \quad (73)$$

in which u_0' is r times the radial $1s$ function and h_1 is given by Eq. (63) with $L=1$ and $u_0' = u_0'(1s)$.

The magnetic field $\mathbf{H}_2(0)$ due to the exchange of $3p$ with $1s$ involves the integral $\int_0^\infty v_0' w_2 r^{-3} dr$. In the same manner as in II, it can be shown that

$$\int_0^\infty v_0' w_2 r^{-3} dr = M(1s, P_1). \quad (74)$$

One thus obtains both for ${}^2P_{3/2}$ and ${}^2P_{3/2}$,

$$\mathbf{H}_2(0) \cdot \mathbf{j} = -(16/3)\mu_0 M(1s, P_1). \quad (75)$$

From Eqs. (69) and (75), the extra magnetic field due to the perturbation of the valence wave function by the closed s and p shells of the core is given by

$$\Delta\mathbf{H}(0) \cdot \mathbf{j} = -\mu_0 \left\{ \sum_n [(16/3)M(ns, P_1)]_{ns} + \sum_n [16M(np, P_0) + (32/5)M(np, P_2)]_{np} \right\}. \quad (76)$$

The resulting correction to δR_m is

$$\delta R_{mv} = -\Delta\mathbf{H}(0) \cdot \mathbf{j} / \mathbf{H}_0(0) \cdot \mathbf{j}. \quad (77)$$

In view of Eqs. (67) and (77), $\delta R_{mv} = \delta R_v$, where δR_v is the correction for the quadrupole coupling, given by (56). Thus the term δR_v is similar to $\delta R_{e,0}$ since it appears both in the magnetic hfs and in the quadrupole coupling. Upon inclusion of δR_v , Eq. (36) for C becomes

$$C = \left[1 - \frac{\delta R_{m'}}{1 - \delta R_{e,0} - \delta R_v} \right] / \left[1 - \frac{R + \delta R_{e'}}{1 - \delta R_{e,0} - \delta R_v} \right]. \quad (78)$$

It may be noted that the same term δR_v also enters into the fine structure. Thus from (64) and (65), one finds that the extra spin density due to the perturbation of $3p$ by $2p$ is given by

$$\Delta\rho_1 = 4\psi_{3p,m_2}^* \psi_{p,m_2}^{(0)} + (8/5)\psi_{3p,m_2}^* \psi_{p,m_2}^{(2)}. \quad (79)$$

From (61), one obtains

$$\int_0^\pi \Delta\rho_1 \sin\theta d\theta = [4v_0' w_{1,0} + (8/5)v_0' w_{1,2}] / r^2 \equiv \xi_{1,2p}. \quad (80)$$

The expression (80) will be called $\xi_{1,2p}$. For the perturbation of $3p$ by $1s$, the spin density is

$$\Delta\rho_2 = (4/3)\psi_{3p,m_2}^* \zeta_{p,m_2}, \quad (81)$$

which gives

$$\int_0^\pi \Delta\rho_2 \sin\theta d\theta = (4/3)v_0' w_2 / r^2 \equiv \xi_{2,1s}. \quad (82)$$

For an atom with several closed s and p shells, we denote by ξ_1 the sum of the $\xi_{1,np}$ for the occupied p shells and by ξ_2 the sum of the $\xi_{2,ns}$ for the s shells. The correction for the fine structure due to the perturbation of the valence function is given by

$$\delta R_{fs} = - \int_0^\infty [(\xi_1 + \xi_2) / r^3] r^2 dr / \langle r^{-3} \rangle, \quad (83)$$

which is equal to δR_v by virtue of (68) and (74).

From the present result and from Eq. (62) of II, one finds that the observed fine structure splitting ν is

proportional to

$$\nu \propto \langle r^{-3} \rangle \left\{ 1 - \delta R_{e,0} - \delta R_v + \frac{\sum_n [K(n\mathcal{p} \rightarrow \mathcal{p}, P_2)]_{n\mathcal{p}}}{\langle r^{-3} \rangle} \right\}. \quad (84)$$

The term involving $K(n\mathcal{p} \rightarrow \mathcal{p}, P_2)$ is very small for the excited states of the alkalis. For Na $3p$ and K $4p$, the values of $(8/5) \sum_n [K(n\mathcal{p} \rightarrow \mathcal{p}, P_2)]_{n\mathcal{p}} / \langle r^{-3} \rangle$ were found to be -0.006 and 0.0025 , respectively, from the calculations reported below. Thus the correction factor for the fine structure contains essentially just those terms, $\delta R_{e,0}$ and δR_v , which are common to both the quadrupole coupling and the magnetic hfs.

The exchange terms due to the induced moment have been evaluated for B $2p$, Na $3p$, and K $4p$, using the perturbed wave functions $u'_{1,1 \rightarrow 1'}$ discussed in Sec. II. For the term $\delta R_e'$ [Eq. (35)], we found the following values: $\delta R_e' = -0.095$ for B $2p$, -0.0294 for Na $3p$, and -0.0194 for K $4p$. For B, the exchange of $2p$ with $1s \rightarrow d$ and with $2s \rightarrow d$ contribute approximately equal amounts. The $1s \rightarrow d$ and $2s \rightarrow d$ terms [Eq. (29)] are -0.046 and -0.049 , respectively. Both for Na $3p$ and K $4p$, the largest term of $\delta R_e'$ is due to the $1s \rightarrow d$ perturbation. The values of this term are -0.0204 and -0.0125 , respectively.

The present results for $\delta R_e'$ will be compared to the corresponding values of R . For B, $\delta R_e'$ is comparable with R ($=0.143$) so that the inclusion of the exchange terms considerably modifies the value of the correction factor C [Eq. (78)]. On the other hand, for Na and K, $\delta R_e'$ is only of the order of $\frac{1}{10}$ of R . From these results and from the value $\delta R_e' = -0.009$ for Cs $6p$ obtained in III, it can be concluded that the effect of $\delta R_e'$ is very small compared to the antishielding given by the direct term R for the excited states of the alkalis.

Besides $\delta R_e'$, we have also calculated the terms $\delta R_{e,0}$ and δR_v which appear both in the quadrupole and the magnetic hfs. For B, $\delta R_{e,0}$ is zero since there are no closed p shells. For Na $3p$ and K $4p$, $\delta R_{e,0}$ is -0.249 and -0.287 , respectively. The value for Na is somewhat larger than that obtained in III (-0.180). This small difference is due to the use of the more accurate values of $u'_{1,1 \rightarrow 1}$ for $2p \rightarrow p$ in the present work. For K, the exchange of $4p$ with $3p \rightarrow p$ gives the largest contribution, -0.210 , while the $2p \rightarrow p$ term is -0.077 .

In order to obtain δR_v , it is necessary to determine the p wave perturbation of the valence wave function $v'_{1,1 \rightarrow 1}$ from Eq. (39). For K, we used the $4p$ function $v_0^2(4p)$ which is orthogonal to the core $2p$ and $3p$ wave functions. After $v'_{1,1 \rightarrow 1}$ is calculated, δR_v is obtained from Eqs. (42), (44), and (56). The resulting values are: $\delta R_v = -0.463$ for B $2p$, $+0.170$ for Na $3p$, and -0.051 for K $4p$. It should be pointed out that only a limited significance can be attached to these numerical values

for δR_v , since the results are very sensitive to the detailed behavior of the radial wave functions. We note that for Na, δR_v is positive and cancels a large part of $\delta R_{e,0}$ ($= -0.249$).

From the preceding results for $\delta R_e'$, $\delta R_{e,0}$, and δR_v , and from the values of R given in Table I, we can calculate the effective R which enters into the denominator of Eq. (78) for C :

$$R_{\text{eff}} \equiv (R + \delta R_e') / (1 - \delta R_{e,0} - \delta R_v). \quad (85)$$

One obtains: $R_{\text{eff}} = +0.033$ for¹⁶ B $2p$, -0.252 for Na $3p$, -0.155 for K $4p$, which can be compared to $R = 0.143$, -0.243 , and -0.188 , respectively. As was anticipated from the discussion of the values of $\delta R_e'$, R_{eff} is considerably different from R for B, whereas for Na and K, the two values are very similar. Thus the additional exchange terms $\delta R_{e,0}$ and δR_v have only a minor influence on C for these excited states.

We will now discuss the magnetic hfs correction term $\delta R_m'$ of Eq. (78). An attempt to obtain $\delta R_m'$ from the Hartree-Fock equations was made in II and III. The calculated values of $\delta R_m'(^2P_{3/2})$ and $\delta R_m'(^2P_{1/2})$ were, however, too large to give agreement with the small observed deviation of $5a(^2P_{3/2})/a(^2P_{1/2})$ from 1 for the light atoms. From Eqs. (32), (35a), and (77), one obtains

$$\frac{5F(1/2)a(^2P_{3/2})}{F(3/2)a(^2P_{1/2})} = \frac{1 - \delta R_m'(^2P_{3/2}) - \delta R_{e,0} - \delta R_v}{1 - \delta R_m'(^2P_{1/2}) - \delta R_{e,0} - \delta R_v} = \frac{1 - \delta \bar{R}_m'(^2P_{3/2})}{1 - \delta \bar{R}_m'(^2P_{1/2})}, \quad (86)$$

where $\delta \bar{R}_m'(^2P_j)$ is defined by

$$\delta \bar{R}_m'(^2P_j) \equiv \delta R_m'(^2P_j) / (1 - \delta R_{e,0} - \delta R_v). \quad (87)$$

From the calculations of II and III, it was found that the largest term of $\delta R_m'$ [which is given by Eqs. (56) and (56a) of II] is that due to the excitation of s electrons of the core into unoccupied s states as a result of the exchange with the valence electron. This conclusion is in agreement with Schwartz's treatment¹⁷ of the hfs anomaly in Ga. Unfortunately, it seems that the value of the perturbed $ns \rightarrow s$ wave functions at $r=0$ cannot be obtained reliably from the present treatment of the Hartree-Fock equations. A similar disagreement of the $ns \rightarrow s$ terms given by the Hartree-Fock equations has been obtained recently by Abragam, Horowitz, and Pryce.¹⁸ It may be noted that we have carried out additional calculations of the $ns \rightarrow s$ effect for B $2p$ and Na $3p$. For B, the value of the complete $ns \rightarrow s$ term was considerably too large and was found to be very

¹⁶ For B $2p$, the large value of $\delta R_e'$ indicates that a more complete investigation of the core effects would be necessary to obtain the actual value of C .

¹⁷ C. Schwartz, Phys. Rev. **99**, 1035 (1955).

¹⁸ Abragam, Horowitz, and Pryce, Proc. Phys. Soc. (London) **A230**, 169 (1955).

sensitive to the $1s$ and $2s$ functions used in the calculation. For Na, the total $ns \rightarrow s$ term was quite small ($+0.009$ for ${}^2P_{3/2}$, -0.002 for ${}^2P_{1/2}$), but this appears to be due to a fortuitous cancellation of the perturbed wave functions for $1s \rightarrow s$ and $2s \rightarrow s$. In view of the inadequacy of the calculations, it seems appropriate to obtain $\delta\bar{R}'_m$ from the experimental values of $a({}^2P_{3/2})/a({}^2P_{1/2})$. Schwartz¹⁷ has shown that the major part of $\delta\bar{R}'_m({}^2P_j)$ is due to $ns \rightarrow s$ excitation. With this assumption, one finds

$$\delta\bar{R}'_m({}^2P_{3/2}) \cong -5\delta\bar{R}'_m({}^2P_{1/2}). \quad (88)$$

Upon inserting (88) into (86), one obtains

$$\delta\bar{R}'_m({}^2P_{3/2}) = (\rho - 1)/(\rho + 5), \quad (89)$$

where ρ is the ratio $5F(1/2)a({}^2P_{3/2})/F(3/2)a({}^2P_{1/2})$.

The values of ρ are very close to 1 for the light atoms. For B $2p$ and Cl $3p^5$, $\rho = 1.0034$ and 1.011 , respectively. For these cases, we can safely neglect $\delta\bar{R}'_m$ in the expression for C . On the other hand, for the ground states of heavy atoms, the difference $\rho - 1$ is quite large. If this is also found for the excited states, there may be an appreciable $\delta\bar{R}'_m$ term in the equation for C for the states of Rb and Cs discussed above.

IV. CONCLUSIONS

Values of the core correction for the nuclear quadrupole coupling have been obtained for 11 atomic ground states and excited states. For the excited p states of the alkalis, the direct Coulomb terms give a net anti-shielding. The corresponding values of R are of order -0.1 to -0.3 . For the ground states of B, Cl, and Cu, we have obtained positive values of R , indicating a net shielding. However, there are appreciable exchange terms for B, and probably also for the ground states of some of the other light atoms. Hence the values of R for the ground states cannot be used without making the corrections for the exchange terms. By contrast, the exchange terms are very small for the excited states, so that the correction factor C for the quadrupole moment is approximately $1/(1-R)$ for these states.

The dependence of the calculated values of R on the

core wave functions has been investigated for Cl $3p^5$ and K $4p$. The angular term $\langle\gamma_{\text{ang}}/r^3\rangle$ is quite insensitive; for Cl, it decreases by only 11% if the Hartree-Fock wave functions are replaced by Hartree functions in the calculations. On the other hand, $\langle\gamma_{\text{rad}}/r^3\rangle$ depends strongly on the core wave functions. Thus for K, R_{rad} changes from -0.247 for Hartree-Fock functions to -0.362 if Hartree functions for the K^+ core are used to obtain $\gamma_{\text{rad}}(r)$. We have also compared the core correction terms for two different choices of the valence wave function for the K, Rb, and Cs excited states. The resulting values of R differ by ~ 0.10 to 0.15 . This difference is due mainly to the strong dependence of $\langle\gamma_{\text{rad}}/r^3\rangle$ on the radial distribution of the valence wave function. It can be concluded that there is an uncertainty of the order of 0.15 in the values of R for excited states because of possible inaccuracies in the core and valence wave functions used in the calculations.

In connection with the radial modes of excitation $u'_{1,l \rightarrow l}$ which enter into $\langle\gamma_{\text{rad}}/r^3\rangle$, we note that the existence of these modes has received strong support from the values of the quadrupolar relaxation time T_1 in magnetic resonance experiments.¹⁹ T_1 is proportional to $1/Q_{\text{ion}}^2$, where Q_{ion} is the total quadrupole moment of the ion. As was shown in IV and V, the total induced moment Q_{iT} is very large, especially for heavy ions where the ratio $|Q_{iT}|/Q$ is of the order of 100. This result is in agreement with the fact that T_1 is smaller by a factor 10^3 – 10^4 than would be expected from the nuclear Q alone. Since Q_{iT} is almost entirely due to the radial modes, this provides a good confirmation for the calculation of these terms. As pointed out in IV, there is also evidence for this effect from the quadrupole coupling in polar molecules.

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¹⁹ J. van Kranendonk, *Physica* **20**, 781 (1954); F. Reif, *Phys. Rev.* **100**, 1597 (1955).