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# The polarization of a closed-shell core of an atomic system by an outer electron

## II. Evaluation of the polarizabilities from observed spectra

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**Abstract.** The dipole polarizabilities of four closed-shell ions,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$ , are evaluated from observed spectra, using theoretical values of the quadrupole polarizabilities taken from the literature and including a number of corrections, in particular a non-adiabatic correction and perturbation corrections up to the fourth order. These additional, previously neglected, corrections are partly positive and partly negative, and nearly cancel each other: consequently the results, in which the probable error is about 1%, are close to results previously obtained from observed spectra.

### 1. Introduction

The determination of the polarizabilities of positive ions from the observed spectra of the systems obtained by attaching one electron to each of these ions depends on the fact that, when the azimuthal quantum number of the outer electron is sufficiently large, the outer orbital penetrates the core only slightly, and then the deviation of the energy levels from the corresponding hydrogenic levels is caused mainly by the additional attractive force exerted by the dipole and higher multipole moments of the core on the outer electron. These moments themselves are produced by the electrostatic field of the outer electron. In previous work (Mayer and Mayer 1933, Sternheimer 1954, Bockasten 1956, 1964, Risberg 1955, 1956, Edlén and Risberg 1956) the polarization of the core has been treated adiabatically, i.e. the effect of the kinetic energy operator of the outer electron on the distortion on the core has been neglected. However, Eissa and Öpik (1967) have found that the non-adiabatic effect on the energy levels of the outer electron, although not very large, is not negligible, and so it is of interest to try to redetermine the polarizabilities from the observed spectra, taking the non-adiabatic effect into account. In order to achieve a real improvement in accuracy, it is also necessary to take into account a number of other corrections; the purpose of this paper is to investigate these, and to include them along with the dynamic correction in a redetermination of the polarizabilities from observed spectra.

We do this calculation on four ions, namely  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$ , hoping to obtain more reliable values of the dipole polarizabilities of these systems. Quite apart from any value that a knowledge of these polarizabilities may have in itself, the dipole polarizability is a quantity on which certain methods of calculating atomic properties can be tested, and so it is desirable to have reliable values for comparison with the results of purely theoretical determinations.

### 2. Determination of the polarizabilities from the second-order energy change

As explained by Eissa and Öpik (1967), whose notation we shall use except where otherwise stated, we define an unperturbed Hamiltonian  $\mathcal{H}^0$ , which represents the outer electron as moving in the field of the spherically symmetrical undistorted core, and a perturbing term  $W(\mathbf{R}, \mathbf{r})$ , which is the difference between the actual instantaneous interaction and the spherically averaged interaction of the outer electron with the core. According to the results of that paper, we can approximately express the contribution from the dipole and the quadrupole polarizations of the core to the second-order perturbation  $E^{(2)}$  of an energy level as

$$E_{\text{d}q}^{(2)} = -\frac{1}{2}\alpha_d(y_0^d \langle R^{-4} \rangle + y_2^d \langle R^{-6} \rangle) - \frac{1}{2}\alpha_q(y_0^q \langle R^{-6} \rangle + y_2^q \langle R^{-8} \rangle) \quad (1)$$

where  $d$  refers to the dipole and  $q$  to the quadrupole polarization, the averages are over the charge distribution of the outer electron, and numerical values of the coefficients  $y_0$  and  $y_2$  are given by Eissa and Öpik (1967).

We shall now endeavour to extract the values of  $E_{dq}^{(2)}$  for the  $^2F$  and, in some cases, the  $^2G$  states from the spectroscopically observed energies. We might then try writing down equation (1) for two of these states, and solving the resulting linear equations for the dipole and the quadrupole polarizability,  $\alpha_d$  and  $\alpha_q$ . Since the coefficient of  $\alpha_q$  in (1) is always much smaller than that of  $\alpha_d$ , the value of  $\alpha_q$  obtained in this way is exceedingly sensitive to the approximations made, and is not reliable. We can obtain a more accurate value of the dipole polarizability  $\alpha_d$  by using a calculated value of  $\alpha_q$  and solving one of the equations (1) at a time for  $\alpha_d$ . Thus, each of the energy levels considered will give us a separate value of  $\alpha_d$ , and the requirement that these values for the same core evaluated from different energy levels should agree provides us with a semi-empirical means of treating the region of small values of  $R$  more accurately than would otherwise be possible.

The values of the  $y$  coefficients are not very sensitive to the values of the polarizabilities used in calculating them, and it is usually possible to make a sufficiently good initial guess of  $\alpha_d$  to make it unnecessary to do this calculation iteratively.

### 3. Determination of the second-order dipole-quadrupole energy changes from observed energy levels

The second-order dipole-quadrupole energy change  $E_{dq}^{(2)}$  is by no means simply equal to the difference between the observed energy and the corresponding hydrogenic energy—there are a number of other corrections, which we have to estimate theoretically. It will be seen that some of these estimates are very crude; fortunately, however, the quantities themselves are then usually very small, and we take the view that even a very crude estimate is better than neglecting such a quantity altogether.

We express the observed energy  $E$  of a  $^2F$  or a  $^2G$  state as follows:

$$E = E^0 + E_{dq}^{(2)} + E_{mult}^{(2)} + E^{(3)} + E^{(4)} \quad (2)$$

where

$$E^0 = E_{hyd} + E_{rel} + E_{pen} \quad (3)$$

is of the zeroth order in the perturbation  $W(\mathbf{R}, \mathbf{r})$ ,  $E_{hyd}$  being the non-relativistic hydrogenic energy,  $E_{rel}$  the relativistic correction, and  $E_{pen}$  the penetration correction;  $E_{mult}^{(2)}$  is the second-order change arising from multipole polarizabilities other than the dipole and the quadrupole polarizabilities,  $E^{(3)}$  and  $E^{(4)}$  are the third-order and the fourth-order changes, and we neglect changes of higher orders than the fourth (except that our practical method of calculating  $E^{(4)}$  is such that it automatically includes some of the higher-order changes).

#### 3.1. The zero-order energy

The zero-order energy, given by (3), differs from the non-relativistic hydrogenic energy mainly because the potential energy of the outer electron at small values of  $R$  is much more negative than  $-(Z-N)/R$ ,  $Z$  being the nuclear charge and  $N$  the number of electrons in the core. In this region the difference between the resulting radial wave function of the outer electron and the corresponding hydrogenic function is not very small in comparison with these radial functions themselves, and so the energy change  $E_{pen}$  cannot be calculated by the first-order perturbation theory. Instead, we integrate numerically the Hartree-Fock equation for the outer electron and hence determine the energy; to eliminate systematic numerical errors, we also integrate the radial Schrödinger equation for the corresponding hydrogenic orbital, using the same step lengths (*nearly* the same in the case of Na). The difference in the energies is  $E_{pen}$ , and the error in this quantity is probably less than the experimental error in the spectroscopic levels.

Mayer and Mayer (1933), using the first-order perturbation theory, underestimated some of the penetration energies very considerably.

We calculate the relativistic corrections  $E_{rel}$  by the hydrogenic formula (Condon and Shortley 1935, § 3<sup>b</sup>). This should be satisfactory, because most of the charge density of the outer electron in these states is well outside the core.

Table 1. The penetration corrections

	4 <sup>2</sup> F	6 <sup>2</sup> F	9 <sup>2</sup> F	5 <sup>2</sup> G	6 <sup>2</sup> G	9 <sup>2</sup> G
Na	0.035	0.021	0.008			
Mg <sup>+</sup>	1.907	1.130	0.421	0.005	0.006	0.003
K	0.592	0.345	0.125			
Ca <sup>+</sup>	34.400	19.727	7.252	0.182	0.197	0.104

The tabulated quantity is  $-10^5 \times 2E_{\text{pen}}$ , where  $E_{\text{pen}}$  is the penetration energy in atomic units (27.2 eV).

### 3.2. The third-order change in the energy

According to Dalgarno (1961, p. 184), the third-order energy change is given in terms of the first-order change in the wave function  $\Psi^{(1)}(\mathbf{R}, \mathbf{x})$  by

$$E^{(3)} = \langle \Psi^{(1)} | W(\mathbf{R}, \mathbf{r}) | \Psi^{(1)} \rangle \quad (4)$$

since  $E^{(1)} = 0$  in our problem. We include only the dipole and the quadrupole term in  $W$ . Using the notation and results of Eissa and Öpik (1967), except that we use subscripts d and q to refer to dipole and quadrupole terms, respectively, and omitting a term of the order of  $\langle R^{-9} \rangle$ , we obtain

$$E^{(3)} = \langle X_d | w_q | X_d \rangle \int_{R_0}^{\infty} (\psi^0)^2 \beta_d^2 R^{-7} dR \\ + 2 \langle X_d | w_d | X_q \rangle \int_{R_0}^{\infty} (\psi^0)^2 \beta_d \beta_q R^{-7} dR. \quad (5)$$

The integrals over  $R$  are calculated numerically, using the zero-order radial functions obtained by solving the Hartree-Fock equations as explained in § 3.1.

For the core matrix elements in (5) we obtain the following formulae in terms of Sternheimer's (1959) distortion functions, *provided* that these functions are first orthogonalized to the undistorted orbitals of the core, and multiplied by the ratio of experimental to Sternheimer polarizability to minimize the errors of the uncoupled approximation:

$$\langle X_d | w_d | X_d \rangle = \int_0^{\infty} \left[ \frac{16}{15} \{u'(ns \rightarrow p)\}^2 + \frac{16}{15} \{u'(np \rightarrow d)\}^2 \right. \\ \left. + \frac{32}{15} u'(np \rightarrow s) u'(np \rightarrow d) \right] r^2 dr \quad (6)$$

$$\langle X_d | w_d | X_q \rangle = \int_0^{\infty} \left\{ \frac{16}{15} u'(ns \rightarrow p) u'(ns \rightarrow d) + \frac{48}{25} u'(np \rightarrow d) u'(np \rightarrow f) \right. \\ \left. + \frac{16}{75} u'(np \rightarrow d) u'(np \rightarrow p) + \frac{16}{15} u'(np \rightarrow s) u'(np \rightarrow p) \right\} r dr \quad (7)$$

where  $n$  is the principal quantum number of the outermost shell of the core. This method of correcting Sternheimer's wave functions has been tested by Eissa and Öpik (1967), who find that it gives the quantities  $\langle X_d | X_d \rangle$  with an error of about 10%.

We use formulae (6) and (7) for the monovalent ions. Sternheimer does not give distortion functions for  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ , so we obtain the core matrix elements for these ions from the values for the isoelectronic monovalent ions by a scaling procedure: the functions are assumed uniformly contracted in the same ratio as the charge distribution of the outermost shell, and in addition the change in  $\langle X | X \rangle$  is explicitly included. Such a scaling method, applied to polarizabilities as a test, predicts them with an error of about 10%.

The error in  $E^{(3)}$  may be about 20%, in addition to the error arising from the arbitrariness of the choice of  $R_0$ .

### 3.3. The fourth-order change in the energy

The fourth-order energy change arises in two ways. First, the polarization potential energy

$$U_{\text{pol}} = -\frac{1}{2}\alpha_d\beta_d R^{-4} - \frac{1}{2}\alpha_q\beta_q R^{-6} - \dots \quad (8)$$

distorts the orbital of the outer electron, and consequently the energy change deviates from the expectation value of  $U_{\text{pol}}$  by a quantity which is of the second order in  $U_{\text{pol}}$  and therefore of the fourth order in  $W(\mathbf{R}, \mathbf{r})$ , since  $U_{\text{pol}}$  itself is of the second order. This deviation may be called the external fourth-order change  $E_{\text{ext}}^{(4)}$ . Secondly, even in the presence of a uniform electric field  $F$ , the change in the energy of the core is not exactly proportional to  $F^2$  but is more accurately expressed as  $-\frac{1}{2}\alpha_d F^2 - \frac{1}{24}\gamma F^4$ , where the last term may be called the internal fourth-order change  $E_{\text{int}}^{(4)}$ . Values of the constant  $\gamma$ , called the dipole hyperpolarizability, have been calculated by Langhoff *et al.* (1966), so we can estimate  $E_{\text{int}}^{(4)}$ . In doing so, we take into account the non-adiabatic effect on the first-order distortion of the core. There is an additional, more direct, non-adiabatic effect which we have not attempted to include.

The external fourth-order change is obtained as follows. We solve the radial Schrödinger equation with  $U_{\text{pol}}$  included as far as the quadrupole term; the resulting eigenvalue is

$$E' = E'^0 + E_{\text{dq}}^{(2)} + E_{\text{ext}}^{(4)} \quad (9)$$

where, strictly speaking,  $E_{\text{ext}}^{(4)}$  also includes some higher-order contributions (which makes the calculation even more accurate).  $E_{\text{dq}}^{(2)}$  for the *same* polarization potential (i.e. with the input value of  $\alpha_d$  and therefore *not* equal to the final value of that quantity), is calculated by (1), and

$$E'^0 = E_{\text{hyd}} + E_{\text{pen}}$$

is the eigenvalue obtained by solving the radial Schrödinger equation without  $U_{\text{pol}}$  (see § 3.1). So  $E_{\text{ext}}^{(4)}$  can be obtained from (9).

It may be felt that the calculated values of the hyperpolarizability  $\gamma$  are somewhat uncertain but, if so, this will not greatly affect our results, because  $E_{\text{int}}^{(4)}$  is only about 10% to 20% of  $E_{\text{ext}}^{(4)}$ . The error in  $E_{\text{ext}}^{(4)}$  should be negligible, except in so far as it depends on the choice of  $R_0$ , to which, however,  $E_{\text{ext}}^{(4)}$  is insensitive.

**Table 2. Samples of the higher corrections and the second-order dipole-quadrupole energy change for comparison**

(1)	(2)	(3)	(4)	(5)	(6)	(7)
Na	4f	1.4	0.021	-0.014	-0.008	-3.66
Mg <sup>+</sup>	4f	1.2	0.476	-0.258	-0.27	-29.08
	5g	1.2	0.012	-0.005	-0.003	-3.94
K	4f	2.2	0.220	-0.462	-0.121	-20.39
	6f	2.2	0.113	-0.202	-0.069	-7.13
	9f	2.2	0.040	-0.068	-0.025	-2.28
Ca <sup>+</sup>	4f	2.0	5.064	-10.039	-4.04	-194.31
	5g	2.4	0.191	-0.272	-0.07	-26.43
	6g	2.4	0.166	-0.205	-0.07	-16.97
	9g	2.4	0.071	-0.078	-0.03	-5.64

(1), system; (2), outer orbital; (3),  $R_0$ ; (4),  $10^5 \times 2E^{(3)}$ ; (5),  $10^5 \times 2E^{(4)}$ ; (6),  $10^5 \times 2E_{\text{mult}}^{(2)}$ ; (7),  $10^5 \times 2E_{\text{dq}}^{(2)}$ .

$E^{(3)}$ ,  $E^{(4)}$  and  $E_{\text{mult}}^{(2)}$  are, respectively, the third-order, the fourth-order and the higher multipole corrections and  $E_{\text{dq}}^{(2)}$  is the second-order dipole-quadrupole energy change, all in atomic units (27.2 eV).  $R_0$  is the lower limit of the radial integrations in atomic units for which these particular values apply.

The near equality of the magnitudes of  $E^{(3)}$  and  $E^{(4)}$  in table 2 is not due to any failure of the perturbation series to converge, but arises because  $E^{(3)}$  is entirely 'internal' in the sense in which we have here used this word. (An 'external' contribution to  $E^{(3)}$ , if it existed, would have to be of the order  $\frac{2}{3}$  in the polarization potential!) And  $E_{\text{int}}^{(4)}$  is, indeed, much smaller in magnitude than  $E^{(3)}$ .

### 3.4. The higher multipole contribution

We represent the higher multipole contribution to the second-order energy by

$$E_{\text{mult}}^{(2)} = -\frac{1}{2}\alpha_0 \langle R^{-8} \rangle \quad (10)$$

where  $\alpha_0$  is the octupole polarizability, for which we use the values calculated by Burns (1959). It is true that this quantity will be strongly decreased in magnitude by the dynamical effect, but on the other hand we are neglecting the hexadecapole and higher polarizabilities, and these two errors have opposite signs.

The error in  $E_{\text{mult}}^{(2)}$  is of the same order of magnitude as  $E_{\text{mult}}^{(2)}$  itself.

### 3.5. The experimental energy

Values of the experimental energy  $E$  are taken from the papers by Risberg (1955, 1956) and by Edlén and Risberg (1956). Values of  $-2E$  are obtained by dividing the term values by the Rydberg constant for the atom under consideration; thus, because of the differing nuclear masses, our unit of energy is slightly different for different atoms.

To avoid random errors, we have, in cases where this makes a noticeable difference, used smoothed values of the energy levels, calculated by formulae given by Risberg and by Edlén and Risberg in their papers, except in the case of potassium, where the smoothing formula seems to introduce a slight systematic error. (This could be rectified by redetermining the coefficients in the formula, but this is not worth doing.)

We estimate the error in the series limit from the consideration that, if the correct energy levels can be fitted by the formulae used for this purpose by Risberg and by Edlén and Risberg, then this cannot be true of these same levels after they have all been shifted by a constant amount through an error in the series limit. By determining the amount of shift needed to make the fit so poor that the deviations from it are clearly noticeable, we arrive at estimates of error limits in substantial agreement with the estimates given by Risberg and by Edlén and Risberg, namely, that the error in the series limit should not exceed  $0.03$  or  $0.04 \text{ cm}^{-1}$  in the cases considered, and is probably even smaller in the case of  $\text{Ca}^+$ .

## 4. Treatment of the region of small values of $R$

Our expressions for the various contributions to the energy, other than the zero-order energy, would be strictly accurate only if the outer orbital did not penetrate into the core at all. The actual  $f$  and  $g$  orbitals that we use are, of course, slightly penetrating, and it is easy to see that if, in calculating the various energy terms, we choose the lower limit  $R_0$  of our integrations so large that only a negligible part of the charge distribution of the core is outside the radius  $R_0$ , then the magnitudes of these terms are underestimated, while a choice of  $R_0$  much less than  $1 \text{ A.U.}$  would overestimate them. So there exists an optimum value of  $R_0$ , say  $R_{\text{opt}}$ , which would yield an accurate value for the *total* polarization energy, even though the individual terms in it might require different values of  $R_0$  to give an accurate value for each of them separately. Because of the close similarity of the radial functions  $P(nl|R)$  of the outer orbitals at small values of  $R$  for a given value of  $l$  but different values of  $n$  (in fact, the ratios  $P(nl|R)/P(n'l|R)$  depend only slightly on  $R$  at small values of  $R$ ), the values of  $R_{\text{opt}}$  for the same  $l$  but different values of  $n$  are expected to be almost equal. Then the requirement that different spectral terms of the same series should yield values of the polarizability in close agreement with each other makes it possible to estimate  $R_{\text{opt}}$ , and, by considering deviations from it which would make the discrepancies too large to be accounted for by other errors, we can estimate the error arising from this source.

Instead of actually determining  $R_{\text{opt}}$ , we can determine the optimum value of the polarizability  $\alpha_d$  corresponding to  $R_{\text{opt}}$  directly as follows. Let  $V_{\text{pol}}$  be an effective polarization

potential energy, so that

$$E_p(nl) = \int_0^\infty V_{\text{pol}}(R) \{P(nl|R)\}^2 dR$$

is the polarization energy of the state specified by the quantum numbers  $n, l$  of the outer orbital. Let  $U_{\text{pol}}$  be our theoretical expression for the polarization potential energy, so that our theoretical expression for the polarization energy is

$$E_p'(nl) = \int_{R_0}^\infty U_{\text{pol}}(R) \{P(nl|R)\}^2 dR.$$

Now  $U_{\text{pol}}$  is practically equal to  $V_{\text{pol}}$  well outside the core region, say for  $R \geq R'$ ; on the other hand, for  $R \leq R'$  it is a good approximation to write

$$P(nl|R) = P(nl|R')p_l(R)$$

where  $p_l$  is independent of  $n$  and  $R''$  is some value of  $R$  such that  $0 < R'' < R'$ . It follows that

$$E_p(nl) - E_p'(nl) = \{P(nl|R'')\}^2 \left[ \int_0^{R'} V_{\text{pol}} \{p_l(R)\}^2 dR - \int_{R_0}^{R'} U_{\text{pol}} \{p_l(R)\}^2 dR \right] \quad (11)$$

to a good approximation, where the quantity in the square brackets is, indeed, unknown, but almost independent of  $n$ , since both  $V_{\text{pol}}$  and  $U_{\text{pol}}$  are expected to be almost independent of  $n$  for a given  $l$ . We eliminate this unknown quantity by requiring that the values of  $\alpha_d$  resulting from the use of two terms in the same spectral series should agree; this leads to two linear equations in which the unknowns are  $\alpha_d$  and the quantity in the square brackets in equation (11). If this method is correct, then the resulting value of  $\alpha_d$  should be insensitive to the choice of  $R_0$  and  $R''$  and values obtained by the use of different pairs of states in the same spectral series, and by the use of different spectral series, should agree closely.

Extensive tests were done on the  $^2G$  series of  $\text{Ca}^+$ .  $R_0$  was varied from 1.6 to 3.2,  $R'$  from 2.7 to 3.2, and the pairs 5g, 6g and 5g, 9g were used. The resulting values of  $\alpha_d$  in all these tests varied between 3.256 and 3.264, which is very satisfactory. The  $f$  orbitals of  $\text{Ca}^+$  are rather more strongly penetrating than any of the other orbitals used in this paper, so we do not expect this method to be very accurate when applied to the  $^2F$  levels of  $\text{Ca}^+$ ; even so, values of  $\alpha_d$  between 3.192 and 3.261 were obtained from the  $^2F$  levels, i.e. not too different from those obtained from the  $^2G$  levels.

This method is not applicable in cases where the uncertainty in the result arising from the errors in the experimental energies is comparable with, or greater than, the uncertainty arising from the penetration. For this reason no attempt was made to apply this method to sodium. Instead, our result for sodium is based on the  $4f\ ^2F$  level, which is least sensitive to the approximations.

## 5. Polarization of the outer orbital by the instantaneous dipole moment of the core

It would be expected that the orbital of the outer electron will be able to follow the motion of the core electrons only very slightly, but, as we want results of a rather high accuracy, it is necessary to enquire whether the resulting change in the energy might be large enough to affect our results significantly.

This effect has been investigated by including a term of the form  $\Phi^0\psi^{(1)}$  in the first-order wave function, where  $\Phi^0$  is the undistorted wave function of the core and  $\psi^{(1)}$ , which depends parametrically on the instantaneous dipole moment of the core, is the distortion of the outer orbital. Here it is considered necessary to use a very flexible form of  $\psi^{(1)}$  in the variational calculation; consequently the resulting expressions are somewhat lengthy and will not be reproduced here.

This effect is found always to lower the total energy and the total lowering is of the order of  $\frac{1}{2}\%$  of the total polarization effect. We cannot estimate it accurately, but fortunately most of this effect is found to come from the region of small values of  $R$  and to be proportional to the charge density of the outer electron in that region, so that this part of the effect

is automatically included in the semi-empirical treatment described in the preceding section. The remainder of the effect can be fairly accurately calculated, but the resulting change in our results is found to be negligible.

The smallness of this effect is due to the number of the core electrons being large, and what has just been said does not necessarily apply to Li or Be<sup>+</sup>.

## 6. Results and conclusion

By taking into account the various corrections as explained above, we arrive at the following values of the dipole polarizabilities of the closed-shell ions, all in atomic units (1 A.U. of dipole polarizability equals 0.1482 Å<sup>3</sup>): Na<sup>+</sup>, 0.978; Mg<sup>2+</sup>, 0.489; K<sup>+</sup>, 5.47; Ca<sup>2+</sup>, 3.26. These values are believed to be more accurate than any that have been obtained before. By considering the probable errors in the various correction terms to the energy, as well as in the experimental energies and in our treatment of the region of small values of  $R$ , we estimate the errors in these values at about 1%—possibly a little less for Ca<sup>2+</sup>, and a little more in the case of Na<sup>+</sup> and Mg<sup>2+</sup>.

Our final values of the dipole polarizabilities are in surprisingly close agreement with results previously obtained from observed spectra without taking into account most of our corrections discussed above. Thus, Bockasten (unpublished, quoted by Cohen 1966) obtains the value of 0.995 A.U. for Na<sup>+</sup>, Edlén and Risberg (1956) give the value 3.31 A.U. for Ca<sup>2+</sup> and Risberg (1956) gives the value 5.47 for K<sup>+</sup>, all three within 2% of our values. This close agreement is not due to the smallness of the additional corrections—for instance, omission of the non-adiabatic correction would, in some cases, decrease our values by several per cent—but to the mutual cancellation of the different corrections. However, this could not have been known without actually doing our calculations.

Our dipole polarizabilities also agree as closely as can reasonably be expected with the calculations done by the coupled Hartree-Fock method by Cohen (1966) and by Lahiri and Mukherji (1967 a, b), being in all cases slightly greater than theirs.

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