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Quadrupole Shielding and Antishielding Factors for Several Atomic Ground States*

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The atomic shielding or antishielding factor R for the quadrupole hyperfine structure has been obtained for seven atomic ground states ranging from $F 2p^5$ to $Br 4p^5$. The values of R were determined by means of the perturbed wave functions $v_l(nl \rightarrow l')$, as obtained by solving the inhomogeneous Schrödinger equation for each type of excitation of the core electrons by the nuclear quadrupole moment Q . The resulting values of R have been listed, together with those for four atomic states which had been previously investigated. For the atomic ground states in this region of the Periodic Table, R is generally positive (shielding), and of the order of $+0.1$, except for $Al 3p$ and $Ga 4p$, for which R is negative, because of the antishielding provided by the $2p \rightarrow p$ and $3p \rightarrow p$ perturbations, respectively. The resulting correction factors $C = 1/(1 - R)$ have been applied to the quadrupole moments of 11 nuclear isotopes. We have also obtained the ionic antishielding factor γ_∞ for the Sc^{3+} ion, $\gamma_\infty(Sc^{3+}) \cong -11.2$.

I. INTRODUCTION

The purpose of the present paper is to give the results of calculations of the quadrupole shielding (or antishielding) factor¹ R for several atomic ground states, ranging from $B 2p$ to $Br 4p^5$. Altogether results will be presented for eleven atomic states in this region of the Periodic Table. The results for four of these states have been obtained previously,^{2,3} namely, for $B 2p$, $Al 3p$, $Cu 3d^9 4s^2$, and $Cu 3d^{10} 4p$. For the seven additional states, the present calculations are new; these states consist of $O 2p^4$, $F 2p^5$, $Cl 3p^5$, $Sc 3d$, $Fe^{2+} 3d^6$, $Ga 4p$, and $Br 4p^5$. The method of the calculations is entirely similar to that which has been used in previous papers.¹⁻⁵ In particular, we used the computer programs which have been described in Ref. 2.

The final results for the values of R and of the resulting quadrupole moment correction factor $C = 1/(1 - R)$ are given in Table VIII. In Sec. II, we shall describe the calculations of R and of the associated ionic antishielding factors⁶ γ_∞ . The individual terms of R and γ_∞ for each case are presented in Tables I-VII. We shall also discuss the present results for R , and in particular, the decrease of R (i.e., decrease of shielding) with increasing atomic number Z for the case of the halogen-atom ground states.

In Sec. III, we apply the correction factors C to

the experimental quadrupole moments Q_{expt} of eight nuclei to obtain corrected values Q_{corr} . We note that, in addition, Q_{corr} values have been previously obtained: (a) for three nuclei, namely, Al^{27} , Cu^{63} , and Cu^{65} in Refs. 2 and 3, and (b) for 12 alkali isotopes from hfs measurements in the excited np states (see Ref. 4). In Sec. III of the present paper, the determination of the presently obtained Q_{corr} values has been combined with that of $Q(Al^{27})$, $Q(Cu^{63})$, and $Q(Cu^{65})$, and the results have been presented in Table IX, which thus gives the values of Q_{corr} for 11 nuclei.

Finally, in Sec. IV we give a brief summary and general discussion of the present results.

II. CALCULATIONS OF R

As already mentioned in the Introduction, the calculations of R follow the same lines as in the work of Refs. 1-5. For the unperturbed wave functions of the core electrons u'_0 , we used in all cases the Hartree-Fock wave functions obtained by Clementi.⁷ The effective potential $V_{0,\text{HF}}$ corresponding to these wave functions was obtained by the procedure previously introduced by the author,⁵ namely,

$$V_{0,\text{HF}} - E_{0,\text{HF}} = \frac{1}{u'_0} \frac{d^2 u'_0}{dr^2} - \frac{l(l+1)}{r^2}, \quad (1)$$

where $E_{0,\text{HF}}$ is the effective Hartree-Fock energy eigenvalue and l is the azimuthal quantum number

of the core electron (nl).

The perturbed wave function $v'_1(nl \rightarrow l')$ arising from the potential due to the nuclear quadrupole moment Q is determined by the following equation¹:

$$\left(-\frac{d^2}{dr^2} + \frac{l'(l'+1)}{r^2} + V_0 - E_0\right) v'_1(nl \rightarrow l') = u'_0(nl)[r^{-3} - \langle r^{-3} \rangle_{nl} \delta_{ll'}], \quad (2)$$

where the additional subscript HF in V_0 and E_0 has been omitted for simplicity.

The contribution of the excitation $nl \rightarrow l'$ to the quadrupole shielding factor R is given by a direct term R_D plus an exchange term R_E . The pertinent equations are given by Eqs. (13)–(20') of Ref. 4. As an example, the direct term corresponding to $nl \rightarrow l'$ is given by

$$R_D(nl \rightarrow l') = \frac{c(nl \rightarrow l')}{\langle r^{-3} \rangle_{n_e l_e}} \left[\int_0^\infty w_e^2 dr \left(\frac{1}{r^3} \int_0^r u'_0 v'_1 r'^2 dr' + r^2 \int_r^\infty u'_0 v'_1 r'^{-3} dr' \right) \right], \quad (3)$$

where $c(nl \rightarrow l')$ is an angular coefficient, which has the following values: $\frac{8}{5}$ for $ns \rightarrow d$, $\frac{48}{25}$ for $np \rightarrow p$, $\frac{72}{25}$ for $np \rightarrow f$, $\frac{16}{7}$ for $nd \rightarrow d$, and $\frac{144}{35}$ for $nd \rightarrow g$. In Eq. (3), w_e is r times the radial wave function for the valence electron (or valence hole), $\langle r^{-3} \rangle_{n_e l_e}$ is the average value of r^{-3} for this wave function (with quantum numbers $n_e l_e$), i. e.,

$$\langle r^{-3} \rangle_{n_e l_e} = \int_0^\infty w_e^2 r^{-3} dr, \quad (4)$$

with the following normalization of w_e :

$$\int_0^\infty w_e^2 dr = 1. \quad (5)$$

The exchange term R_E is given by an integral (or a sum of integrals) of the same type as Eq. (3), but involving $v'_1 w_e$ in the integrals over r' and $u'_0 w_e$ in the second integral over r . The values of the coefficients $C(nl \rightarrow l'; n_e l_e; L)$ which replace $c(nl \rightarrow l')$ in Eq. (3) are given by Eq. (20') of Ref. 4 for the case of an external p electron, i. e., $l_e = 1$. For an external d electron, i. e., $l_e = 2$, the corresponding values of $C(nl \rightarrow l'; n_e l_e; L)$ are given in Table II of Ref. 2 (which also lists the values for $l_e = 1$ and $l_e = 3$).

We note that the above values of the coefficients c and C pertain to a valence electron (or hole) in interaction with a filled nl shell. If the interaction takes place with a half-filled shell in which all electrons have the same spin direction, so that all values of the orbital magnetic quantum number m_l are represented (from $m_l = -l$ to $m_l = +l$), then the values of $c(nl \rightarrow l')$ for the direct term must be multiplied by $\frac{1}{2}$. In the present work, the two examples in which this occurs are O $2p^4$ and Fe²⁺ $3d^6$. Thus for oxygen, we assume that there is a "valence" $2p$ electron outside a half-filled $2p^3$ configuration

which is assumed to be in a 4S state ($S = \frac{3}{2}$, $L = 0$), as in the ground state of the nitrogen atom. Similarly, for the Fe²⁺ ion, a single $3d$ electron of opposite spin to a $3d^5$ configuration is assumed to exist outside this configuration, whose spectroscopic state is 6S ($S = \frac{5}{2}$, $L = 0$). In both cases, the relevant values of c , i. e., $c(2p \rightarrow l')$ for oxygen and $c(3d \rightarrow l')$ for iron are $\frac{1}{2}$ of those for a filled $2p$ or $3d$ shell, respectively. On the other hand, since the "valence" electron has opposite spin to that of the half-filled shell, the corresponding exchange terms are zero, i. e., $R_E = 0$.

The wave functions $v'_1(nl \rightarrow l')$ and the electrostatic integrals over $u'_0(nl)$, $v'_1(nl \rightarrow l')$, and $w_e(n_e l_e)$ were obtained by means of the computer programs described previously in Ref. 2. The resulting values of R_D and R_E for the seven cases (O, F, Cl, Sc, Fe²⁺, Ga, and Br) are given in Tables I–VII. For convenience, the contributions $R_D(nl \rightarrow l')$, $R_E(nl \rightarrow l')$, and their sum $R(nl \rightarrow l')$ have been multiplied by 10^2 in the tables.

As has been extensively discussed in previous papers,^{1,2} the terms $R(nl \rightarrow l')$ are of two kinds, namely, the terms for the angular excitations with $l' = l \pm 2$, and those for the radial excitations of the core electrons with $l' = l$. The total of the angular terms is listed in the tables as total (ang), while the corresponding total for the radial terms is listed as total (rad).

The values in the last column of each table give the contributions to the ionic antishielding factor $\gamma_\infty(nl \rightarrow l')$, whose value is given by⁶

$$\gamma_\infty(nl \rightarrow l') = c(nl \rightarrow l') \int_0^\infty u'_0(nl) v'_1(nl \rightarrow l') r^2 dr. \quad (6)$$

Finally, the last row of each table lists the total (angular plus radial) value of $10^2 R_D$, $10^2 R_E$, $10^2 R$, and γ_∞ .

It may be noted that the tabulations for Fe²⁺, Ga, and Br (Tables V–VII) do not include the small terms due to $3d \rightarrow s$. As was pointed out in Ref. 4 [see Eq. (25)], on the basis of earlier calculations,⁶ we have

$$R_D(nd \rightarrow s) \approx -0.07 R_D(nd \rightarrow d), \quad (7)$$

TABLE I. Values of the contributions to R and to γ_∞ from the core excitations $nl \rightarrow l'$ for F $2p^5$.

$nl \rightarrow l'$	$10^2 R_D$	$10^2 R_E$	$10^2 R$	γ_∞
$1s \rightarrow d$	4.686	-2.649	2.037	0.0791
$2s \rightarrow d$	1.454	-1.302	0.152	0.3008
$2p \rightarrow f$	2.318	-1.159	1.159	0.4340
Total (ang)	8.458	-5.110	3.348	0.8139
$2p \rightarrow p$	7.338	-0.611	6.727	-9.325
Total $10^2 R$ or γ_∞	15.796	-5.721	10.075	-8.511

TABLE II. Values of the contributions to R and to γ_∞ from the core excitations $nl \rightarrow l'$ for O $2p^4$.

$nl \rightarrow l'$	$10^2 R_D$	$10^2 R_E$	$10^2 R$	γ_∞
$1s \rightarrow d$	5.356	-2.975	2.381	0.0893
$2s \rightarrow d$	1.726	-1.571	0.155	0.3464
$2p \rightarrow f$	1.349	...	1.349	0.2455
Total (ang)	8.431	-4.546	3.885	0.6812
$2p \rightarrow p$	3.928	...	3.928	-4.779
Total $10^2 R$ or γ_∞	12.359	-4.546	7.813	-4.098

$$R_E(nd \rightarrow s) \approx -0.1 R_E(nd \rightarrow d; L=1). \quad (8)$$

These results are based on the fact that $v'_1(nd \rightarrow s)/v'_1(nd \rightarrow d)$ is of the order of -0.1 throughout the range of r . The resulting values of $R(3d \rightarrow s)$ are very small in all three cases (Tables V–VII). Thus we have found for $R(3d \rightarrow s)$ from Eqs. (7) and (8): -0.0025 for Fe^{2+} , $+0.0014$ for Ga, and $+0.0007$ for Br. Even if there is some uncertainty in these estimates, the actual value of $|R(3d \rightarrow s)|$ is expected to be less than 0.01 in each case, which is of the order of the accuracy of the calculation of the total R values listed in Tables V–VII.

It may be of interest to list the values of $\langle r^{-3} \rangle_{n_e l_e}$ for the valence electron (or valence hole), which were used in the calculations. These values were derived from the valence wave functions obtained by Clementi.⁷ We have (in units of a_H^{-3} , where a_H is the Bohr radius): $\langle r^{-3} \rangle = 4.974$ for O $2p$, 7.546 for F $2p$, 6.755 for Cl $3p$, 1.428 for Sc $3d$, 5.086 for Fe^{2+} $3d$, 2.891 for Ga $4p$, and 11.98 for Br $4p$. In addition, the values of $\langle r^{-3} \rangle$ for the remaining four cases previously calculated are 0.7798 for B $2p$, 1.2960 for Al $3p$, 8.15 for Cu $3d$, and $1.276 a_H^{-3}$ for Cu $4p$.

The final values of R as obtained from Tables I–VII, together with the four values previously determined in Refs. 2 and 3 for B, Al, and Cu,

TABLE III. Values of the contributions to R and to γ_∞ from the core excitations $nl \rightarrow l'$ for Cl $3p^5$.

$nl \rightarrow l'$	$10^2 R_D$	$10^2 R_E$	$10^2 R$	γ_∞
$1s \rightarrow d$	2.167	-1.397	0.770	0.0410
$2s \rightarrow d$	0.845	-0.093	0.752	0.1183
$3s \rightarrow d$	0.558	-0.590	-0.032	0.3886
$2p \rightarrow f$	1.471	-0.340	1.131	0.1588
$3p \rightarrow f$	0.712	-0.356	0.356	0.6399
Total (ang)	5.753	-2.776	2.977	1.3466
$2p \rightarrow p$	-4.690	-0.023	-4.713	-1.540
$3p \rightarrow p$	+6.637	-0.553	+6.084	-29.95
Total (rad)	+1.947	-0.576	+1.371	-31.49
Total $10^2 R$ or γ_∞	+7.700	-3.352	+4.348	-30.14

TABLE IV. Values of the contributions to R and to γ_∞ from the core excitations $nl \rightarrow l'$ for Sc $3d$.

$nl \rightarrow l'$	$10^2 R_D$	$10^2 R_E$	$10^2 R$	γ_∞
$1s \rightarrow d$	3.242	-0.073	3.169	0.0330
$2s \rightarrow d$	6.010	-1.403	4.607	0.0879
$3s \rightarrow d$	4.271	-1.775	2.496	0.2656
$4s \rightarrow d$	0.300	-0.016	0.284	0.8018
$2p \rightarrow f$	8.839	-1.630	7.209	0.1197
$3p \rightarrow f$	5.600	-2.135	3.465	0.3842
Total (ang)	28.262	-7.032	21.230	1.6922
$2p \rightarrow p$	-50.57	+33.73	-16.84	-1.010
$3p \rightarrow p$	+13.77	-8.24	+5.53	-12.198
Total (rad)	-36.80	+25.49	-11.31	-13.208
Total $10^2 R$ or γ_∞	-8.54	+18.46	+9.92	-11.516

are listed in Table VIII, which also gives the corresponding correction factors $C=1/(1-R)$. We note that the value of R for Cu $3d^9 4s^2$ is very slightly different from that obtained in Ref. 2 [see Eq. (38)], namely, $R=0.179$ instead of 0.178 . The difference of 0.001 is due to the interaction of $3d$ with the $4s-d$ excitation mode, which had been inadvertently omitted in the calculations of Ref. 2.

Concerning the values of R in Table VIII, the following comments can be made:

(a) Generally speaking, the values of R for the atomic ground states in the region from B to Br are positive, and of the order of $+0.1$. The two exceptions are Al ($R=-0.063$) and Ga ($R=-0.129$), which have a valence p electron outside a closed np shell. The antishielding provided by the closed np shell ($2p^6$ for Al and $3p^6$ for Ga), and to a lesser extent the antishielding due to the $3d^{10}$ shell in Ga, result in a net antishielding of the nuclear quadrupole moment. However, the effect is small, of the order of -0.1 in both cases. We note that the case of Cu $3d^{10} 4p$, for which R is also nega-

TABLE V. Values of the contributions to R and to γ_∞ from the core excitations $nl \rightarrow l'$ for Fe^{2+} $3d^6$.

$nl \rightarrow l'$	$10^2 R_D$	$10^2 R_E$	$10^2 R$	γ_∞
$1s \rightarrow d$	2.590	-0.078	2.512	0.0265
$2s \rightarrow d$	4.246	-1.156	3.090	0.0679
$3s \rightarrow d$	2.068	-0.809	1.259	0.1790
$2p \rightarrow f$	6.407	-1.354	5.053	0.0919
$3p \rightarrow f$	3.211	-1.181	2.030	0.2764
$3d \rightarrow g$	1.774	...	1.774	0.1954
Total (ang)	20.296	-4.578	15.718	0.8371
$2p \rightarrow p$	-31.579	+24.092	-7.487	-0.724
$3p \rightarrow p$	+17.094	-16.851	+0.243	-8.607
$3d \rightarrow d$	+3.584	...	+3.584	-2.478
Total (rad)	-10.901	+7.241	-3.660	-11.809
Total $10^2 R$ or γ_∞	+9.395	+2.663	+12.058	-10.972

tive (-0.175), is that of an *excited* state. Indeed, the value of R for Cu $3d^{10}4p$ is of the same order and sign as that found for the excited np states of the alkalis, as reported in Ref. 4.

(b) If we consider the halogen atoms, F, Cl, and Br, we note that R decreases with increasing Z , from 0.101 for F to 0.043 for Cl, and to the very small value 0.0042 for Br. This decrease is due to the increasingly antishielding effect of the radial excitation modes $np \rightarrow p$ with increasing Z . This effect nearly cancels the shielding provided by the angular modes for the case of Br. Thus, if we may extrapolate to the next halogen, namely, I, we expect a weak net antishielding, perhaps of the order of $R = -0.05$. Actually, upon considering Tables I (for F), III (for Cl), and VII (for Br) in more detail, we note that the antishielding is provided only by the np shells which are internal to the $n_e p^5$ configuration of the outermost p shell. Thus for F, the $2p \rightarrow p$ excitation of the valence shell actually provides a shielding (0.0673), and for Cl, the antishielding due to the internal $2p$ shell (-0.047) is overcompensated by the shielding due to the external $3p$ shell ($+0.061$), giving a net shielding of 0.014 due to the radial terms. However, for Br, the antishielding due to $2p \rightarrow p$, $3p \rightarrow p$, and $3d \rightarrow d$ predominates slightly over the shielding due to $4p \rightarrow p$, giving a net negative contribution due to the radial modes ($R = -0.018$).

(c) For atoms with an external p electron or hole in the p shell, the exchange term $R_E(n_0s \rightarrow d)$ for the outermost ns shell ($= n_0s$) generally predominates over the direct term $R_D(n_0s \rightarrow d)$, giving a small net antishielding. The relatively large values of the exchange term are presumably due to the large overlap between the valence wave function for n_0p and the function for n_0s . For the more internal $ns \rightarrow d$ excitation modes, $R_E(ns \rightarrow d)$ is generally small, except for $1s \rightarrow d$, where it is

TABLE VI. Values of the contributions to R and to γ_∞ from the core excitations $nl \rightarrow l'$ for Ga $4p$.

$nl \rightarrow l'$	$10^2 R_D$	$10^2 R_E$	$10^2 R$	γ_∞
$1s \rightarrow d$	1.095	-0.746	0.349	0.0221
$2s \rightarrow d$	0.415	-0.036	0.379	0.0552
$3s \rightarrow d$	0.370	-0.049	0.321	0.1324
$4s \rightarrow d$	0.414	-0.459	-0.045	0.6250
$2p \rightarrow f$	0.748	-0.156	0.592	0.0747
$3p \rightarrow f$	0.627	-0.084	0.543	0.2150
$3d \rightarrow g$	0.777	-0.071	0.706	0.2952
Total (ang)	4.446	-1.601	2.845	1.4196
$2p \rightarrow p$	-2.031	-0.017	-2.048	-0.566
$3p \rightarrow p$	-11.010	+0.021	-10.989	-6.680
$3d \rightarrow d$	-5.375	+2.677	-2.698	-3.970
Total (rad)	-18.416	+2.681	-15.735	-11.216
Total $10^2 R$ or γ_∞	-13.970	+1.080	-12.890	-9.796

TABLE VII. Values of the contributions to R and to γ_∞ from the core excitations $nl \rightarrow l'$ for Br $4p^5$.

$nl \rightarrow l'$	$10^2 R_D$	$10^2 R_E$	$10^2 R$	γ_∞
$1s \rightarrow d$	0.951	-0.663	0.288	0.0196
$2s \rightarrow d$	0.324	-0.030	0.294	0.0475
$3s \rightarrow d$	0.266	-0.037	0.229	0.1161
$4s \rightarrow d$	0.277	-0.298	-0.021	0.465
$2p \rightarrow f$	0.610	-0.135	0.475	0.0649
$3p \rightarrow f$	0.429	-0.067	0.362	0.1743
$4p \rightarrow f$	0.297	-0.148	0.149	0.714
$3d \rightarrow g$	0.520	-0.053	0.467	0.216
Total (ang)	3.674	-1.431	2.243	1.817
$2p \rightarrow p$	-1.396	-0.017	-1.413	-0.479
$3p \rightarrow p$	-5.329	+0.003	-5.326	-4.612
$3d \rightarrow d$	-1.778	+0.607	-1.171	-1.626
$4p \rightarrow p$	+6.641	-0.553	+6.088	-73.46
Total (rad)	-1.862	+0.040	-1.822	-80.18
Total $10^2 R$ or γ_∞	+1.812	-1.391	+0.421	-78.36

of the order of 60% of the direct term (with opposite sign, of course).

(d) Referring to Table IV for Sc $3d$, we note the relatively large contributions from the angular, and especially from the radial terms. There is thus a large amount of cancellation both between the direct and exchange terms R_D and R_E for each mode ($nl \rightarrow l'$), and also between the total angular term ($+0.21$) and the total radial term for R (-0.11). In particular, we note the very large values of $R_D(2p \rightarrow p) = -0.51$ and $R_E(2p \rightarrow p) = +0.34$, giving a total $R(2p \rightarrow p) = -0.17$. We believe that the large values of R_D and R_E for scandium are at least partly due to the relatively small value of $\langle r^{-3} \rangle_{3d} = 1.428 a_H^{-3}$, which is in the denominator of the expressions for R_D and R_E [see Eq. (3)]. Because of the large amount of cancellation, it is believed that the final result for Sc, $R = 0.099$, may have an appreciable uncertainty, probably of the order of ± 0.15 .

TABLE VIII. Values of the atomic shielding (or antishielding) factor R and of the resulting correction factor C for the nuclear quadrupole moment.

Element	R	C
B	0.048	1.050
O	0.078	1.085
F	0.101	1.112
Al	-0.063	0.941
Cl	0.043	1.045
Sc	0.099	1.110
Fe ²⁺	0.121	1.138
Cu ($3d$)	0.179	1.218
Cu ($4p$)	-0.175	0.851
Ga	-0.129	0.886
Br	0.0042	1.0042

(e) The values of R for oxygen and fluorine, $R_O = 0.078$ and $R_F = 0.101$, are in reasonable agreement with the corresponding values derived in Ref. 3 from the work of Schaefer, Klemm, and Harris,⁸ namely, $R_O = 0.1285$ and $R_F = 0.0881$ [see Eqs. (28) and (29) of Ref. 3]. We also note that very accurate many-body calculations of core polarization have been carried out by Kelly⁹ for the case of oxygen. These calculations go beyond the present approximation, which is included in his "modified second-order" diagrams (see second paper of Ref. 9; Table III). Our value of $R = 0.078$ may be compared with Kelly's modified second-order value of $-\gamma_q$ which is 0.123. Kelly's total $-\gamma_q$ (including higher-order terms) is $-\gamma_q$ (total) = 0.155.

(f) In connection with the values of γ_∞ listed in Tables I–VII, it should be pointed out that these values cannot be directly used in calculations involving the ionic antishielding factor.⁶ Thus in connection with the halogens (F, Table I; Cl, Table III; and Br, Table VII), the values listed for the total $|\gamma_\infty|$ are considerably smaller than the actual $|\gamma_\infty|$ for the corresponding negative ions, because the calculations were carried out for neutral-atom wave functions (as is appropriate for the calculation of R), and not for the wave functions appropriate to the more loosely bound negative ions. As an example, γ_∞ (from neutral Cl wave functions) = -30.1 , as compared to γ_∞ (Cl⁻ ion) = -56.6 (see second paper of Ref. 6, Table VI). A similar comment applies to the case of oxygen (Table II). As concerns Tables V and VI, the appropriate values of γ_∞ for the trivalent ions Fe³⁺ ($\gamma_\infty = -9.14$) and Ga³⁺ ($\gamma_\infty = -9.50$) have been previously calculated by the author.⁶ Actually in these cases, the difference between γ_∞ for the trivalent ion and γ_∞ calculated with neutral-atom wave functions [minus the contribution of $\gamma_\infty(4s-d)$ for Ga] is only of the order of 10%, and the values of $|\gamma_\infty|$ obtained with the proper trivalent-ion wave functions are appropriately smaller.

For the case of Sc³⁺, we can obtain an estimate of γ_∞ by considering $\gamma_\infty(\text{ang})$ without the $4s-d$ term, $\gamma_\infty(4s-d) = 0.802$ (see Table IV), giving: $\gamma_\infty(\text{ang}, \text{Sc}^{3+}) = 1.692 - 0.802 = 0.890$. Upon adding this result to $\gamma_\infty(\text{rad}) = -13.208$ (see Table IV), we obtain -12.318 . As discussed above, and also in the third paper of Ref. 6 (see p. 268), it is reasonable to divide this result by 1.1, to take into account the tighter binding of the electrons in the trivalent ion. We thus obtain $\gamma_\infty(\text{Sc}^{3+}) = -11.2$, with an overall uncertainty of ± 1.0 .

III. DETERMINATION OF NUCLEAR QUADRUPOLE MOMENTS Q

We have applied the correction factors C of Table VIII to the experimental values Q_{expt} of 11 nuclear isotopes, namely, Al²⁷, Cl³⁵, Cl³⁶, Cl³⁷,

Cu⁶³, Cu⁶⁵, Ga⁶⁷, Ga⁶⁸, Ga⁶⁹, Ga⁷¹, and Ga⁷².

The corrected values of the nuclear quadrupole moments Q_{corr} are given by

$$Q_{\text{corr}} = Q_{\text{expt}} C = Q_{\text{expt}} [1/(1-R)]. \quad (9)$$

For the cases of Al²⁷, and Cu⁶³, Cu⁶⁵, values of Q_{corr} have been obtained previously in Ref. 3 [see Eq. (24)] and Ref. 2 [see Eqs. (42) and (43)], respectively. For the remaining eight Q values, the present determinations of Q_{corr} are new, and had not been obtained previously. The corrected values of Q for all 11 cases are presented in Table IX. The references for the uncorrected values Q_{expt} are also given in this table. It should be noted that the "atomic state" listed in the second column of the table refers to the state of the valence electron or valence shell in the atom.

Upon considering the values of R and C listed in Table VIII, we should discuss the various reasons why it was not possible to apply correction factors C for all of the cases listed in this table.

(i) For the case of boron, as has been discussed in Ref. 3, more accurate calculations of R and of the resulting values of $Q(\text{B}^{10})$ and $Q(\text{B}^{11})$ are available from the work of Schaefer *et al.*⁸ and of Nes-

TABLE IX. Values of the experimental quadrupole moments Q_{expt} (without correction factor C) and of the corresponding corrected moments Q_{corr} [see Eq. (9)]. The values of $C = 1/(1-R)$ are listed in the fourth column of the table. Q_{expt} and Q_{corr} are in units of $b = 10^{-24} \text{ cm}^2$. The references for the values of Q_{expt} are listed in the table.

Nucleus	Atomic state	Q_{expt}	$1/(1-R)$	Q_{corr}
Al ²⁷	3p	+0.149(2) ^a	0.941	+0.140(2)
Cl ³⁵	3p ⁵	-0.06213(2) ^b	1.045	-0.06493(2)
Cl ³⁶	3p ⁵	-0.0172(4) ^c	1.045	-0.0180(4)
Cl ³⁷	3p ⁵	-0.07894(2) ^b	1.045	-0.08249(2)
Cu ⁶⁵	3d ⁹ 4s ²	-0.161(3) ^d	1.218	-0.196(4)
Cu ⁶³	3d ¹⁰ 4p	-0.228(5) ^e	0.851	-0.194(4)
Cu ⁶³	3d ⁹ 4s ²	-0.172(4) ^d	1.218	-0.209(5)
Ga ⁶⁷	4p	+0.22 ^f	0.886	+0.195
Ga ⁶⁸	4p	$\pm 0.0313(16)$ ^g	0.886	$\pm 0.0277(14)$
Ga ⁶⁹	4p	+0.190 ^h	0.886	+0.168
Ga ⁷¹	4p	+0.120 ^h	0.886	+0.106
Ga ⁷²	4p	+0.59 ^f	0.886	+0.52

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bet.¹⁰ However, both the calculations of Schaefer *et al.*⁸ and those of Larsson¹¹ give values of R in good agreement with our result, namely, $R=0.0411$ and $R=0.050$, respectively, as compared to our value $R=0.0478$. In fact, the separate contributions of direct and exchange terms R_D and R_E obtained by Larsson¹¹ are also in good agreement with our results, as discussed in Ref. 3 (see p. 1726).

(ii) For the case of O^{17} , the value of $Q_{\text{expt}} = -0.026 \pm 0.009$ b obtained by Stevenson and Townes¹² has an uncertainty of ± 0.009 b and, moreover, presumably already includes core polarization effects, due to the use of covalently bonded wave functions. We note that the accurate value of $Q(O^{17})$ obtained by Kelly⁹ is -0.0263 b, in good agreement with the result of Schaefer *et al.*,⁸ namely, -0.0256 b. Both of these results include the core polarization corrections (i. e., the effect of R), as was discussed above in Sec. II.

(iii) For the case of fluorine, according to the tables of Fuller and Cohen,¹³ no value of Q has been obtained for the isotopes F^{17} and F^{20} for which the nuclear spin I is larger than $\frac{1}{2}$, and which therefore have a nonvanishing quadrupole moment. This lack of information is presumably due to the short half-lives of these two isotopes (66 and 11 sec, respectively).

(iv) For the cases of the chlorine and gallium isotopes, we note that for some nuclei, the values of Q_{expt} have been recalculated by Korolkov and Makhanek,¹⁴ using revised values of $\langle r^{-3} \rangle$ for the valence electron (or valence hole). The corresponding changes of Q_{expt} are, however, small compared to those produced by the correction factor $C=1/(1-R)$.

(v) Concerning the case of scandium, a large number of quadrupole moments Q_{expt} for various isotopes are known.¹³ In fact, it was the precise determination of Q_{expt} for Sc^{45} by Childs¹⁵ which led us to investigate the values of $C=1/(1-R)$ for additional ground states of light and medium heavy atoms. The uncorrected value $Q_{\text{expt}}(Sc^{45})$ is -0.216 b. If we would apply the correction factor 1.110 of Table VIII, we would obtain $Q_{\text{corr}}(Sc^{45}) = -0.240$ b. However, as pointed out in the discussion of Sec. II, there is a large amount of cancellation between terms pertaining to different excitations ($nl \rightarrow l'$), and also between the direct and exchange terms R_D and R_E for each ($nl \rightarrow l'$). As a result, we estimate that the calculated total value of R has an appreciable uncertainty, namely, ± 0.15 , which is of the order of R itself (0.099). Thus it does not seem justified to apply the calculated correction factor C of Table VIII for the case of the scandium isotopes.

(vi) In connection with the present calculation of R for the ferrous ion Fe^{2+} , we note that there is a

very extensive literature concerning the quadrupole moment of the metastable nucleus Fe^{57m} . Probably the most recent and thorough determination of $Q(Fe^{57m})$ is that of Sharma.¹⁶ This determination attempts successfully to resolve the discrepancy which had been previously found between values of $Q(Fe^{57m})$ obtained from ferrous (Fe^{2+}) vs ferric (Fe^{3+}) compounds. In the determination of $Q(Fe^{57m})$, Sharma used Sternheimer's value¹⁷ of $\gamma_{\infty} = -9.14$ for the ionic antishielding factor for Fe^{3+} , and also a value $R=0.32$ for the atomic shielding factor, which was derived from a calculation of Ingalls.¹⁸ It is believed that the present value of $R=0.121$ is more reliable, and also more reasonable, being much closer to the value of R for $3d^34s^2$ of the neighboring atom Cu ($R_{Cu}=0.179$). It would therefore be of some interest to recalculate $Q(Fe^{57m})$ using the procedure of Sharma, with $R=0.121$ (instead of $R=0.32$).

(vii) The values of Q_{corr} for Cu^{65} and Cu^{63} in Table IX are essentially the same as those previously derived by the author in Ref. 2 [see Eqs. (42), (43), and following discussion]. The only difference is that $Q_{\text{corr}}(Cu^{63})$ is here obtained directly from the measurements of Fischer, Hühnermann, and Kollath¹⁹ [i. e., from the value of $B(Cu^{63}, ^2D_{5/2}) = 6.20(15)$ mK, on p. 164], instead of applying the ratio²⁰ $Q^{63}/Q^{65} = 1.0806$ to the calculated $Q_{\text{corr}}(Cu^{65}) = -0.195 \pm 0.004$ b, to obtain $Q_{\text{corr}}(Cu^{63}) = -0.211 \pm 0.004$ b, as was done in Ref. 2. It may be noted that the value -0.209 ± 0.005 b of Table IX is in agreement with the former value, within the small uncertainties of the measurements.

(viii) Concerning the small shielding factor $R=0.0042$ for bromine [which results from a near cancellation of the radial and angular terms (see Table VII)], we conclude that the resulting correction factor $C=1.0042$ is so close to unity, that it does not seem appropriate to apply the factor C , since the corrections so obtained would be much smaller than the experimental errors of the quadrupole moment determinations. Thus even for the largest value of Q_{expt} ,²¹ namely, $\pm 0.73 \pm 0.03$ b for Br^{82} , the corrections would amount to only 0.0031 b, a factor of 10 smaller than the experimental uncertainty.

IV. SUMMARY AND DISCUSSION

In the present work, we have obtained the shielding or antishielding factors R for seven atomic ground states. The results for R and the corresponding correction factors $C=1/(1-R)$ are given in Table VIII. These results have been combined with those previously obtained in Refs. 2 and 3 for two excited states of Cu, and for the ground states B $2p$ and Al $3p$.

The correction factors C thus obtained have been applied to the experimentally determined quadrupole

moments Q_{expt} of 11 nuclei, namely, Al²⁷, Cl³⁵, Cl³⁶, Cl³⁷, Cu⁶³, Cu⁶⁵, Ga⁶⁷, Ga⁶⁸, Ga⁶⁹, Ga⁷¹, and Ga⁷². The resulting values of Q_{corr} are listed in Table IX.

However, we should discuss a possible reservation in connection with the above results. Thus it should be pointed out that the values of R calculated in the present work correspond to the single-particle excitations $nl \rightarrow l'$ by the nuclear quadrupole moment. Two-particle excitations brought about by the nuclear quadrupole interaction combined with the electrostatic interaction between the core electrons and the valence electron have not been considered. In the work of Nesbet²² for the lithium 2^2P state, such effects have been included by means of an atomic Bethe-Goldstone calculation. The result of Nesbet²² is that although the first-order result $R = 0.1188$ agrees closely with the value found by the present author, namely, $R = 0.1156$ (Ref. 2, Table VII), when the double excitations of both $1s$ and $2p$ electrons are considered, the result is reduced to $R = 0.0255$. On the other hand, the Brueckner-Goldstone calculations of Lyons, Pu, and Das²³ give $R = 0.1700$ for Li $2p$. The point as to what is the correct value of R appears therefore to be an open question. In order to resolve these discrepancies, Hameed and Foley²⁴ have recently recalculated R for the Li 2^2P state, and their result appears to be in rough agreement with that of Nesbet. However, it should be pointed out that Nesbet's result may be peculiar to the lithium 2^2P state. Especially for the excited np states of the alkalis (see Ref. 4), the double-excitation effect involving the valence electron may be considerably less important, on account of the decrease of the overlap between the valence (np) electron and the core electrons with increasing n . On the other hand, for the atomic ground states, where this overlap can be large, no such argument can be made. Thus it would be of interest to calculate the double-excitation terms for some of the cases of Table VIII. Unfortunately, the Bethe-Goldstone calculations of the type carried out by Nesbet become increasingly complicated with increasing Z . In any case, the single-excitation terms calculated in the present work should be of interest, independently of the magnitude of the double-excitation terms. Thus the single-excitation terms obtained here could be compared with those obtained in a more complete calculation including the higher-order terms.

It should be emphasized that with the first-order treatment used in the present paper, we have obtained remarkable agreement between the two corrected values of Q for the copper isotope Cu⁶⁵, when the uncorrected values of Q (Q_{expt}) are obtained from the $3d^9 4s^2$ and $3d^{10} 4p$ excited states. The uncorrected values of Q differ by more than

40% [see Eqs. (42) and (43) of Ref. 2]. In this connection, it should be noted that although Cu $3d^9 4s^2$ is an excited state, its $\langle r^{-3} \rangle_{3d}$ value is quite large, namely, $7.52 a_H^{-3}$ for the Hartree-Fock wave functions²⁵ used in the calculations.² Thus the $3d$ wave function for copper is rather internal, and since its magnitude of $\langle r^{-3} \rangle_{ni}$ is similar to (and usually larger than) the values of $\langle r^{-3} \rangle_{ni}$ for the ground states considered in the present work, it may be hoped that the second-order corrections will also be unimportant for the present calculations. Of course, it should be noted that if the second-order corrections should be important for Cu $3d^9 4s^2$ and $3d^{10} 4p$, they would have to affect both states equally, in order to preserve the agreement of the corrected Q values. Such a coincidence appears to be unlikely.

In addition to the evidence for the copper excited states, there is good evidence from the hfs of Tb¹⁵⁹ for both the configurations $4f^9 6s^2$ and $4f^8 5d 6s^2$, which have been extensively investigated by Childs.²⁶ As was discussed in Ref. 4 (see p. 847), Childs found a ratio between $a_{4f}/a_{5d} (= 2.96)$ and $b_{4f}/b_{5d} (= 2.02)$ of 1.47. This ratio can be regarded as a measure of $(1 - R_{5d})/(1 - R_{4f})$ for terbium. Although the present author's calculations are not as complete for the rare earths as for the copper excited states, nevertheless the best estimates are $R_{5d} = -0.3 \pm 0.1$ and $R_{4f} = +0.10 \pm 0.05$. Upon taking the ratio

$$\frac{1 - R_{5d}}{1 - R_{4f}} = \frac{1.3 \pm 0.1}{0.90 \pm 0.05} = 1.44 \pm 0.14, \quad (10)$$

we find very good agreement with the result of Childs²⁶ for the ratio of the hyperfine constants a and b in the two configurations.

Besides the striking evidence of shielding and antishielding effects for different atomic states of copper and terbium, there is additional evidence in favor of the values of R calculated by the present theory. This evidence has been summarized in the paper of Sternheimer and Peierls,⁴ and in an earlier paper by the present author.²⁷ To give a brief summary, the work of zu Putlitz and co-workers^{28,29} has shown that when the quadrupole moments of Rb⁸⁷ and Cs¹³⁴ are obtained from different excited atomic np states, there is appreciably better agreement between the values obtained from different states, when the correction factors $C_{ni} = 1/(1 - R_{ni})$ for each state are appropriately applied, than without these correction factors. As an example, Bucka, zu Putlitz, and Rabold²⁹ have shown that

$$Q_{5p, \text{expt}}/Q_{7p, \text{expt}}(\text{Rb}^{85}, \text{Rb}^{87}) = 1.07 \pm 0.03, \quad (11)$$

which can be compared with the calculated ratio⁴ $C_{7p}/C_{5p} = 0.840/0.796 = 1.055$. The improved agreement when the calculated values of C_{ni} are applied, is shown specifically in Table XIII of the paper of

Sternheimer and Peierls.⁴

In addition to the work on the alkali-metal excited np states, there is the earlier work of Murakawa,³⁰ who has shown from the interpretation of experimental hfs data that for the elements in the neighborhood of lutetium ($Z=71$) [and also for lanthanum ($Z=57$)], there is a weak antishielding for the $6p$ electron ($R_{6p} \sim -0.1$), whereas for the $5d$ electron, there is a considerably stronger antishielding ($R_{5d} \sim -0.4$), in good general agreement with the calculations (see Ref. 2, Table VI). Also, there are good indications from several Mössbauer-type experiments³¹ that for the rare earths, R_{4f} for the $4f$ electrons is of the order of $+0.1$ to

$+0.2$ (shielding), in good agreement with our calculations.²⁷ Thus there is extensive evidence from a number of atomic states that the first-order perturbation theory for R used in the present work gives good agreement with the experimental results on the hyperfine structure.

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