# Nuclear Quadrupole Coupling in Polar Molecules\*

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The effect of an external charge on the nuclear electric quadrupole coupling has been investigated for various ions. These results presumably apply to the case of polar molecules. The quadrupole moment induced by the nuclear quadrupole moment Q is 46.5Q, 8.7Q, 50.2Q, and 86.8Q for the Cl<sup>-</sup>, Cu<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup> ions, respectively. When an external charge interacts with the ion as in a polar molecule, the induced moment is added to Q, so that the quadrupole coupling is multiplied by a factor of order 10–100. This model of a polar molecule disregards the exchange repulsion between the ions. Evidence is presented from several molecules which seems to confirm the existence of the induced quadrupole moment, although there is only partial agreement with the experimental values. It is shown that the contribution to the quadrupole coupling due to the induced dipole moment in second order is small compared to the induced quadrupole effect.

### I. INTRODUCTION

T has been previously shown<sup>1,2</sup> that the nuclear quadrupole moment induces a quadrupole moment in the electron distribution of the atom. This induced moment interacts with the valence electron and contributes to the hyperfine splitting. The same effect is expected to take place for molecules where the atom core around the nucleus whose quadrupole coupling is considered interacts both with the valence electrons and the other atom cores and nuclei in the molecule. Consider, for simplicity, the case of a polar diatomic molecule, e.g., NaCl. The quadrupole coupling at the Cl nucleus includes the interaction of the moment induced in the Cl<sup>-</sup> ion with the Na<sup>+</sup> ion. Since the Na<sup>+</sup> ion is almost wholly external to the CI<sup>-</sup> electron distribution, the effect of penetration is small and the interaction energy due to the Cl<sup>-</sup> core is of the order of the interaction of the total Cl<sup>-</sup> induced moment with a unit charge placed at the position of the Na nucleus. The total induced moment  $|Q_{iT}|$  has been calculated for the Cl<sup>-</sup>, Cu<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup> ions, as representative examples, and was found to be very large, having values 46.5Q, 8.7Q, 50.2Q, and 86.8Q, respectively. Here Q is the nuclear quadrupole moment, and the sign of  $Q_{iT}$  is such as to reinforce the effect of the nuclear Q. The largest contribution to  $Q_{iT}$  is due to the radial excitations of the p and d shells, i.e., to the excitation of p electrons into higher p states and similarly to  $nd \rightarrow d$ terms. These modes of excitation have been described previously1 as antishielding effects, and are distinguished from the angular excitations such as  $ns \rightarrow d$  and  $np \rightarrow f$ which tend to shield the nuclear Q.

The purpose of this paper is to point out the existence

of the antishielding effect for molecules and to describe the calculations which give the order of magnitude of this effect. In general, if the magnitude of the induced moment is  $|\gamma_{\infty}|Q$ , the quadrupole coupling q will be of order  $2e(1+|\gamma_{\infty}|)/R^3$  rather than  $2e/R^3$ , which would be its value without the induced moment; here R is the internuclear distance. Since  $|\gamma_{\infty}|$  is of order 10–100 for medium and heavy ions, the order of magnitude of the experimental values of q can be compared with the present calculations. At present q can be deduced for only very few cases. It will be shown that for some of these q is much larger than  $2e/R^3$ . This fact may be taken as an indication of the presence of antishielding, although other effects may also play a role in determining q. We also discuss the contributions from the dipole perturbation of the wave functions to the nuclear quadrupole coupling and show that these terms are generally small.

### II. CALCULATION OF THE INDUCED QUADRUPOLE MOMENT

The calculation of the radial modes of excitation by the nuclear Q has been described previously in I. Here we will merely summarize the procedure of the calculation by taking the 3p shell of  $Cl^-$  as an example. For the m=0 states (m= magnetic quantum number) it was shown that the nuclear Q gives rise to the following  $3p \rightarrow p$  perturbation:

$$u_{1, p} = (2/5)(3/2)^{\frac{1}{2}} Q u'_{1, p} \cos\theta, \qquad (1)$$

where  $u_{1,p}$  is r times the perturbation of the wave function,  $\theta$  is the angle which the radius vector (of length r) makes with the axis of Q, and  $u'_{1,p}$  is the solution of

$$-\frac{d^2u'_{1,p}}{dr^2} + \left[\frac{2}{r^2} + V_0 - E_0\right]u'_{1,p} = u'_0 \left(\frac{1}{r^3} - \left\langle\frac{1}{r^3}\right\rangle_{3p}\right).$$
 (2)

Here  $V_0$  is the effective potential for the 3p electrons,  $E_0$  is the unperturbed energy,  $\langle 1/r^3 \rangle_{3p}$  is the average

<sup>\*</sup> The work carried out at Brookhaven National Laboratory was done under the auspices of the U. S. Atomic Energy Commission.

<sup>&</sup>lt;sup>†</sup> Supported by a grant from the National Science Foundation. <sup>1</sup> R. M. Sternheimer, Phys. Rev. 80, 102 (1950); 84, 244 (1951).

The second paper will be referred to as I. <sup>2</sup> R. M. Sternheimer and H. M. Foley, Phys. Rev. **92**, 1460 (1953).

value of  $1/r^3$  for the 3p state, and  $u_0'$  is r times the radial part of the unperturbed wave function, normalized according to  $\int_0^\infty u'_0^2 dr = 1$ . For  $u'_0$  we took the Hartree-Fock function<sup>3</sup> for Cl<sup>-</sup> which gives  $\langle 1/r^3 \rangle_{3p} = 5.7a_{\rm H}^{-3}$ . Equation (2) was integrated numerically starting from r=0 by means of the power series,

$$u'_{1, p} = a_1 r + a_2 r^2 + a_3 r^3 + \dots + b_2 r^2 \log r + b_3 r^3 \log r + \dots, \quad (3)$$

where the  $a_i$  and  $b_i$  are constant coefficients which are determined by inserting Eq. (3) into (2) and equating powers of r.  $a_2$  is arbitrary and was taken as 0. This coefficient corresponds to the part of  $u'_{1,p}$  proportional to  $u'_0$  (solution of the homogeneous equation) which is determined below. The resulting values of  $u'_{1,p}$  for two radii near  $r=0.02a_{\rm H}$  are used to start the numerical integration. In order to be consistent with  $u'_0$ , the square bracket on the left-hand side of (2), which will be denoted by P, was obtained from  $u'_0$  as follows:

$$P(r_n) = \left[ u'_0(r_n + \delta) - 2u'_0(r_n) + u'_0(r_n - \delta) \right] / \delta^2 u'_0(r_n),$$
(4)

where  $r_n$  is a selected radius and  $\delta$  is the interval of integration. The values of  $u'_{1,p}$  are obtained from

$$u'_{1, p}(r_{n}+\delta) = \{2+\delta^{2}[P(r_{n})-I(r_{n})/u'_{1, p}(r_{n})]\} \times u'_{1, p}(r_{n})-u'_{1, p}(r_{n-1}), \quad (5)$$

where  $I(r) = u'_0(r^{-3} - \langle r^{-3} \rangle_{3p})$  is the expression on the right-hand side of (2). It can be shown that the resulting  $u'_{1,p}$  should be well-behaved for large r, because of the property  $\int_0^{\infty} I u'_0 dr = 0$ . In actual cases, this is not true because of the finite  $\delta$  used in the integration, and it is necessary to use a suitable cut-off procedure. No serious error is introduced by this treatment. The perturbation must be made orthogonal to  $u'_0$ . As shown in I, this is achieved by subtracting a suitable multiple of  $u'_0$ . One obtains

where

$$\alpha = \int_0^\infty u'_{1, p} u'_0 dr. \tag{6a}$$

(6)

 $\vec{u}'_{1, p}$  together with  $u'_0$  is shown in Fig. 4 of I. The total induced moment  $Q_{iT}(3p \rightarrow p)$  due to  $3p \rightarrow p$  is given by<sup>1</sup>

 $\bar{u'}_{1, p} = u'_{1, p} - \alpha u'_{0},$ 

$$Q_{iT}(3p \rightarrow p) = (48/25)Q \int_{0}^{\infty} u'_{0} \bar{u}'_{1, p} r^{2} dr = -46.4Q, \quad (7)$$

where the - sign indicates that, in view of  $Q(\operatorname{Cl}^{35,87}) < 0$ , there is an excess of electrons near  $\theta = 0^{\circ}$  and  $180^{\circ}$  at large r. Thus the effect of  $Q_{iT}(3p \rightarrow p)$  at large r is to reinforce the nuclear Q. The sign of  $Q_{iT}(3p \rightarrow p)$  can be explained in terms of the orthogonality of  $\overline{u}'_{1,p}$ and  $u'_{0}$ . Near r=0, there is a lack of electrons for  $\theta \cong 0^{\circ}$  and  $180^{\circ}$  in view of the positive potential energy  $-e^{2}Q(3\cos^{2}\theta - 1)/4r^{3}$  in the field of Q. Hence  $Qu'_{0}\overline{u}'_{1,p}$ 

TABLE I. Induced quadrupole moment for the Cl<sup>-</sup>, Cu<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup> ions.  $\gamma_{\infty}$  is the ratio of the total induced moment to Q, and the values listed above  $\gamma_{\infty}$  are the contributions of the radial and angular modes to  $\gamma_{\infty}$ .

Ion	C1-	Cu+	Rb <sup>+</sup>	Cs+
$ \begin{array}{c} \hline \gamma_{\infty}(2p \rightarrow p) \\ \gamma_{\infty}(3p \rightarrow p) \\ \gamma_{\infty}(3d \rightarrow d) \\ \gamma_{\infty}(4p \rightarrow p) \\ \gamma_{\infty}(4d \rightarrow d) \end{array} $	-1.5 -46.4	-0.60 -6.4 -3.7	-0.47 -3.4 -1.2 -47.3	-0.21 -1.6 -0.38 -8.4 -3.4
$\gamma_{\infty}(5p \rightarrow p)$ $\gamma_{\infty}(\text{ang})$ $\gamma_{\infty}$	$^{+1.4}_{-46.5}$	$+2.0 \\ -8.7$	$^{+2.2}_{-50.2}$	-75.7 +2.9 -86.8

is negative near r=0, and because of the orthogonality,  $Qu'_{0}\bar{u}'_{1,p}>0$  for large r. Thus  $Q_{iT}(3p \rightarrow p)$  is positive.

The calculation of the  $2p \rightarrow p$  excitation for Cl<sup>-</sup> proceeds in the same manner as  $3p \rightarrow p$  and gives  $Q_{iT}(2p \rightarrow p) = -1.5Q$ . It may be noted that these calculations for Cl<sup>-</sup> are identical with those reported in I. except that we have integrated over the induced moment distribution to find the total induced moment. The wave function calculations for the angular modes<sup>4</sup>  $(ns \rightarrow d, np \rightarrow f)$  give  $Q_{iT, ang} = +1.42Q$  (shielding). Thus the total induced moment is  $Q_{iT} = -46.5Q$ , so that the effect of Q is increased at large distances by a factor  $1+|Q_{iT}|/Q=47.5$ . In the following  $Q_{iT}/Q$  will be denoted by  $\gamma_{\infty}$ . The terms of  $\gamma_{\infty}$  due to various modes will be written  $\gamma_{\infty}(2p \rightarrow p), \gamma_{\infty}(3p \rightarrow p), \cdots$ , where the parenthesis indicates the mode of excitation. For convenience these terms are listed in Table I. The large magnitude of  $Q_{iT}(3p \rightarrow p)$  is due partly to the factor  $r^2$ in the induced moment density. Since  $u'_{0}\bar{u}'_{1,p}r^{2}$  has its maximum at  $r=3.4a_{\rm H}$ ,  $r^2$  contributes roughly a factor 12 to the result.

The same procedure as for  $Cl^-$  was used for  $Cu^+$ ,  $Rb^+$ and  $Cs^+$ . For  $Cu^+$ , we used the Hartree-Fock functions obtained by Hartree.<sup>5</sup> The radial modes for the p shells are found from the same equations as for  $Cl^-$ . Figure 1 shows the  $3p \rightarrow p$  wave  $\bar{u}'_{1,p}$  and the induced moment  $Q_i(3p \rightarrow p)/Q = (48/25)u'_0\bar{u}'_{1,p}r^2$  together with the unperturbed 3p function  $u'_0$ . It is seen that  $\bar{u}'_{1,p}$  has one more node than  $u'_0$  and that the induced moment is antishielding  $(Q_i < 0)$  outside the last node of  $\bar{u}'_{1,p}$ . For 3d, the  $3d \rightarrow d$  excitation is obtained by a calculation similar to that given in I for the  $np \rightarrow p$  waves. After summing over the states in the 3d shell, one finds for the induced moment

$$Q_{iT}(3d \to d) = (16/7)Q \int_0^\infty u'_0 \bar{u}'_{1,d} r^2 dr, \qquad (8)$$

where  $u'_0$  is r times the radial 3d function, normalized

<sup>&</sup>lt;sup>8</sup> D. R. Hartree, Proc. Roy. Soc. (London) A156, 56 (1936).

<sup>&</sup>lt;sup>4</sup>A small error was found in the earlier calculations of the angular modes. The values of  $q_0(r)$  shown in Fig. 5 of I are too large for  $r > 1.2a_{\rm H}$ . These values should be:  $q_0(2.0) = 0.528$ ,  $q_0(3.0) = 0.279$ ,  $q_0(4.0) = 0.113$ . The quadrupole correction factor given in reference 17 is practically unchanged.

<sup>&</sup>lt;sup>5</sup> D. R. Hartree, Proc. Roy. Soc. (London) A157, 490 (1936).



FIG. 1.  $3p \rightarrow p$  perturbation  $\bar{u'}_{1,p}$  for Cu<sup>+</sup>, induced moment density  $Q_i/Q$  and unperturbed 3p function  $u_0'$ . The induced moment is -6.4Q.

according to  $\int_0^{\infty} u'_0^2 dr = 1$ , and  $\bar{u'}_{1,d}$  is that solution of

$$-\frac{d^{2}\bar{u}'_{1,d}}{dr^{2}} + \left(\frac{6}{r^{2}} + V_{0} - E_{0}\right)\bar{u}'_{1,d} = u_{0}'\left(\frac{1}{r^{3}} - \left\langle\frac{1}{r^{3}}\right\rangle_{3d}\right), (9)$$

which is orthogonal to  $u'_0$ . Here  $E_0$  is the unperturbed 3d energy and  $\langle 1/r^3 \rangle_{3d}$  is the average of  $1/r^3$  over the 3d wave function. The contributions of the  $m=0, \pm 1$  and  $\pm 2$  states to Eq. (8) are  $Q \int_0^\infty u'_0 \bar{u'}_{1,d} r^2 dr$  times 32/49, 16/49, and 64/49, respectively.

The shielding due to the angular modes was obtained by interpolation of the result for Cl<sup>-</sup> mentioned previously and similar wave function calculations for Cs<sup>+</sup> which will be reported soon. These calculations give  $Q_{iT, ang} = 2.95Q$  for Cs<sup>+</sup>. In order to obtain  $Q_{iT, ang}$  for Cu<sup>+</sup> by interpolation, we have considered besides  $Q_{iT, ang}/Q$  for Cl<sup>-</sup>(1.42) the values for<sup>1</sup> Al(1.06) and Na(0.62). One thus obtains  $Q_{iT, ang} \cong 2.0Q$  for Cu<sup>+</sup>.

In order to obtain the induced moment distribution  $Q_{i,ang}(r)$  which is needed below, we used the Thomas-Fermi model according to which<sup>1</sup>

$$Q_{i, \text{ang}}(r)dr = 0.2998Q(\chi x)^{\frac{1}{2}}(x/r)dr, \qquad (10)$$

where  $\chi$  and x are the Thomas-Fermi function and variable, respectively, and  $x = (Z^{\frac{1}{2}}/0.8853)r$ , where r is in units  $a_{\text{H}}$ . Since the Thomas-Fermi model is not valid for large r, an exponential decrease of  $Q_{i,\text{ang}}$  was assumed for  $x \gtrsim 9$ , in place of Eq. (10). The exponential was adjusted so that the total induced moment is  $\cong 2.0Q$ . We note that the precise treatment of  $Q_{i,\text{ang}}(r)$ is not important in the present problem, because  $Q_{iT,\text{ang}}$ is generally small compared to the induced moment due to the radial modes.

The various terms of  $\gamma_{\infty}$  for Cu<sup>+</sup> are given in Table I.  $\gamma_{\infty}$  is smaller than for Cl<sup>-</sup>, although it still represents a large effect. An important reason for this difference is that the Cu<sup>+</sup> 3*p* function is more internal than the Cl<sup>-</sup> 3*p* function; the outermost maximum of  $u'_0$  is at  $r=0.6a_{\rm H}$  as compared to 1.5a<sub>H</sub> for Cl<sup>-</sup>. As a result the maximum of  $u'_0\bar{u'}_{1, p}r^2$  is at a smaller value of r, 1.15 $a_{\rm H}$  as compared to  $3.4a_{\rm H}$ , and the difference in the effective  $r^2$  explains in part the smaller  $Q_{iT}(3p \rightarrow p)$  for Cu<sup>+</sup>.

For Rb<sup>+</sup> and Cs<sup>+</sup> the Hartree functions<sup>6</sup> were used. These functions are presumably not as accurate as the Hartree-Fock functions used for Cl<sup>-</sup> and Cu<sup>+</sup>, but should give the correct order of magnitude of the effect. The results are listed in Table I. The large value of  $Q_{iT}(4p \rightarrow p)$  for Rb<sup>+</sup> and  $Q_{iT}(5p \rightarrow p)$  for Cs<sup>+</sup> is again correlated with the position of the outermost maximum of  $u'_{0}\bar{u}'_{1,p}r^{2}$  which occurs at  $r=2.7a_{\rm H}$  and  $3.1a_{\rm H}$ , respectively.

The contribution of the induced moment to the quadrupole coupling q at a nucleus (A) of a polar diatomic molecule can be easily obtained if the molecule is completely ionic and if the ion centered at the other nucleus (B) can be represented by a unit point charge. q is then given by  $(2e/r^3)[1-\gamma(R)]$ , where

$$\gamma(r) = (1/Q) \left[ \int_0^r Q_i dr' + r^5 \int_r^\infty Q_i r'^{-5} dr' \right].$$
(11)

Here  $Q_i dr$  is the induced moment due to all modes between r and r+dr.  $\gamma$  is 0 at r=0 and approaches  $Q_{iT}/Q=\gamma_{\infty}$  for large r. The general behavior of  $1-\gamma(r)$ is the same for the four cases studied, as shown by Fig. 2.  $1-\gamma(r)$  is generally less than 1 up to some radius  $r\sim 1.5a_{\rm H}$  where the antishielding by the outermost (and possibly next to outer) p shell becomes effective. Then  $1-\gamma$  increases rapidly to the asymptotic value  $1-\gamma_{\infty}$ . At the common internuclear distances  $(R\sim 5a_{\rm H}), 1-\gamma$ is  $\gtrsim 90$  percent of the asymptotic value. Thus the  $\gamma_{\infty}$ given in Table I can be used to estimate the effect of the induced moment on q.

The effect of the extent of the charge distribution of the ion centered at nucleus *B* is expected to be small if  $\gamma$  is close to  $\gamma_{\infty}$  and does not vary appreciably over the dimensions of the ion at *B*. The general expression



FIG. 2.  $1-\gamma(r)$  for Cl<sup>-</sup>, Cu<sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup>. The function  $(1-\gamma)Q(3\cos^2\theta-1)/2r^3$  gives the total quadrupole potential.

<sup>6</sup> D. R. Hartree, Proc. Roy. Soc. (London) A143, 506 (1934); 151, 101 (1935). for q is

$$q = 2e \left\{ \frac{Z_B [1 - \gamma(R)]}{R^3} - \int \frac{(1 - \gamma)(3 \cos^2\theta_A - 1)\rho_B}{2r_A^3} dV \right\},$$
(12)

where  $Z_B$  is the charge of nucleus B,  $r_A$  and  $\theta_A$  are polar coordinates with origin at A and with respect to the internuclear axis,  $\rho_B$  is the charge density of the ion at B, and dV is the volume element. In the following we will frequently use q' defined as  $q' \equiv q/2e$ .

The numerical integration to obtain the perturbed wave functions introduces some error, although a large number of intervals  $\delta$  (~50 for the external shells) was used. It is estimated that the values of Table I are accurate within  $\pm 25$  percent for Cl<sup>-</sup> and  $\pm 50$  percent for the other ions.

The effect of the polarization of the closed shells can also be obtained by considering the perturbation of the ion by the external charge and calculating the contribution of the perturbed wave functions to the electric field gradient at nucleus A. The equivalence of this result with that obtained from the induced moment has been shown previously<sup>2</sup> and can be used as a check on the calculations.

The values of  $Q_{iT}$  obtained above are not exactly self-consistent. In order to obtain self-consistent values of the perturbations  $\bar{u}'_1$  one must replace the right-hand sides of Eqs. (2) and (9) by

$$I' = u'_{0} \left[ \frac{1 - \gamma}{r^{3}} - \left( \frac{1 - \gamma}{r^{3}} \right) \right],$$
(13)

and solve the resulting equations. This was done for Cl<sup>-</sup>. The effect of using I' was found to be small and reduces the total induced moment  $Q_{iT}$  by only  $\sim 10$ percent. The reason for the smallness of this effect is that  $\bar{u}'_{1,p}$  is largely determined by the inner parts of the atom where  $\gamma$  is relatively small and positive (shielding). A similar result was found for the  $5p \rightarrow p$ wave of Cs<sup>+</sup> where the use of I' leads to  $Q_{iT}(5p \rightarrow p) =$ -72.2Q as compared to -75.7Q obtained from Eq. (2). Thus it can be concluded that the values of Table I are self-consistent to the accuracy of the calculations.

The data for the polar molecules for which q can be obtained appear to give support to the existence of a strong antishielding. For  $K^{39}Br^{81}$  the values<sup>7</sup>  $(eqQ)_{Br}/h$  $= 8.555 \text{ Mc/sec and}^8 Q(\text{Br}^{81}) = 0.280 \times 10^{-24} \text{ cm}^2 \text{ give}$  $q' = 0.0650 a_{\rm H}^{-3}$ . Without the induced moment one would expect  $q'=1/R^3$  which is  $0.00660a_{\rm H}^{-3}$  (using<sup>7</sup> R=2.82A). If  $\kappa$  denotes the ratio  $q'/(1/R^3)$ , we have  $\kappa = 9.85$ .  $\kappa$  may be compared with  $1 - \gamma_{\infty}$  for the neighboring ion Rb<sup>+</sup>, which is 51.2. These values differ considerably, showing that other effects besides the antishielding must play a role. On the other hand the fact that  $\kappa$  is ~10 indicates that a large amplifying effect of the type of the antishielding probably does exist.

For NaCl<sup>35</sup>, the values<sup>9</sup>  $(eqQ)_{Cl}/h = 5.6 \text{ Mc/sec and}^{10}$  $Q(Cl^{35}) = -0.07894 \times 10^{-24} \text{ cm}^2 \text{ lead to } q' = 0.151 a_{H}^{-3}$ , as compared to  $1/R^3 = 0.01127 a_{\rm H}^{-3}$  (using<sup>11</sup> R = 2.36A). Thus one obtains  $\kappa = 13.4$  which is again of order 10 but considerably smaller than  $1-\gamma_{\infty}=47.5$ . For<sup>9</sup> NaI<sup>127</sup>,  $(eqQ)_{I}/h = -260 \text{ Mc/sec and}^{12} Q(I^{127}) = -0.59 \times 10^{-24}$ cm<sup>2</sup> lead to  $q' = 0.938 a_{\rm H}^{-3}$ , whereas  $1/R^3 = 0.00744 a_{\rm H}^{-3}$ (with<sup>11</sup> R=2.71A). The resulting value of  $\kappa$  is 126. This ratio agrees fairly well with  $1 - \gamma_{\infty} = 87.8$  for the neighboring ion Cs<sup>+</sup>. The antishielding by the outer pelectrons represents the effect of a small covalency, as is discussed below.

For K<sup>39</sup>Cl<sup>35</sup> the quadrupole coupling<sup>13</sup> is close to zero for the state with vibrational quantum number v=0. Upon using<sup>13</sup>  $(eqQ)_{Cl}/h = -0.075, -0.237, and -0.393$ Mc/sec for v=1, 2, and 3, respectively, one obtains q' = 0.00202, 0.00639, and 0.0106 $a_{\rm H}^{-3}$  for  $v = 1, 2, and 3, d_{\rm H}^{-3}$ respectively. We remark that q' for v=3 exceeds  $1/R^3$ which is  $0.00778a_{\rm H}^{-3}$  (using<sup>13</sup> R = 2.67A).<sup>14</sup> These data for KCl seem to indicate that another effect which tends to cancel the antishielding is of importance for this molecule.

Concerning the use of calculations for a positive ion, e.g., Cs<sup>+</sup>, to obtain the induced quadrupole moment for the neighboring negative ion with the same electron core (I<sup>-</sup>) one may expect that  $Q_{iT}$  will be larger for the negative ion since the outermost electrons (5p) are more loosely bound and hence can be polarized more easily in the latter case. In order to obtain an estimate of this effect, the  $3p \rightarrow p$  wave for K<sup>+</sup> was calculated, in order to compare it with  $3p \rightarrow p$  for Cl<sup>-</sup>. Using the Hartree-Fock<sup>15</sup> 3p function for K<sup>+</sup>, we found  $\gamma_{\infty}(3p \rightarrow p)$ = -18.2 as compared to -46.4 for Cl<sup>-</sup>. Thus the effect of the additional binding of the positive ion reduces  $\gamma_{\infty}(3p \rightarrow p)$  by more than a factor of 2. Referring to the cases of Br- and I- which are involved in the comparison with the experimental data, it is likely that  $1-\gamma_{\infty}$  is larger than the values obtained for Rb<sup>+</sup> and Cs<sup>+</sup>, respectively. This would improve the agreement with experiment for NaI where the theoretical value of  $1 - \gamma_{\infty}$  for Cs<sup>+</sup> is 87.8 as compared to  $\kappa = 126$ . For KBr an increase of  $1-\gamma_{\infty}$  above the value for Rb<sup>+</sup> (51.2) would lead to a worse disagreement with  $\kappa = 9.85$ .

#### **III. HYDROGENIC WAVE FUNCTIONS**

It is of interest that the radial and angular perturbations of the wave functions can be obtained exactly for

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<sup>12</sup> J. E. Mack, Revs. Modern Phys. 22, 64 (1950).
<sup>13</sup> Lee, Fabricand, Carlson, and Rabi, Phys. Rev. 91, 1395

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<sup>&</sup>lt;sup>7</sup> Fabricand, Carlson, Lee, and Rabi, Phys. Rev. **91**, 1403 (1953). <sup>8</sup> J. G. King and V. Jaccarino, Phys. Rev. **91**, 209 (1953).

<sup>&</sup>lt;sup>14</sup>We note that although q' is close to zero, the variation of q' with v is of the same order of magnitude ( $\sim 2/3$  as large) as for q' at the Br nucleus in KBr. From the data of reference 7 for  $(eqQ)_{\rm Br}/h$  in K<sup>39</sup>Br<sup>79</sup> one finds q'=0.0651, 0.0713, and 0.0775 $a_{\rm H}^{-3}$ for v=0, 1 and 2, respectively.

<sup>&</sup>lt;sup>15</sup> D. R. Hartree, Proc. Roy. Soc. (London) A166, 450 (1938).

the case of a hydrogenic potential  $V_0 = -2Z/r$ , where Z is the atomic number. This will be done first for the radial modes for 2p and 3p which give rise to the antishielding. Instead of obtaining this effect from the induced quadrupole moment, we consider the perturbation of the core wave functions by the field of the external charge and the resulting contribution to the field gradient at the nucleus.<sup>2</sup> For a unit charge placed at a distance R, the contribution to q' is  $(48/25)R^{-3} \times \int_0^\infty u'_0 \tilde{u}'_1/r^3 dr$ , where  $\tilde{u}'_1$  is that solution of

$$-\frac{d^{2}\tilde{u}'_{1}}{dr^{2}} + \left[\frac{l(l+1)}{r^{2}} - \frac{2Z}{r} + \frac{Z^{2}}{n^{2}}\right]\tilde{u}'_{1} = u'_{0}(r^{2} - \langle r^{2} \rangle) \quad (14)$$

which is orthogonal to the unperturbed p function  $u'_0$ ; *n* and *l* are the principal and orbital quantum numbers, respectively;  $\langle r^2 \rangle$  is the average of  $r^2$  over  $u'_0$ . The normalization is  $\int_0^\infty u'_0^2 dr = 1$ .

For  $2p \rightarrow p$ , we have

$$u'_{0} = (Z^{5/2}/24^{1/2})r^{2} \exp(-Zr/2),$$
 (15)

whence  $\langle r^2 \rangle = 30/Z^2$ . Equation (14) is solved by assuming that  $\tilde{u}'_1$  has the form

$$\tilde{u}'_1 = (Z^{5/2}/24^{1/2})(c_2r^2 + c_4r^4 + c_5r^5) \exp(-Zr/2).$$
 (16)

The coefficients  $c_4$  and  $c_5$  are determined from Eq. (14) and  $c_2$  is chosen such as to make  $\tilde{u}_1'$  orthogonal on  $u'_0$ . One finds

$$\tilde{u}'_{1} = \frac{Z^{5/2}}{24^{1/2}} \left[ -\frac{160}{Z^4} r^2 + \frac{3}{Z^2} r^4 + \frac{1}{3Z} r^5 \right] \exp\left(-Zr/2\right).$$
(17)

This gives

$$\int_{0}^{\infty} (u'_{0}\tilde{u}'_{1}/r^{3})dr = -67/(12Z), \qquad (18)$$

so that the contribution to q' is

$$\Delta q' = (48/25)R^{-3} \int_0^\infty (u'_0 \tilde{u}'_1/r^3) dr = -268/(25ZR^3).$$
(19)

 $\gamma_{\infty}(2p \rightarrow p)$  is given by  $\Delta q'/(1/R^3) = -268/25Z$ . The negative sign corresponds to the antishielding.

In a similar manner, the perturbation due to the  $3p \rightarrow p$  mode was obtained. We find

$$\tilde{u}'_{1} = \frac{(2Z/3)^{5/2}}{3} \left[ -\frac{3645r^{2}}{2Z^{4}} + \frac{1215r^{3}}{4Z^{3}} + \frac{18r^{4}}{Z^{2}} -\frac{r^{5}}{Z} - \frac{r^{6}}{12} \right] \exp\left(-\frac{Zr}{3}\right), \quad (20)$$

and  $\gamma_{\infty}(3p \rightarrow p) = -1008/25Z$ .

An attempt was made to correlate this result for 3pwith the Hartree function values of Table I. We can obtain an effective Z such that the formula for  $\gamma_{\infty}(3p \rightarrow p)$  gives the same value as the calculation by means of the Hartree functions. Thus the values of Table I lead to  $Z_{eff} = 0.87, 6.3, 11.9, and 25.2$  for Cl<sup>-</sup>, Cu<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup>, respectively. One may expect that  $Z_{eff}$  is related to the charge of the nucleus screened by the electron distribution. Using Slater's screening constants,<sup>16</sup> one finds  $Z_0 = Z - 11.25$  for the effective charge of the central field for 3p. One thus obtains  $Z_0 = 5.75$ , 17.75, 25.75, and 43.75 for Cl<sup>-</sup>, Cu<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup>, respectively. These values of  $Z_0$  are considerably larger than the  $Z_{eff}$ required to give the results obtained from the Hartree functions. This lack of agreement is perhaps not surprising since the Hartree 3p wave functions have only a remote similarity to hydrogenic functions. On the other hand, the main features of the hydrogenic perturbed functions  $\tilde{u}'_1$  such as the sign and the number of nodes, are in agreement with the Hartree function calculations.

For the angular excitations of the internal shells we obtain the induced quadrupole moment from the following equation for the perturbation due to the nuclear Q,

$$-\frac{d^2u'_1}{dr^2} + \frac{l(l+1)u'_1}{r^2} - \frac{2Zu'_1}{r} + \frac{Z^2u'_1}{n^2} = \frac{u'_0}{r^3}.$$
 (21)

For the  $1s \rightarrow d$  wave the result has been given previously,<sup>2</sup>

$$u_1' = (Z^{3/2}/3) [1 + (Z/3)r] \exp(-Zr), \qquad (22)$$

and the contribution to  $\gamma_{\infty}$  is

$$\gamma_{\infty}(1s \to d) = \frac{8}{5} \int_{0}^{\infty} u'_{0} u'_{1} r^{2} dr = \frac{2}{3Z}.$$
 (23)

For  $2s \rightarrow d$ , one finds

$$u'_{1} = \frac{Z^{3/2}}{6\sqrt{2}} \left[ 1 - \frac{Z}{6}r - \frac{Z^{2}}{24}r^{2} \right] \exp(-Zr/2), \qquad (24)$$

whence  $\gamma_{\infty}(2s \rightarrow d) = 4/3Z$ . For  $2p \rightarrow f$ , the perturbation is

$$u'_{1} = \frac{Z^{5/2}}{24\sqrt{6}} \left[ r + \frac{Z}{10} r^{2} \right] \exp(-Zr/2), \qquad (25)$$

so that  $\gamma_{\infty}(2p \rightarrow f) = 48/25Z$ . For  $3p \rightarrow f$  one finds

$$u'_{1} = \frac{(2Z/3)^{5/2}}{36} \left[ r - \frac{Z}{15} r^{2} - \frac{Z^{2}}{135} r^{3} \right] \exp(-Zr/3), \quad (26)$$

so that  $\gamma_{\infty}(3p \rightarrow f) = 78/25Z$ .

For  $3s \rightarrow d$ , the degeneracy of the 3s and 3d states makes it necessary to use a more refined treatment. Since the hydrogenic case is at best only a very crude representation for 3s, a solution was not obtained.

We note that the hydrogenic results for the angular modes are in quite good agreement with the values 16 J. C. Slater, Phys. Rev. 36, 57 (1930).

obtained from the Hartree wave functions, if one uses  $Z_{eff}$  equal to the screened  $Z_0$  defined above. Thus for  $Cl^-$ , the induced moment is 0.113Q for  $2s \rightarrow d$  and 0.157Q for  $2p \rightarrow f$ , as obtained from the Hartree functions. These values lead to  $Z_{eff}=11.8$  for  $2s \rightarrow d$  and 12.2 for  $2p \rightarrow f$ , in good agreement with  $Z_0=12.85$  derived from Slater's screening constants.<sup>16</sup>

# IV. INDUCED DIPOLE EFFECT

Aside from the induced quadrupole moment, there is a further induced effect which contributes to the quadrupole coupling for polar molecules. This effect arises by virtue of the dipole moment induced near nucleus Aby the ion surrounding B. In second order the dipole perturbation contributes to q.

We first consider the perturbation of an s state. The complete Schroedinger equation to second order is

$$(H_0+H_1)(u_{0,ns}+w_1+w_2) = (E_0+E_2)(u_{0,ns}+w_1+w_2),$$
(27)

where  $H_0$  and  $E_0$  are the unperturbed Hamiltonian and energy, respectively,  $H_1$  is the dipole perturbation,  $u_{0,ns}$  is the *ns* function (times *r*),  $w_1$  is the first-order perturbation of the wave function,  $w_2$  and  $E_2$  are the second-order terms in the wave function and the energy, respectively. Assuming that the ion at *B* acts as a positive point charge,  $H_1$  is given by  $-(2r/R^2)\cos\theta$ (Rydberg units) for r < R. Upon equating the first- and second-order terms in (27), one obtains

$$(H_0 - E_0)w_1 = -H_1 u_{0, ns}, \tag{28}$$

$$(H_0 - E_0)w_2 = -H_1w_1 + E_2u_{0, ns}.$$
(29)

The contribution to q arises from the two second-order terms in the density,  $w_1^2$  and  $2u_{0,ns}w_2$ . Since  $w_1$  is a p wave, Eq. (28) becomes

$$-\frac{d^2w_1}{dr^2} + \left(\frac{2}{r^2} + V_0 - E_0\right)w_1 = \frac{2}{R^2}u_{0,ns}r\cos\theta, \quad (30)$$

where  $V_0$  is the effective spherical potential. Here and in the following the wave functions are normalized to a volume element  $r^2 dr \sin\theta d\theta$ . Upon introducing  $u'_{0,ns} \equiv u_{0,ns}\sqrt{2}$ ,  $w_1$  can be written

$$w_1 = w'_1 \sqrt{2} \cos\theta / R^2, \qquad (31)$$

where  $w'_1$  satisfies

$$-\frac{d^2w'_1}{dr^2} + \left(\frac{2}{r^2} + V_0 - E_0\right)w'_1 = u'_{0, ns}r.$$
 (32)

Note that

$$\int_{0}^{\infty} u^{\prime 2}{}_{0, ns} dr = 1.$$
 (33)

The contribution  $\Delta q'_1$  due to the  $w_1^2$  terms for both s

electrons is

$$\Delta q'_{1} = -2 \int_{0}^{\infty} \int_{0}^{\pi} \frac{w_{1}^{2} (3 \cos^{2}\theta - 1)}{2r^{3}} dr \sin\theta d\theta$$
$$= -\frac{16}{15R^{4}} \int_{0}^{\infty} \frac{w_{1}'^{2}}{r^{3}} dr. \quad (34)$$

In order to obtain  $w_2$ , we substitute the expressions for  $H_1$  and  $w_1$  in Eq. (29), giving

$$(H_{0}-E_{0})w_{2} = \left[\frac{E_{2}u'_{0,ns}}{\sqrt{2}} + \frac{2\sqrt{2}w'_{1}r}{3R^{4}}\right] + \frac{2\sqrt{2}w'_{1}r(3\cos^{2}\theta - 1)}{3R^{4}}, \quad (35)$$

where the right-hand side has been written as a sum of s and d functions. Thus  $w_2$  has both an s and a d part. Only the d part is of interest here since the overlap of the s part with  $u_{0,ns}$  does not contribute to q. If we write the d function part of  $w_2$ , as

$$w_{2,d} = (2\sqrt{2}/3R^4) w'_{2,d} (3\cos^2\theta - 1), \qquad (36)$$

the radial function  $w'_{2,d}$  is determined by

$$-\frac{d^2w'_{2,d}}{dr^2} + \left(\frac{6}{r^2} + V_0 - E_0\right)w'_{2,d} = w'_1r.$$
(37)

In view of Eq. (36), the density due to the overlap of  $w_{2,d}$  and  $u_{0,ns}$  for both s electrons is

$$\rho_2 = (8/3R^4) u'_{0, ns} w'_{2, d} (3 \cos^2 \theta - 1).$$
(38)

The contribution to q' is

$$\Delta q'_{2} = -\int \rho_{2} [(3 \cos^{2}\theta - 1)/2r^{3}] dV$$
  
=  $-(32/15R^{4}) \int_{0}^{\infty} (u'_{0, ns} w'_{2, d}/r^{3}) dr.$  (39)

For the dipole perturbation of 1s states, Eqs. (32) and (37) can be solved exactly if one assumes that  $u'_{0,1s}$  is a hydrogenic function,

$$u'_{0,1s} = 2Z^{\frac{3}{2}}r \exp(-Zr).$$
 (40)

 $w'_1$  is then given by

$$w'_1 = Z^{-\frac{1}{2}r^2} \exp(-Zr) [1 + (Z/2)r],$$
 (41)

and Eq. (31) yields

$$\Delta q'_1 = -19/(30Z^3R^4). \tag{42}$$

Upon inserting  $w'_1$  into Eq. (37), one can easily verify that the solution is

$$w'_{2} = Z^{-\frac{1}{2}} \left( \frac{15}{32Z^{2}} r^{3} + \frac{5}{16Z} r^{4} + \frac{1}{16} r^{5} \right) \exp(-Zr).$$
 (43)

Eq. (39) now gives

$$\Delta q'_2 = -\frac{14}{(15Z^3R^4)},\tag{44}$$

so that the complete term for the dipole excitation of 1s is

$$\Delta q'_{1s, D} = -47/(30Z^3R^4). \tag{45}$$

The ratio of  $\Delta q'_{1s,D}$  to the ionic term will be denoted by  $\rho_{1s,D}(=-47/30Z^3R)$ . For q at the Cl nucleus in NaCl  $(R=4.46a_{\rm H})$ ,  $\rho_{1s,D}=-7.2\times10^{-5}$ . Although the terms due to 1s (and other inner shells) are negligible for Cl<sup>-</sup>, it will be seen below that the term due to the outermost shell (3p) is quite appreciable. We note that for the perturbation of ns, the normalization condition and the determination of  $E_2$  enter only into the calculation of the s part of  $w_2$ , but do not affect  $w'_{2,d}$ .

For the electrons in a p shell, the dipole perturbation gives rise to excited d and s states in first order, and in second order gives excited p and f states, as shown in Fig. 3. In this figure an arrow corresponds to the application of the perturbation. The subscripts indicate the unperturbed state and the type of perturbation (dipole or quadrupole) which is being considered. Primes are used to distinguish the various s, p, d, f functions from each other. The contributions to q arise from the terms of type  $(d_{np, D}, d_{np, D})$ ,  $(np, p_{np, D})$ ,  $(np, f_{np, D})$  and  $(np, p'_{np, D})$ , where  $(np, p_{np, D})$  is the density due to the overlap of np with  $p_{np, D}$ , and the notation for the perturbed wave functions is the same as in Fig. 3. For brevity, the subscript np will be omitted in the following.

By a procedure similar to that used for the s states, one finds, for the total contribution of a p shell,

$$\Delta q'_{np,D} = -\frac{1}{R^4} \left[ \frac{16}{15} J(d_D, d_D) + \frac{32}{75} J(3p, p_D) + \frac{96}{125} J(f_D, f_D) + \frac{32}{15} J(3p, p'_D) \right]. \quad (46)$$

Here J(a,b) is defined as

$$J(a,b) = \int_0^\infty \left[ w'_i(a) w'_j(b) \right] / r^3 dr, \qquad (47)$$

where  $w'_i(a)$  and  $w'_j(b)$  are the radial functions (times r) for the perturbed waves a and b, respectively. The subscript (i,j) indicates the order of the perturbation. The  $w'_i$  are determined by the equations,

$$M_2 w'_1(d_D) = u'_{0, n_P} r, (48)$$

$$M_0 w'_1(s_D) = u'_{0, n_P} r, (49)$$

$$M_1 w'_2(p_D) = w'_1(d_D) r - \lambda_1 u'_{0, np}, \qquad (50)$$

$$M_3 w'_2(f_D) = w'_1(d_D)r, (51)$$

$$M_1 w'_2(p'_D) = w'_1(s_D) r - \lambda_2 u'_{0, np}, \qquad (52)$$



FIG. 3. Perturbations arising in first and second order from dipole and quadrupole parts of potential produced by external charge. (a) Quadrupole perturbation. (b) Dipole perturbation.

where

$$M_{l} = -\frac{d^{2}}{dr^{2}} + \frac{l(l+1)}{r^{2}} + V_{0} - E_{0}, \qquad (53)$$

and  $u'_{0,np}$  is r times the radial np function, normalized according to

$$\int_{0}^{\infty} u^{\prime 2}{}_{0, np} dr = 1.$$
 (53a)

The parameters  $\lambda_i$  are proportional to the second-order energy terms  $(E_2)$  and are given by

$$\lambda_1 = \int_0^\infty w'_1(d_D) r u'_{0, np} dr, \qquad (54)$$

$$\lambda_2 = \int_0^\infty w_1'(s_D) r u'_{0, np} dr.$$
 (55)

It is seen that the right hand sides of Eqs. (50) and (52) are orthogonal on  $u'_{0,np}$ . These equations determine  $w'_2(p_D)$  and  $w'_2(p'_D)$ , respectively, except for the addition of an arbitrary multiple of  $u'_{0,np}$ . This part of the perturbation is determined by the normalization conditions which are

$$\int_{0}^{\infty} \{ [w_{1}'(d_{D})]^{2} + 2u'_{0, np}w'_{2}(p_{D}) \} dr = 0, \quad (56)$$
$$\int_{0}^{\infty} \{ [w'_{1}(s_{D})]^{2} + 2u'_{0, np}w'_{2}(p'_{D}) \} dr = 0. \quad (57)$$

The calculation of these perturbed wave functions and of the resulting  $\Delta q'_{3p,D}$  [Eq. (46)] was carried through for the 3p shell of Cl<sup>-</sup>. The first-order perturbations  $w'_1(d_D)$  and  $w'_1(s_D)$  were obtained by numerical integration of Eqs. (48) and (49), and then

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the second-order perturbations were found from Eqs. (50)–(52). We give here the contributions to  $\Delta q'_{3p, D} R^3$ , which is the ratio of  $\Delta q'_{3p, D}$  to the ionic term. These values are proportional to 1/R and pertain to NaCl  $(R=4.46a_{\rm H})$ ; they will be called  $\rho_D(a,b)$ . We have:  $\rho_D(d_D,d_D) = -0.2$ ,  $\rho_D(3p,p_D) = +4.8$ ,  $\rho_D(3p,f_D) = -0.2$ ,  $\rho_D(3p,p'_D) = +6.5$ .

The principal reason for calculating the induced dipole effect was to determine whether it tends to cancel the first-order antishielding discussed earlier. The total contribution  $\sum (a,b)\rho_D(a,b)$  is +10.9. It should be noted that the sign of the  $\rho_D$  is independent of the sign of the external charge, since  $\rho_D$  involves the square of  $H_1$ . For an external positive charge the induced dipole effect has the same sign as the antishielding, while for an external negative charge (e.g., Na coupling in NaCl) the induced dipole effect tends to reduce the magnitude of q (shielding). Thus the possibility of cancellation would occur only in the latter case. However, the results for Cl<sup>-</sup> appear to indicate that the induced dipole effect will be rather small compared to the first-order terms (10.9 as compared to 46.5). Moreover, the values of  $\rho_D$  given above are probably overestimates for the following reason. The perturbation was taken as  $-(2r/R^2)\cos\theta$  for all r, whereas for r > R, we have  $H_1 = -(2R/r^2) \cos\theta$ . The outermost maximum of  $w'_2(p_D)$  is at  $r=4.7a_{\rm H}$  which is outside  $R(=4.46a_{\rm H})$ for NaCl. Thus the perturbing potential is effectively too large, resulting in an overestimate of  $w'_2(p_D)$  and hence of  $J(3p,p_D)$ . The same remark applies for the other perturbed functions.

## V. SECOND-ORDER QUADRUPOLE EFFECT

Besides the induced dipole effect, there is another second-order contribution to q which arises from applying twice the quadrupole part of the potential of the external charge. This term is  $-(r^2/R^3)(3\cos^2\theta-1)$ for r < R, and in first order gives rise to the induced quadrupole effect. The second-order term is evaluated in the same manner as the induced dipole effect.

For the excitation of an s state, one obtains the functions shown in Fig. 3. In first-order *ns* is excited to a d wave  $(d_{ns,Q})$  and in second order one obtains s, d, and g functions. The contribution to q' is given by

$$\Delta q'_{ns, Q} = -\frac{1}{R^6} \left[ \frac{16}{35} J(d_{ns, Q}, d_{ns, Q}) + \frac{32}{35} J(ns, d'_{ns, Q}) \right], (58)$$

where J(a,b) is defined by Eq. (47). The radial functions  $w'_1(d_{ns, Q})$  and  $w'_2(d'_{ns, Q})$  are determined by

$$M_2 w'_1(d_{ns, Q}) = u'_{0, ns} r^2, \tag{59}$$

$$M_2 w'_2(d'_{ns,Q}) = w'_1(d_{ns,Q})r^2.$$
(60)

For the excitation of a p state, Fig. 3 shows the perturbed wave functions which arise in first and second order. In the following the subscript np of these functions will be omitted. One finds for the complete p shell,

$$\Delta q'_{np, Q} = -\frac{1}{R^6} \left[ \frac{48}{125} J(p_Q, p_Q) + \frac{576}{875} J(f_Q, f_Q) + \frac{96}{125} J(np, p'_Q) + \frac{288}{875} J(np, f'_Q) + \frac{288}{875} J(np, p''_Q) + \frac{1152}{875} J(np, f''_Q) \right].$$
(61)

The radial functions which are involved in the J(a,b) are determined by the equations:

$$M_{1}w'_{1}(p_{Q}) = u'_{0,np}(r^{2} - \langle r^{2} \rangle_{np}), \qquad (62)$$

$$M_3 w'_1(f_Q) = u'_{0, np} r^2, (63)$$

$$M_{1}w'_{2}(p'_{Q}) = w'_{1}(p_{Q})(r^{2} - \langle r^{2} \rangle_{np}) - \lambda_{3}u'_{0, np}, \quad (64)$$

$$M_3 w'_2(f'_Q) = w'_1(p_Q)r^2, \tag{65}$$

$$M_1 w'_2(p''_q) = w'_1(f_q) r^2 - \lambda_4 u'_{0,np}, \tag{66}$$

$$M_3 w'_2(f''_{Q}) = w'_1(f_{Q})r^2, \tag{67}$$

where

$$\lambda_3 = \int_0^\infty w'_1(p_Q) r^2 u'_{0, n_P} dr, \qquad (68)$$

$$\lambda_4 = \int_0^\infty w'_1(f_Q) r^2 u'_{0, np} dr.$$
 (69)

The normalization conditions are

$$\int_{0}^{\infty} \{ [w'_{1}(p_{Q})]^{2} + 2u'_{0, np} w'_{2}(p'_{Q}) \} dr = 0, \quad (70)$$

$$\int_{0}^{\infty} \{ [w'_{1}(f_{Q})]^{2} + 2u'_{0,np}w'_{2}(p''_{Q}) \} dr = 0.$$
 (71)

Equations (62)-(67) were solved numerically for the 3p state of Cl<sup>-</sup>, and the second-order quadrupole effect was calculated from Eq. (61). We will give the values of  $\rho_Q(a,b)$  defined as the ratio of the terms of Eq. (61) to  $1/R^3$ .  $\rho_Q$  varies as  $1/R^3$  and the following values pertain to NaCl:  $\rho_Q(p_Q, p_Q) = -0.6$ ,  $\rho_Q(f_Q, f_Q) = -0.003$ ,  $\rho_Q(3p,p'_Q) = +9.8, \ \rho_Q(3p,f'_Q) = -0.006, \ \rho_Q(3p,p''_Q) =$  $+1.1, \rho_Q(3p, f''_Q) = -0.016$ . The complete second-order quadrupole term  $\sum (a,b)\rho_Q(a,b)$  is +10.3. However, as for the induced dipole effect, the perturbed waves are overestimated because of the use of the perturbing potential  $-(r^2/R^3)(3\cos^2\theta-1)$  for all r. Thus it is likely that the actual second-order effect for  $Cl^{-}[(\Delta q'_{3p,D})]$  $+\Delta q'_{3p,Q}R^3$  is considerably smaller than the value 21.2 obtained from the  $\rho_D$  and  $\rho_Q$  given above. A value of  $\sim 10$  would be hardly outside the limits of error of the first-order antishielding. Aside from 3p, only the 3s shell is expected to give an appreciable second-order

term. The inner shells make a very small contribution to the second-order effects.

It can be concluded that the induced dipole and second-order quadrupole effects for Cl<sup>-</sup> are rather small compared to the first-order antishielding. This result seems to indicate that at least for the case of Cl<sup>-</sup> the first-order antishielding should give a good approximation to the effect of an external charge on the quadrupole coupling.

## VI. CONCLUSIONS

While the experimental values of the quadrupole coupling give some support to the present calculations of the antishielding, it should be stressed that the case of KCl and the rather poor agreement for NaCl and KBr show that other effects are of importance for at least some molecules. In fact, the strong repulsive exchange forces which exist between ions at short internuclear distances may be expected to produce distortions of the charge distribution which contribute to the quadrupole coupling. The possible importance of this effect is suggested by the fact that the repulsive forces are as important as the Coulomb attraction between the ions treated as point charges in determining the internuclear distance. Hence one might expect that the exchange repulsion has a similarly large effect on the quadrupole coupling.

The present calculations are essentially concerned with a model of polar molecules and correspond to a weak valence bond. Thus the radial distortion  $(n \not \rightarrow \phi)$ for Cl<sup>-</sup> in NaCl may be regarded as a pulling away of the Cl<sup>-p</sup> electrons by the Na<sup>+</sup> ion. As a result there are fewer p electrons of Cl<sup>-</sup> near r = 0 along the internuclear axis, and this results in a positive contribution to q'. If there is a strong valence bond so that the electron has an appreciable probability to be localized on the other ion, the model is expected to be a poor representation. However, with the exception of the exchange forces, it should be well suited for polar molecules.

It should be emphasized that the antishielding effects which predominate for the case of an external charge are quite different in character from the shielding effects discussed previously<sup>1</sup> for atomic valence electrons. The former are due to the radial modes of excitation, while the latter involve the angular modes. The essential difference between the molecular and the atomic case arises from the penetration of the atomic valence electrons. Thus, as shown by Fig. 2, the total induced effect for Cl is very small  $(1 - \gamma \sim 1)$  and in fact shielding up to  $r \sim 1a_{\rm H}$  where most of the quadrupole coupling for the 3p electron takes place. This accounts for the small shielding effect<sup>1</sup> found for 3p of Cl, and the same effect occurs in other atomic cases. From the previous calculations for Cl it was believed that the antishielding is generally small compared to the shielding for the atomic ground states.<sup>17</sup> This problem is being investigated at present by one of us (R.M.S.) using the results for heavy ions obtained here and some additional calculations. It appears that the shielding generally predominates for the light atoms  $(Z \leq 30)$  for which quadrupole correction factors have been given.<sup>17</sup> For medium and heavy atoms the antishielding may be larger than the shielding due to the angular modes. These considerations do not affect the previous results<sup>17</sup> for Cl and Al in which the effect of the radial modes was taken into account.

For excited atomic states, preliminary calculations have shown that there is a weak net antishielding due the external distribution of these wave functions. Thus even for the lowest excited (p) states of the alkalis, one obtains a weak antishielding, because of the small penetration. For the Na 3p state, a preliminary calculation gives  $\sim 10$  percent antishielding.

For the case of a polar molecule, in contrast to atomic states, the other ion is at a distance  $R \sim 5a_{\rm H}$  and the large magnitude of the antishielding can be understood in terms of the rapid increase of  $1-\gamma(r)$  with r (see Fig. 2). However, it should be noted that even a contribution of  $100/R^3$  is considerably smaller than the atomic value of q' which would be involved in molecules having a typical valence bond. Thus the present considerations hardly affect the discussion of covalent molecules.18

It should be noted that the induced quadrupole moment is fairly small for the light elements for which the 3p shell is not occupied. For Al, the  $2p \rightarrow p$  antishielding is  $\gamma_{\infty}(2p \rightarrow p) = -2.19$  while the angular modes give  $\gamma_{\infty}(ang) = 1.06$  so that the total induced moment is -1.13Q. For Na a calculation of the  $2p \rightarrow p$  and the angular perturbations gives  $\gamma_{\infty}(2p \rightarrow p) = -2.73$  and  $\gamma_{\infty}(\text{ang}) = 0.62$  so that  $Q_{iT} = -2.11Q$ .  $Q_{iT}$  is also expected to be small for the elements between B and F for which the 2p shell is not complete.

The Thomas-Fermi model gives a fairly good approximation to the angular (shielding) modes of excitation. but appears not to include the radial (antishielding) modes. As has been shown here, the latter arise mostly from the valence electrons and depend on the position of the ion in the periodic table. It is well known that the Thomas-Fermi model does not generally include effects of this kind.

<sup>&</sup>lt;sup>17</sup> R. M. Sternheimer, Phys. Rev. 86, 316 (1952). <sup>18</sup> C. H. Townes and B. P. Dailey, J. Chem. Phys. 20, 35 (1952). The quoted statement by one of us (H.M.F.) that a shielding takes place in the presence of external charges was based on the Thomas-Fermi results together with preliminary calculations for the s electrons of Cl<sup>-</sup>.