PHYSICAL REVIEW A VOLUME 1, NUMBER 2 FEBRUARY 1970

Quadrupole Polarizabilities of Various Ions and the Alkali Atoms*

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(Received 10 October 1969)

The quadrupole polarizability α_q which measures the induced quadrupole moment produced by an external field gradient has been calculated for three ions: Rb^+, Cs^+, and Bi^{5+}, and for the neutral alkali atoms. The present calculations for Rb^+ and Cs^+, using the appropriate Hartree-Fock wave functions, represent a considerable improvement over our previous calculations, in which Hartree wave functions (without exchange) were employed. The values obtained for α_q of the alkali atoms are very large, ranging from 60.0 Å^5 for Li to 440.8 Å^5 for Cs. In Sec. III, we have collected the values of α_q for 11 ions, as obtained using the author's method of direct solution of the inhomogeneous wave equation. Wherever possible, these values have been compared to those obtained by other methods. The agreement is generally very good.

I. INTRODUCTION

The purpose of this paper is to present the results of calculations of the quadrupole polarizability α_q of several ions and the alkali atoms. The quadrupole polarizability is defined as the ratio of the induced quadrupole moment Q_{ind} of the ion (or atom) to the external field gradient $\partial E_z/\partial z$, which gives rise to Q_{ind}. Thus,

$$\alpha_q \equiv -eQ_{\text{ind}}\left(\frac{\partial E_z}{\partial z}\right)^{-1}$$

in the same manner as the dipole polarizability α_d is defined as $\alpha_d \equiv p_{\text{ind}}/E$, where E is the external (homogeneous) electric field and p_{ind} is the resulting induced dipole moment. Effects of the quadrupole polarizability of the ion core were originally considered by Mayer and Mayer,[1] in connection with their discussion of the spectral term defects of the alkalis. Subsequently, the polarizability α_q was defined, and the values of α_q were calculated by Sternheimer[2,3] for various ions. In recent years, values of α_q have been calculated by a number of authors.[4]

In the present paper, we have obtained improved values of α_q for the Rb^+ and Cs^+ ions, as well as values of α_q for Bi^{5+} and for the neutral alkali atoms, for which, to our knowledge, no previous systematic calculations have been carried out. For Rb^+ and Cs^+, the present calculations can be regarded as a direct extension of the previous work by the author,[3] in which $\alpha_q(Rb^+)$ and $\alpha_q(Cs^+)$ were obtained using the Hartree wave functions, which were the only ones available at that time (in 1957). The present calculations were carried out using the corresponding Hartree-Fock functions, which have been calculated in the meantime by Freeman and Watson.[5] As was expected, the use of the Hartree-Fock wave functions results in a considerable decrease of α_q, as a consequence of the contraction of the Rb^+ and Cs^+ ion cores due to the exchange effect. The present results for α_q of the alkali atoms were obtained using the same valence wave functions as were employed in our previous work[6,7] on the dipole polarizabilities α_d of the alkali atoms. In Sec. III, we give a summary table of the quadrupole polarizabilities α_q which have been obtained by the present method of direct solution of the inhomogeneous Schrödinger equation for the perturbed wave functions.

II. CALCULATIONS OF α_q

The method of calculation was the same as was employed in our previous papers, in particular, Refs. 2 and 3. Thus, the perturbed radial wave functions $u_1'(nl\to l')$ ($l'=l$ or $l\pm2$) are the solutions of the following inhomogeneous equation:

$$\left(-\frac{d^2}{dr^2}+\frac{l'(l'+1)}{r^2}+V_0-E_0\right)u_1'(nl\to l') = u_0'(nl)\left(r^2-\langle r^2\rangle_{nl}\delta_{ll'}\right) , \qquad (1)$$

where u_0' is r times the radial part of the unperturbed (nl) wave function of the core electron. The effective values of $V_0(r)-E_0$ (V_0 = unperturbed potential; E_0 = unperturbed energy eigenvalue) were obtained in the same manner as in our previous work,[2,3,8] from the equation

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

The method of solution of Eq. (1) has been described in several previous papers.[2,3,8] We employed the program of inward integration of Eq. (1). A CDC-6600 computer program[9] was again used to integrate the differential equations.

In terms of $u_1'(nl \to l')$, the contribution to the quadrupole polarizability $\alpha_q(nl \to l')$ is given by

$$\alpha_q(nl \to l') = c(l \to l')(0.0415\ \text{Å}^5) \int_0^\infty u_0' u_1' r^2 dr, \qquad (3)$$

where $0.0415\ \text{Å}^5 = a_H{}^5$ (a_H = Bohr radius), and $c(l \to l')$ has the following values for a closed nl shell: $c(s \to d) = c(d \to s) = \frac{8}{5}$; $c(p \to p) = \frac{48}{25}$; $c(d \to d) = \frac{16}{7}$; $c(p \to f) = \frac{72}{25}$; $c(d \to g) = \frac{144}{35}$; $c(f \to h) = \frac{16}{3}$.

The wave functions $u_1'(nl \to l')$ have been tabulated in a separate paper.[10] In the present paper, we will give only the resulting values of $\alpha_q(nl \to l')$ and of the total α_q.

For the case of Rb^+, we used the Hartree-Fock wave functions of Watson and Freeman,[5] except for the Rb^+ 4s state, where the Hartree-Fock-Slater wave function of Herman and Skillman[11] was employed. In all cases, the outermost shell of the ion (or the valence electron for an alkali atom) gives by far the predominant contribution to α_q. Thus, in listing the results for various ions in Table I, n_0 denotes the principal quantum number of the outermost shell, i.e., $n_0 = 4$ for Rb^+. In obtaining α_q (total), we have also included an almost negligible contribution due to $3d \to g$, namely, $\alpha_q(3d \to g) = 0.00176\ \text{Å}^5$, as indicated in the footnote to the table.

The resulting $\alpha_q(\text{Rb}^+) = 1.592\ \text{Å}^5$ may be compared with our previous result,[3] $2.990\ \text{Å}^5$, based on Hartree wave functions. Thus, the use of Hartree-Fock wave functions decreases α_q by a factor of 1.88. This reduction is more important than that previously found for the dipole polarizability $\alpha_d(\text{Rb}^+)$, where a reduction factor of $\frac{2.92}{2.02} = 1.45$ can be deduced from the results of Ref. 7.

For the case of Cs^+, we also used Hartree-Fock wave functions obtained by Freeman and Watson.[12] The resulting perturbed wave functions $u_1'(nl \to l')$ are tabulated in Ref. 10, and the values of $\alpha_q(n_0 l \to l')$ are listed in Table I of the present paper. Here we have $n_0 = 5$. In the same manner as for Rb^+ (and also for Pr^{3+} and Tm^{3+}), the largest contribution within the outermost shell ($n_0 = 5$) is due to the $n_0 p \to f$ excitation of the $n_0 p$ electrons. As indicated in Table I, the final value $\alpha_q(\text{Cs}^+) = 4.907\ \text{Å}^5$ includes a small contribution, $0.0125\ \text{Å}^5$, arising from $\alpha_q(4d \to g)$. When we compare the present result with our previous (Hartree-function) value,[3] namely, $7.80\ \text{Å}^5$, we find that the use of the Hartree-Fock wave functions leads to a reduction of $\alpha_q(\text{Cs}^+)$ by a factor of 1.59. The corresponding reduction factor for the dipole polarizability $\alpha_d(\text{Cs}^+)$ is $\frac{5.60}{3.76} = 1.49$, as can be deduced from our previous results of Ref. 7.

The next two columns of Table I pertain to the results which we have previously obtained[13] for α_q of the Pr^{3+} and Tm^{3+} rare-earth ions. Here we have again $n_0 = 5$. In addition to the $n_0 = 5$ terms previously calculated in Ref. 13, the final results α_q (total) include a small contribution $\alpha_q(4s, 4p, 4d)$ pertaining to the 4s, 4p, and 4d shells, which has been evaluated in the paper of Sternheimer, Blume, and Peierls[14] (see Tables VIII and IX of Ref. 14).

Finally, the last column of the table pertains to the present calculations for the Bi^{5+} ion. It should be noted that we had originally intended to carry out a calculation for the trivalent Bi^{3+} ion, i.e., the ion with external configuration $5s^2 5p^6 5d^{10} 6s^2$. However, the wave functions used in the calculations, namely those of Herman and Skillman,[11] pertain to the neutral Bi atom. As a result, the 6s wave function $u_0'(6s)$ of Herman and Skillman[11] is considerably more external than that for Bi^{3+} because of the shielding provided by the three 6p

TABLE I. Contributions to the quadrupole polarizability α_q of five heavy ions. The rows above α_q (total) list the terms $\alpha_q(n_0 l \to l')$ due to the various modes of excitation of the (outermost) shell with highest principal quantum number n_0. The sum α_q (total) also includes the dominant term due to the subshells with principal quantum number $n_0 - 1$, as indicated in footnotes (a)–(e). All values are in units Å^5.

Ion	Rb^+	Cs^+	Pr^{3+}	Tm^{3+}	Bi^{5+}
$\alpha_q(n_0 s \to d)$	0.2132	0.842	0.300	0.1200	0.01074
$\alpha_q(n_0 p \to p)$	0.3649	0.925	0.273	0.1284	0.00548
$\alpha_q(n_0 p \to f)$	1.012	3.127	1.140	0.4755	0.02122
$\alpha_q(n_0 d \to s)$					0.1001
$\alpha_q(n_0 d \to d)$					0.04101
$\alpha_q(n_0 d \to g)$					0.1131
α_q(total)	1.592[a]	4.907[b]	1.731[c]	0.7284[d]	0.2921[e]

[a] This result includes $\alpha_q(3d \to g) = 1.76 \times 10^{-3}\ \text{Å}^5$.

[b] This result includes $\alpha_q(4d \to g) = 1.25 \times 10^{-2}\ \text{Å}^5$.

[c] This result includes $\alpha_q(4s, 4p, 4d) = 1.78 \times 10^{-2}\ \text{Å}^5$ (see Ref. 14).

[d] This result includes $\alpha_q(4s, 4p, 4d) = 4.53 \times 10^{-3}\ \text{Å}^5$ (see Ref. 14).

[e] This result includes $\alpha_q(4f \to h) = 4.3 \times 10^{-4}\ \text{Å}^5$.

electrons in the neutral Bi atom. In Table I, we again have $n_0 = 5$. It may be noted that since wave functions for the neutral Bi atom were used for the $n = 5$ shell (and also for $4f$), these wave functions are slightly more external than those which would be rigorously appropriate for the Bi^{5+} ion. However, for the $n = 5$ shell, the corresponding differences of the $u_0'(nl)$ are less important than those which would be involved for $u_0'(6s)$.

In addition to the results listed in Table I (for Bi^{5+}), we have also obtained the functions $u_1'(6s \to d)$ and $v_1'(6s \to d)$, as calculated from the function $u_0'(6s)$ of Ref. 11. Here the function $v_1'(6s \to d)$ pertains to the perturbation produced by the potential due to the nuclear quadrupole moment Q. Thus, $v_1'(6s \to d)$ is determined by the following equation:

$$\left(-\frac{d^2}{dr^2} + \frac{6}{r^2} + V_0 - E_0\right) v_1'(6s \to d) = \frac{u_0'(6s)}{r^3} \quad . \tag{4}$$

As discussed above, the function $u_1'(6s \to d)$ thus obtained from the neutral-atom Bi wave function $u_0'(6s)$ cannot be used to obtain a reliable value of $\alpha_q(6s \to d)$ for the Bi^{3+} ion. Nevertheless, the value of $\alpha_q(6s \to d)$ thus calculated can be employed to set an absolute upper limit on the actual $\alpha_q(6s \to d)$ for Bi^{3+}. This upper limit turns out to be 3.235 Å^3. A reasonable estimate of the actual $\alpha_q(6s \to d)$ is 1–2 Å^5, so that the total $\alpha_q(\mathrm{Bi}^{3+})$ is also of this order of magnitude, in view of the smallness of the contribution of the $n = 5$ subshells (0.2921 Å^5; see Table I).

From $v_1'(6s \to d)$, we can obtain the contribution of $6s \to d$ to the ionic antishielding factor[15] γ_∞. We find

$$\gamma_\infty(6s \to d) = \tfrac{8}{5} \int_0^\infty u_0'(6s) v_1'(6s \to d) r^2\, dr = 1.817 \quad . \tag{5}$$

Of course, this positive (shielding) contribution to $\gamma_\infty(\mathrm{Bi}^{3+})$ is small compared to the total $\gamma_\infty(\mathrm{Bi}^{3+})$, which is antishielding on account of the $nl \to l$ modes, and which was calculated[16] to be ~ -42.4.

In connection with the present calculations for Bi^{5+} and Bi^{3+}, it should be emphasized that these calculations are nonrelativistic, being based on the wave functions of Herman and Skillman.[11] Important relativistic corrections (perhaps as high as 50%) may be expected, in view of the large value of Z (= 83) for Bi.

The remainder of the present work was devoted to a calculation of α_q for the alkali atoms Li, Na, K, Rb, and Cs. The term $\alpha_q(ns \to d)$ due to the valence electron (ns) is overwhelmingly predominant. To this term we will add the effective contribution of the alkali ion core, which will be discussed below.

The values of $\alpha_q(ns \to d)$ are given by

$$\alpha_q(ns \to d) = \tfrac{4}{5}(0.0415\ \text{Å}^5) \int_0^\infty u_0'(ns) \times u_1'(ns \to d) r^2\, dr . \tag{6}$$

We note that the coefficient $c(s \to d) = \frac{8}{5}$ in Eq. (3) is replaced here by $\frac{4}{5}$, since there is a single valence (ns) electron.

The values of $u_1'(ns \to d)$ are determined by the following equation, which is a special case of Eq. (1):

$$\left(-\frac{d^2}{dr^2} + \frac{6}{r^2} + V_0 - E_0\right) u_1'(ns \to d) = u_0'(ns) r^2 \quad . \tag{7}$$

In these calculations, we used the same valence wave functions $u_0'(ns)$ as in our previous calculations[6, 7] of the dipole polarizabilities $\alpha_d(ns \to p)$. Thus, for Li and Na, we used wave functions obtained from the effective potentials of Seitz[17] and Prokofjew,[18] respectively. For the case of K, a potential derived by the author in Ref. 6 was used to calculate $u_0'(4s)$. For Rb, the $5s$ wave function given by Callaway and Morgan[19] was employed. Finally, for Cs we used the $6s$ wave function obtained by Sternheimer[20] ($E_0 \cong E_{0,\,\mathrm{expt}} = -0.2862$ Ry). All of these wave functions have the property that they reproduce the observed ionization potentials, i.e., $E_0 \cong E_{0,\,\mathrm{expt}}$.

The resulting values of $\alpha_q(ns \to d)$, as obtained from Eq. (6), are as follows (in units Å^5):

$$\begin{aligned} &\text{for Li:} && \alpha_q(2s \to d) = 59.99\,; \\ &\text{for Na:} && \alpha_q(3s \to d) = 74.82\,; \\ &\text{for K:} && \alpha_q(4s \to d) = 211.53\,; \\ &\text{for Rb:} && \alpha_q(5s \to d) = 261.7\,; \\ &\text{for Cs:} && \alpha_q(6s \to d) = 443.6\ . \end{aligned} \tag{8}$$

The qualitative features of these results are similar to those obtained previously[6, 7] for the dipole polarizabilities, namely (in units Å^3):

$$\begin{aligned} &\alpha_{v,a}(\mathrm{Li}) = 24.92; && \alpha_{v,a}(\mathrm{Na}) = 23.18; \\ &\alpha_{v,a}(\mathrm{K}) = 47.36; && \alpha_{v,a}(\mathrm{Rb}) = 51.06; \\ &\alpha_{v,a}(\mathrm{Cs}) = 71.31; && \end{aligned} \tag{9}$$

(see Table I of Ref. 7). Thus, in both cases we have $\alpha_{d,q}(\mathrm{Li}) \sim \alpha_{d,q}(\mathrm{Na})$; $\alpha_{d,q}(\mathrm{K}) \sim \alpha_{d,q}(\mathrm{Rb})$, with a large increase in both polarizabilities (α_d and α_q) in going from Na to K, and also in going from Rb to Cs.

It should be noted that the values of α_q obtained here (and also those of α_d) apply only to the isolated atoms in a gas or in an atomic beam. The reason is that the maxima of $|u_1'(ns \to d)|$ occur at very large radii, ranging from $r_{\max} = 6.6a_{\mathrm{H}}$ for Li to $r_{\max} = 7.45a_{\mathrm{H}}$ for Rb and $r_{\max} = 6.9a_{\mathrm{H}}$ for Cs. These values of $r_{\max}$ are large compared to typical internuclear distances in a solid or in a molecule. In these latter environments, we expect that $|u_1'(ns \to d)|$ at large r will be considerably decreased from its value for an isolated atom, because the perturbing function is longer r^2 [Eq. (1)], when r exceeds the internuclear distances involved.

The maximum values of $|u_1'(ns \to d)|$, which are attained at $r_{\max}$, are very large, which, of course, partly accounts for the large resulting values of α_q [Eq. (6)]. Thus, the maximum $|u_1'| = 31.44$ at $r = r_{\max} = 6.6a_H$ for Li. Similarly, the maximum $|u_1'| = 75.8$ at $r_{\max} = 7.45a_H$ for Rb, and $|u_1'|_{\max} = 110.8$ at $r_{\max} = 6.9a_H$ for Cs.

In order to obtain the total polarizabilities of the alkali atoms, we must add the effective ion-core contribution to the valence-electron terms $\alpha_q(ns \to d)$ given in Eq. (8). In the same manner as in Refs. 6 and 7, we note that $\alpha_{q,\,\mathrm{ion,\,eff}}$ would be simply equal to the quadrupole polarizability of the alkali ion [e.g., $\alpha_q(\mathrm{Li}^+), \ldots, \alpha_q(\mathrm{Cs}^+)$], if it were not for the induced field gradient $(\partial E_z/\partial z)_{\mathrm{ind}}$ produced by the valence electron itself, which tends to shield the core from the external field gradient $(\partial E_z/\partial z)_{\mathrm{ext}}$. Thus, the total field gradient at the position of the ion core is given by

$$\left(\frac{\partial E_z}{\partial z}\right)_{\mathrm{total}} = \left(\frac{\partial E_z}{\partial z}\right)_{\mathrm{ext}} + \left(\frac{\partial E_z}{\partial z}\right)_{\mathrm{ind}} . \qquad (10)$$

In the same manner as in Eq. (20) of Ref. 7, we can write

$$\left(\frac{\partial E_z}{\partial z}\right)_{\mathrm{ind}} = -\,\xi(ns \to d;\, r)_q \left(\frac{\partial E_z}{\partial z}\right)_{\mathrm{ext}} . \qquad (11)$$

As indicated, $\xi(ns \to d;\, r)_q$ is a function of r, which depends on $u_0'(ns)$ and $u_1'(ns \to d)$ of the valence electron. As a particular case of $\xi(ns \to d;\, r)_q$, we have at the nucleus

$$\xi(ns \to d;\, r = 0)_q = \gamma_\infty(ns \to d) \quad , \qquad (12)$$

where $\gamma_\infty(ns \to d)$ is the contribution to the quadrupole shielding factor[15] γ_∞ due to the valence electron [see also Eq. (5)].

In the same manner as in Eq. (22) of Ref. 7, we find that $\xi(ns \to d; r)_q$ is given by

$$\xi(ns \to d;\, r)_q = \tfrac{4}{5}\Big(\int_r^\infty u_0' u_1' \, r'^{-3} dr' + r^{-5} \times \int_0^r u_0' u_1' r'^2 \, dr' \Big) \ , \qquad (13)$$

where $u_0' = u_0'(ns)$ and $u_1' = u_1'(ns \to d)$. The first integral on the right-hand side of (13) represents the effect of the perturbed valence density outside the distance r (i.e., $r' > r$), whereas the second integral represents the effect of the quadrupole moment induced in the valence electron distribution at smaller distances, i.e., $r' < r$.

The function $\xi(ns \to d;\, r)_q$ for each alkali atom was obtained by means of the same computer program[9] as was employed in the calculation of $\alpha_q(ns \to d)$ for the valence electron [Eq. (6)].

For the present purpose of obtaining $\alpha_{q,\,\mathrm{ion,\,eff}}$, we must obtain $\xi(ns \to d;\, r_1)_q$ at the radius r_1 at which the principal perturbation $u_1'[(n-1)p \to f]$ of the ion core has its outermost maximum. Thus, for Cs, the principal perturbation of the ion core is $5p \to f$, as is shown by the values of $\alpha_q(nl \to l')$ in Table I. We note, however, that for Li the relevant core perturbation is $1s \to d$, since there is no closed p shell in this case. The values of r_1 thus obtained from the perturbed wave functions calculated by the author [3, 10] are as follows: $r_1 = 1.4a_{\mathrm{H}}$ for Li, $1.8a_{\mathrm{H}}$ for Na; $2.6a_{\mathrm{H}}$ for K; $2.8a_{\mathrm{H}}$ for Rb; and $3.2a_{\mathrm{H}}$ for Cs.

The values of $\xi(ns \to d;\, r_1)_q$ will be simply denoted by $\xi_q(r_1)$. Thus, the effective total field gradient at the location of the $[(n\text{-}1)p \to f]$ maximum is given by

$$\left(\frac{\partial E_z}{\partial z}\right)_{\mathrm{total}} = \left(\frac{\partial E_z}{\partial z}\right)_{\mathrm{ext}} [1 - \xi_q(r_1)], \qquad (14)$$

and therefore, the contribution of the ion core to the quadrupole polarizability of the alkali atom is approximately given by

$$\alpha_{q,\,\mathrm{ion,\,eff}} = \alpha_q(\mathrm{ion})[\,1 - \xi_q(r_1)], \qquad (15)$$

where $\alpha_q(\mathrm{ion})$ is the ion-core quadrupole polarizability, which will be obtained from Ref. 3 and the present calculations.

The values of $\xi_q(r_1)$, as obtained from Eq. (13), are as follows: 0.73 for Li; 0.75 for Na; 1.07 for K; 1.21 for Rb and 1.56 for Cs. It is seen that for K, Rb, and Cs, $\xi_q(r_1)$ is actually larger than 1, resulting in an overshielding and a (small) negative $\alpha_{q,\,\mathrm{ion,\,eff}}$. A similar effect was found for the effective contribution of the ion core to the dipole polarizability,[6, 7] i.e., $\xi_{v,\,b}(r_1) > 1$ in the notation of Ref. 7. However, because of the smallness of $\alpha_q(\mathrm{ion})$ as compared to the direct valence-electron contribution $\alpha_q(ns \to d)$ [Eq. (8)], the resulting corrections $\alpha_{q,\,\mathrm{ion,\,eff}}$ are negligible in all cases, except for Cs. Thus, from Eq. (15), we obtain the following values for $\alpha_{q,\,\mathrm{ion,\,eff}}$ (in units Å^5): 0.0013 for Li; 0.0159 for Na; − 0.051 for K; − 0.334 for Rb; and − 2.75 for Cs. Upon dividing these results by the corresponding $\alpha_q(ns \to d)$ [Eq. (8)], we obtain a ratio of only − 0.0062 for Cs, and (numerically) smaller values for the other alkalis.

The final values of α_q(total) for the alkali atoms, upon inclusion of $\alpha_{q,\,\mathrm{ion,\,eff}}$, are as follows (in units Å^5):

$$\alpha_q(\mathrm{Li}) = 59.99; \qquad \alpha_q(\mathrm{Na}) = 74.84;$$

$$\alpha_q(\mathrm{K}) = 211.48; \qquad \alpha_q(\mathrm{Rb}) = 261.4; \tag{16}$$

$$\alpha_q(\mathrm{Cs}) = 440.8.$$

III. RESULTS AND DISCUSSION

The results for α_q obtained in Ref. 3 and in the present work have been tabulated in Table II, which includes values for 11 ions besides those for helium and the alkali atoms. For comparison, the last column of the table lists values of α_q obtained by other workers.[21–29]

For the case of helium, the most accurate value is probably that of Dalgarno and McNamee.[24] These authors used the fully coupled Hartree-Fock approximation, in the terminology of Dalgarno.[30] However, our result, obtained in Ref. 3, is too large by only 1.4% (0.0993 versus 0.0979). For Li$^+$ and Be^{++}, our results differ negligibly from those of Dalgarno and McNamee.[24] The corresponding results of Das and Bersohn[21] and those of Langhoff and Hurst[27] were obtained by a variational method, which is somewhat less reliable than the numerical method used here.

For the Na$^+$ ion, our value (0.0634) is very close to that obtained by Lahiri and Mukherji[28] (0.0632) from the more accurate fully coupled Hartree-Fock method. The other values for Na$^+$ are also reasonably close to the result of Ref. 28.

For Cl$^-$, our result (13.77) is in moderately good agreement with the value which Lahiri and Mukherji[29] have obtained from their more accurate calculations (11.92). The discrepancy is about 15%. It should be remembered that the outermost ($3p$) electron of Cl$^-$ is very loosely bound and, therefore, relatively small changes in its wave function $u_0'(3p)$ at large r and the resulting changes of $u_1'(3p \to p)$ and $u_1'(3p \to f)$ can lead to relatively large changes of $\alpha_q(3p \to p)$ and $\alpha_q(3p \to f)$, for which the integrand contains the factor r^2 [see Eq. (3)]. In fact, the very wide variation of the values of α_q for different positive ions (from 6.4×10^{-4} for Be^{++} to 4.91 for Cs$^+$) is a direct result of the strong dependence of α_q on the outermost regions of the electron wave functions. Of course, neutral atoms and negative ions can have much larger values of α_q than positive ions, for the same reason.

In connection with the results for Cl$^-$, we note

TABLE II. Values of the quadrupole polarizability α_q (in units Å^5) for several ions and for the alkali atoms. The values obtained by the author in Ref. 3 and in the present work are given in the second column of the table. Column 3 lists the values of α_q obtained in other calculations.

Ion	α_q (present work and Ref. 3)	α_q (other calculations) [a–i]
He	0.0993	0.0949,[a] 0.0979,[d] 0.0979[g]
Li$^+$	4.73×10^{-3}	4.71×10^{-3},[a] 4.72×10^{-3},[d] 4.70×10^{-3}[g]
Be^{++}	6.37×10^{-4}	6.33×10^{-4},[a] 6.42×10^{-4},[g]
Na$^+$	0.0634	0.0670,[a] 0.0649,[b] 0.0639,[g] 0.0632[h]
Cl$^-$	13.77	13.1,[c] 13.05,[e] 11.79 and 19.44,[g] 11.92[i]
K$^+$	0.733	0.721,[b] 0.717,[e] 0.719,[g] 0.674[i]
Cu$^+$	1.280	
Rb$^+$	1.592	
Cs$^+$	4.907	
Pr^{3+}	1.731	1.752[f]
Tm^{3+}	0.729	0.718[f]
Bi^{5+}	0.2921	
Li	59.99	
Na	74.84	
K	211.5	
Rb	261.4	
Cs	440.8	

[a] Reference 21.

[b] Reference 22.

[c] Reference 23.

[d] Reference 24.

[e] Reference 25.

[f] Reference 26.

[g] Reference 27.

[h] Reference 28.

[i] Reference 29.

that the two values of Langhoff and Hurst,[27] namely, 11.79 and 19.44, were obtained for two choices of the unperturbed (Hartree-Fock) wave functions. Thus, $\alpha_q = 11.79$ Å^5 was obtained with the recently calculated Cl^- wave functions of Clementi *et al.*,[31] whereas the larger result, namely $\alpha_q = 19.44$ Å^5, was obtained using the earlier wave functions of Watson and Freeman,[32] which are presumably more external. In our previous work,[3] we used the original wave functions of Hartree and Hartree,[33] which are presumably intermediate between those of Refs. 31 and 32. Since the Clementi wave functions were also used in the work of Lahiri and Mukherji,[29] with almost the same result for α_q as in Ref. 27 (11.92, as compared to 11.79), it is quite likely that most if not all of the difference between our result (13.77) and that of Lahiri and Mukherji[29] (11.92) is due to the use of the slightly different zero-order wave functions in the two calculations.

For the case of K^+, our value is in very good agreement with those of Refs. 22, 25, and 27, and is only 8.8% larger than the value obtained by Lahiri and Mukherji[29] (0.733 versus 0.674). As in the case of Cl^-, the difference may be simply due to the use of slightly different zero-order wave functions in the two calculations.

For the cases of Pr^{3+} and Tm^{3+}, our values of α_q are in very good agreement with those of Ghatikar *et al.*,[26] as was to be expected since the same method and the same zero-order wave functions[34] were used in both calculations.

In connection with the preceding discussion of the slight differences of α_q as obtained by different calculations, it should be emphasized that the main purpose of the present calculations is to present a set of values of α_q for a number of ions and neutral atoms, for possible use in calculations of the internal field gradients in solids. The very wide variations in α_q values for different ions, which was pointed out above, is much more important than the small differences ($\lesssim 10\%$) between the results of various calculations for a given ion. Of course, as has been shown by Burns and Wikner,[23] the values of α_q (and of α_d) tend to decrease when the ion is imbedded in a solid. Nevertheless, this reduction is much less important for the positive ions than for negative ions, and, therefore, the values of Table II (except those for Cl^- and for the alkali *atoms*) may be used with some confidence to give the correct value (probably to $\lesssim 30\%$) for the corresponding ions in solids.

ACKNOWLEDGMENT

I wish to thank Dr. R. F. Peierls for the two computer programs pertaining to the integration of Eqs. (1) and (3), without which the present calculations would not have been possible in the limited time available.

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

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PHYSICAL REVIEW A VOLUME 1, NUMBER 2 FEBRUARY 1970

Exact Magnus-Force Formula for Three-Dimensional Fluid-Core Vortices[*]

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The two-dimensional Magnus formula $\vec{f}_m = \rho(\vec{v}_s - \vec{V}_v) \times \vec{\kappa}$ can be extended to three-dimensional fluid-core vortices of arbitrary core structure by a precise redefinition of the stream velocity vector $\vec{v}_s$, vortex velocity vector $\vec{V}_v$, and circulation vector $\vec{\kappa}$. For example, $\vec{V}_v$ becomes the velocity, in a plane slicing the vortex core, of the "center of mass" of the vorticity. The exact three-dimensional formula is derived by analyzing the motion of vorticity relative to the fluid particles – a relative motion caused by the action of nonconservative forces on the vortex core (e.g., the electric force on a charged vortex ring in superfluid helium). The analysis deals with the vorticity field $\vec{\omega} \equiv \vec{\nabla} \times \vec{v}$ and, thus, can lead to simple formulas and insights in cases where the velocity field $\vec{v}$ may be impossibly complicated. Examples introduced are (i) the concept of a "conserved vorticity current," (ii) a possible classical mechanism for the creation or destruction of vortex lines in superfluid helium, and (iii) a simple technique for analyzing the effect of viscosity on the structure of a vortex core.

Traditionally, the Magnus force is the lift force on a cylinder moving through a fluid when there is a net circulation of fluid about the cylinder.[1,2] One can also calculate the lift or Magnus force $\vec{f}_m$ (per unit length) exerted by a uniform stream on a two-dimensional singular core vortex; the result is simply[2]

$$\vec{f}_m = -\rho\vec{U} \times \vec{\kappa}\,, \tag{1}$$

where ρ is the fluid density, $\vec{U}$ the velocity of the singular core relative to the stream, and $\vec{\kappa}$ the total circulation of the vortex.

In the past few years, the use of the Magnus-force concept has proved to be a lucid and powerful technique for analyzing the motion of vortices in superfluid helium.[3–5] Detailed predictions about the motion of charged vortex rings, predictions based on the simple Magnus formula in Eq. (1), have been accurately verified by experiment[4] despite the lack of a derivation of the Magnus formula for curved three-dimensional vortices undergoing nonuniform motion. Here we derive an exact Magnus formula for three-dimensional vortices with localized but otherwise arbitrary fluid-core structures. The exact formula, which reduces to Eq. (1) for the case of two-dimensional circular-core vortices in