

hyperfine splittings will also give information regarding the hyperfine structure constant and magnetic moments of the nuclei; however, it is not likely that these measurements can be made to any greater accuracy than by existing methods.

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## Electronic Polarizabilities of Ions\*

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The dipole polarizability  $\alpha_d$  and the quadrupole polarizability  $\alpha_q$  have been calculated for several ions by solving the Schrödinger equation satisfied by the first-order perturbation of the wave functions of the electrons of the core. The results for  $\alpha_d$  of the helium-like ions are in good agreement with those obtained previously by an analytic method. The calculated quadrupole polarizability  $\alpha_q$  of the alkali ions increases very rapidly with increasing  $Z$ , from  $0.056 \text{ \AA}^6$  for  $\text{Na}^+$  to  $7.80 \text{ \AA}^6$  for  $\text{Cs}^+$ .

### I. INTRODUCTION

THE electronic polarizabilities of a number of ions have been calculated previously by means of a numerical solution of the Schrödinger equation satisfied by the perturbation of the wave functions of the electrons of the core.<sup>1</sup> For the unperturbed wave functions, the Hartree or Hartree-Fock wave functions of the core were used. The calculated results for the dipole polarizability  $\alpha_d$  were shown to be in reasonable agreement with the experimental data. The purpose of this paper is to give the results of additional calculations of the dipole polarizability  $\alpha_d$  of the helium-like ions and of the quadrupole polarizability  $\alpha_q$  of several helium-like and alkali ions.

### II. DIPOLE POLARIZABILITY

The method of calculation of  $\alpha_d$  was the same as that used in I. Thus, for the helium-like ions, which involve only the  $1s \rightarrow p$  excitation,  $\alpha_d$  is given by

$$\alpha_d = (8/3) \int_0^\infty u'_0 u'_{1,0 \rightarrow 1} r dr, \quad (1)$$

where  $u'_0$  is  $r$  times the radial  $1s$  function, normalized according to:  $\int_0^\infty (u'_0)^2 dr = 1$ ;  $u'_{1,0 \rightarrow 1}$  is  $r$  times the radial part of the  $1s \rightarrow p$  perturbation, and is determined by

$$\left( -\frac{d^2}{dr^2} + \frac{2}{r^2} + V_0 - E_0 \right) u'_{1,0 \rightarrow 1} = u'_0 r. \quad (2)$$

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<sup>1</sup> R. M. Sternheimer, Phys. Rev. **96**, 951 (1954). This paper will be referred to as I.

In Eq. (2),  $V_0$  is the spherical potential and  $E_0$  is the unperturbed  $1s$  eigenvalue. Actually the function,

$$P \equiv V_0 - E_0 = (1/u'_0)(d^2 u'_0/dr^2), \quad (3)$$

is obtained directly from the second derivative of  $u'_0$ , as shown by Eq. (53) of I. We note that Eq. (1) gives  $\alpha_d$  in units  $a_H^3$  ( $a_H = \text{Bohr radius}$ ) and must be multiplied by  $(0.529)^3 = 0.148$  to obtain  $\alpha_d$  in units  $\text{Å}^3$ .

For the helium-like ions, values of  $\alpha_d$  have been presented in Table II of I. In obtaining these values,  $u'_{1,0 \rightarrow 1}$  was not derived by numerical solution of the Schrödinger Eq. (2), but was obtained analytically in the following manner. One notes that for a hydrogenic wave function  $u'_0$ ,

$$u'_0 = 2Z^{3/2} r \exp(-Zr), \quad (4)$$

with atomic number  $Z$ , the perturbation is given by

$$u'_{1,0 \rightarrow 1} = Z^{-3/2} r^2 (1 + \frac{1}{2} Zr) \exp(-Zr). \quad (5)$$

The zero-order wave functions  $u'_0$  for the helium-like ions which were used in I and in the present work are the wave functions obtained by Löwdin,<sup>2</sup> which are of the following form:

$$u'_0 = c_1 [2Z_1^{3/2} r \exp(-Z_1 r)] + c_2 [2Z_2^{3/2} r \exp(-Z_2 r)], \quad (6)$$

where  $Z_1$  and  $Z_2$  are two effective values of the atomic number;  $c_1$  and  $c_2$  are coefficients. In the work of I we assumed that  $u'_{1,0 \rightarrow 1}$  is given to a good approximation by a linear combination of the functions (5), corresponding to  $Z_1$  and  $Z_2$ , i.e., we took [see Eq. (71) of I]:

$$u'_{1,0 \rightarrow 1} = c_1 [Z_1^{-3/2} r^2 (1 + \frac{1}{2} Z_1 r) \exp(-Z_1 r)] + c_2 [Z_2^{-3/2} r^2 (1 + \frac{1}{2} Z_2 r) \exp(-Z_2 r)]. \quad (7)$$

<sup>2</sup> P. O. Löwdin, Phys. Rev. **90**, 120 (1953).

TABLE I. Calculated values of the dipole polarizability  $\alpha_d$  and quadrupole polarizability  $\alpha_q$  of several helium-like ions. The second column lists the present values obtained from a numerical solution of Eqs. (2) and (10), while the third column gives the values determined analytically in I. The values of  $\alpha_d$  and  $\alpha_q$  are in units  $\text{A}^3$  and  $\text{A}^5$ , respectively.

Ion	Numerical	Analytic
$\alpha_d(\text{H}^-)$	13.4	16.1
$\alpha_d(\text{He})$	0.224	0.236
$\alpha_d(\text{Li}^+)$	0.0307	0.0316
$\alpha_d(\text{Be}^{++})$	$8.25 \times 10^{-3}$	$8.3 \times 10^{-3}$
$\alpha_q(\text{H}^-)$	66.5	71.1
$\alpha_q(\text{He})$	0.0993	0.101
$\alpha_q(\text{Li}^+)$	$4.73 \times 10^{-3}$	$4.77 \times 10^{-3}$
$\alpha_q(\text{Be}^{++})$	$6.37 \times 10^{-4}$	$6.40 \times 10^{-4}$

It was shown in I that for the case of  $\text{Li}^+$  and presumably also for the heavier helium-like ions ( $\text{Be}^{++}$ ,  $\text{B}^{3+}$ ,  $\text{C}^{4+}$ ), the approximation of using Eq. (7) for  $u'_{1,0 \rightarrow 1}$  introduces a negligible error in the calculated value of  $\alpha_d$ . Thus for  $\text{Li}^+$ , the value of  $\alpha_d$  obtained by means of Eq. (7) is  $0.0316 \text{ A}^3$  as compared to a value of  $0.0306 \text{ A}^3$  gotten by solving Eq. (2) numerically for  $u'_{1,0 \rightarrow 1}$ , with  $V_0 - E_0$  determined directly from the Löwdin function  $u'_0$  by means of Eq. (3).

Recently Wikner and Das<sup>3</sup> have obtained values of  $\alpha_d$  for the helium-like ions by means of a variational method. In order to compare with their results, it seemed of interest to recalculate the values of  $\alpha_d$  for several helium-like ions by numerical solution of the Schrödinger equation. The procedure of the numerical integration has been described<sup>4</sup> in I. The results are given in the upper part of Table I, which lists both the present values obtained numerically and the previous values of I. It is seen that the previously used analytic approximation is already quite good for He, where the error is only 5%. For  $\text{Be}^{++}$ , the analytic approximation agrees within 1% with the numerical result, so that the values given in I for  $\alpha_d$  of  $\text{B}^{3+}$  and  $\text{C}^{4+}$ , ( $0.00308 \text{ A}^3$  and  $0.00139 \text{ A}^3$ , respectively) are probably also accurate within 1%. The only case where there is an appreciable discrepancy between the two results is that of  $\text{H}^-$ , where the extended charge distribution is probably responsible for the inaccuracy of the analytic approximation. Thus the maximum of  $u'_{1,0 \rightarrow 1}$  for  $\text{H}^-$  occurs at  $r = 6a_{\text{H}}$ , and there are significant contributions to the integral of (1) up to radii  $r \sim 12a_{\text{H}}$ .

The present results are in good agreement with the variational results of Wikner and Das.<sup>3</sup> These authors have used for  $u'_0$  the wave functions of Green, Mulder, Lewis, and Woll,<sup>5</sup> which differ slightly from the Löwdin functions<sup>2</sup> used in the present work. They have obtained the following values for  $\alpha_d$  (in units  $\text{A}^3$ ): for  $\text{H}^-$ : 14.88; for He: 0.218; for  $\text{Li}^+$ : 0.0305; for  $\text{Be}^{++}$ : 0.00813; for

$\text{B}^{3+}$ : 0.00303. Except for  $\text{H}^-$ , the agreement between these values and ours is very good. Wikner and Das<sup>3</sup> have given a critical comparison of these calculated results with the experimental values of  $\alpha_d$  for the helium-like ions.

### III. QUADRUPOLE POLARIZABILITY

The quadrupole polarizability<sup>6</sup>  $\alpha_q$  measures the quadrupole moment induced in the ion  $Q_{\text{ind}}$  by an externally applied field gradient  $\partial E_x / \partial x$ , in the same manner as the ordinary (dipole) polarizability  $\alpha_d$  is related to the induced dipole moment. The quantity  $\alpha_q$  is defined as follows<sup>1</sup>:

$$\alpha_q = -\frac{eQ_{\text{ind}}}{\partial E_x / \partial x}. \quad (8)$$

Values of  $\alpha_q$  for several helium-like ions and for  $\text{Na}^+$  and  $\text{Cs}^+$  have been previously obtained (see Table III of I). For the helium-like ions,  $\alpha_q$  (in units  $a_{\text{H}}^5$ ) is given by<sup>1</sup>

$$\alpha_q = (8/5) \int_0^\infty u'_0 u'_{1,0 \rightarrow 2} r^2 dr, \quad (9)$$

where  $u'_{1,0 \rightarrow 2}$  is  $r$  times the radial wave function for the  $1s \rightarrow d$  perturbation;  $u'_{1,0 \rightarrow 2}$  is determined by:

$$\left( -\frac{d^2}{dr^2} + \frac{6}{r^2} + V_0 - E_0 \right) u'_{1,0 \rightarrow 2} = u'_{0r^2}. \quad (10)$$

In the work of I,  $u'_{1,0 \rightarrow 2}$  was not obtained from Eq. (10) for the helium-like ions, but instead, in the same manner as for  $\alpha_d$ , use was made of the analytic form of  $u'_{1,0 \rightarrow 2}$  for the case of a hydrogenic field [see Eq. (102) of I]. Thus  $u'_{1,0 \rightarrow 2}$  was taken as

$$u'_{1,0 \rightarrow 2} = c_1 \left[ \frac{1}{2} Z_1^{-1/2} r^3 \left( 1 + \frac{2}{3} Z_1 r \right) \exp(-Z_1 r) \right] + c_2 \left[ \frac{1}{2} Z_2^{-1/2} r^3 \left( 1 + \frac{2}{3} Z_2 r \right) \exp(-Z_2 r) \right], \quad (11)$$

where  $c_1$ ,  $c_2$ ,  $Z_1$ , and  $Z_2$  are the parameters of the Löwdin wave function, Eq. (6). In order to determine the accuracy of Eq. (11) for  $u'_{1,0 \rightarrow 2}$ , we have obtained  $u'_{1,0 \rightarrow 2}$  by solving Eq. (10) numerically. The resulting values of  $\alpha_q$  are listed in the lower part of Table I, together with the values previously obtained by means of the  $u'_{1,0 \rightarrow 2}$  of Eq. (11). It is seen that for  $\text{H}^-$ , the analytic method overestimates  $\alpha_q$  by 7%, but that for He, the analytic approximation is already very good. For  $\text{Li}^+$  and  $\text{Be}^{++}$  the error is less than 1%, and therefore, the values for  $\text{B}^{3+}$  and  $\text{C}^{4+}$ , given in Table III of I are probably accurate to within 1% ( $1.40 \times 10^{-4} \text{ A}^5$  and  $4.31 \times 10^{-5} \text{ A}^5$  for  $\text{B}^{3+}$  and  $\text{C}^{4+}$ , respectively).

Results for  $\alpha_q$  for  $\text{Na}^+$  and  $\text{Cs}^+$  have been obtained in I. These values have been recalculated to somewhat higher accuracy in the present work, and we have also obtained results for  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{Cu}^+$ , and  $\text{Rb}^+$ . For these ions with several closed shells, only the outermost shell

<sup>3</sup> E. G. Wikner and T. P. Das, Phys. Rev. **107**, 497 (1957). I would like to thank Dr. Das for sending me a copy of this paper before publication.

<sup>4</sup> Reference 1, p. 955.

<sup>5</sup> Green, Mulder, Lewis, and Woll, Phys. Rev. **93**, 757 (1954).

<sup>6</sup> J. E. Mayer and M. G. Mayer, Phys. Rev. **43**, 605 (1933).

makes a significant contribution<sup>1</sup> to  $\alpha_q$ . It has been shown in I that  $\alpha_q$  is given by

$$\alpha_q = \frac{8}{5}(J_{0 \rightarrow 2})_{n_0 s} + \left( \frac{48}{25}J_{1 \rightarrow 1} + \frac{72}{25}J_{1 \rightarrow 3} \right)_{n_0 p} + \left( \frac{8}{5}J_{2 \rightarrow 0} + \frac{16}{7}J_{2 \rightarrow 2} + \frac{144}{35}J_{2 \rightarrow 4} \right)_{n_0 d}, \quad (12)$$

where  $n_0$  is the principal quantum number of the highest filled shell,  $J_{l \rightarrow l'}$  is the radial integral corresponding to the  $n_0 l \rightarrow l'$  excitation.  $J_{l \rightarrow l'}$  is given by

$$J_{l \rightarrow l'} = \int_0^\infty u'_0 u'_{1, l \rightarrow l'} r^2 dr, \quad (13)$$

where  $u'_0$  is the unperturbed radial  $n_0 l$  wave function and  $u'_{1, l \rightarrow l'}$  is the radial wave function for the perturbation and is determined by the equation:

$$\left[ -\frac{d^2}{dr^2} + \frac{l'(l'+1)}{r^2} + V_0 - E_0 \right] u'_{1, l \rightarrow l'} = u'_0 (r^2 - \langle r^2 \rangle_{n_0 l} \delta_{ll'}). \quad (14)$$

Here  $\langle r^2 \rangle_{n_0 l}$  is the average value of  $r^2$  over the unperturbed function  $u'_0$ . As is seen from Eq. (14), this term enters only for  $n_0 p \rightarrow p$  and  $n_0 d \rightarrow d$  excitations.

Equation (14) was integrated numerically in all cases. For  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{K}^+$ , and  $\text{Cu}^+$ , the Hartree-Fock functions<sup>7-10</sup> were used for the  $u'_0$ . For  $\text{Rb}^+$  and  $\text{Cs}^+$ , only Hartree functions (excluding exchange effects) are available.<sup>11,12</sup> The  $n_0 p \rightarrow p$  and  $n_0 d \rightarrow d$  perturbations  $u'_{1, l \rightarrow l'}$  have been previously obtained by Sternheimer and Foley.<sup>13</sup> For the perturbations with  $l' \neq l$ , the calculations were carried out as follows. First Eq. (14) was integrated numerically inward starting from large  $r$ . Then Eq. (14) was integrated outward starting from small  $r$  by means of an appropriate power series expansion. The two solutions were joined at an intermediate radius ( $r \sim 0.5a_H$ ), and the resulting function  $u'_{1, l \rightarrow l'}$  was used in Eq. (13) to obtain  $J_{l \rightarrow l'}$ . It may be noted that the inward integration must be repeated several times with various assumed values of  $u'_{1, l \rightarrow l'}(r_1)$  at the large radius  $r_1$  at which the integration is started. Unless  $u'_{1, l \rightarrow l'}(r_1)$  has the correct value, the function  $u'_{1, l \rightarrow l'}(r)$  will diverge near  $r=0$ . Of course, the actual solution is found by the procedure of joining with the internal solution at small  $r$ . This situation is similar to that which arises in

<sup>7</sup> V. Fock and M. Petrashen, *Physik. Z. Sowjetunion* **6**, 368 (1934).

<sup>8</sup> D. R. Hartree and W. Hartree, *Proc. Roy. Soc. (London)* **A156**, 45 (1936).

<sup>9</sup> D. R. Hartree and W. Hartree, *Proc. Roy. Soc. (London)* **A166**, 450 (1938).

<sup>10</sup> D. R. Hartree and W. Hartree, *Proc. Roy. Soc. (London)* **A157**, 490 (1936).

<sup>11</sup> D. R. Hartree, *Proc. Roy. Soc. (London)* **A151**, 96 (1935).

<sup>12</sup> D. R. Hartree, *Proc. Roy. Soc. (London)* **A143**, 506 (1934).

<sup>13</sup> R. M. Sternheimer and H. M. Foley, *Phys. Rev.* **102**, 731 (1956).

TABLE II. Calculated values of the quadrupole polarizability  $\alpha_q$ . The rows above  $\alpha_q$  list the contributions to  $\alpha_q$  of the various modes of excitation of the (outermost) shell with highest principal quantum number  $n_0$ . All values are in units  $\text{A}^5$ .

Ion	$\text{Na}^+$	$\text{Cl}^-$	$\text{K}^+$	$\text{Cu}^+$	$\text{Rb}^+$	$\text{Cs}^+$
$\alpha_q(n_0 s \rightarrow d)$	0.0133	0.635	0.132	0.00451	0.324	0.884
$\alpha_q(n_0 p \rightarrow p)$	0.0173	5.38	0.183	0.00380	0.759	1.702
$\alpha_q(n_0 p \rightarrow f)$	0.0256	7.75	0.418	0.00937	1.907	5.21
$\alpha_q(n_0 d \rightarrow s)$				0.840		
$\alpha_q(n_0 d \rightarrow d)$				0.192		
$\alpha_q(n_0 d \rightarrow g)$				0.230		
$\alpha_q$	0.0562	13.77	0.733	1.280	2.990	7.80

the calculation of the dipole polarizability [Eq. (58) of I].<sup>4</sup>

The results of the calculations of  $\alpha_q$  are given in Table II. It is estimated that each of the terms is accurate to  $\pm 5\%$ . For  $\text{Na}^+$  and  $\text{Cs}^+$ , the present results differ very little from those previously published<sup>1</sup> ( $\alpha_q$  for  $\text{Na}^+ = 0.0562 \text{ A}^5$  as compared to the previous value  $0.058 \text{ A}^5$ ; for  $\text{Cs}^+ : 7.80 \text{ A}^5$  as compared to  $7.62 \text{ A}^5$ ). The significant increase of  $\alpha_q$  in going from  $\text{K}^+$  to  $\text{Cl}^-$  shows that  $\alpha_q$  is very sensitive to the radius of the charge distribution. There is also a large increase with increasing  $Z$  for the alkali ions, in going from  $\text{Na}^+$  to  $\text{Cs}^+$ .

For the case of  $\text{Cu}^+$ , it may be noted that the inner electrons among the  $n_0=3$  group, i.e.,  $3s$  and  $3p$ , contribute very little to  $\alpha_q$ , which is due almost entirely to the  $3d$  electrons. This result is in accordance with the fact that  $\alpha_q$  depends essentially<sup>1</sup> on  $[\langle r^2 \rangle_{n_0 l}]^2 / \langle \Delta E \rangle$ , where  $\langle \Delta E \rangle$  is a mean energy denominator for quadrupole excitation. The value of  $[\langle r^2 \rangle_{n_0 l}]^2$  is a factor of  $\sim 4$  times larger for  $3d$  than for  $3s$  and  $3p$ . Moreover  $\langle \Delta E \rangle$  is considerably larger for  $3s$  and  $3p$  than for  $3d$  ( $\sim 10 \text{ ry}$  for  $3s$  and  $3p$ , as compared to  $\lesssim 1 \text{ ry}$  for  $3d$ ). Within the  $3d$  group, the  $3d \rightarrow s$  term is  $\sim 4$  times larger than the  $3d \rightarrow d$  or  $3d \rightarrow g$  term. This is due to the fact that the energy of the  $4s$  state  $E_{4s}$  is very close to the  $3d$  energy  $E_{3d}$ . Thus  $u'_{1, 2 \rightarrow 0}$  for the  $3d \rightarrow s$  excitation contains a contribution  $a_{4s} u'_{0, 4s}$ , where  $u'_{0, 4s}$  is the unperturbed  $4s$  function and the coefficient  $a_{4s}$  is given by

$$a_{4s} = \left[ \int_0^\infty u'_{0, 3d} r^2 u'_{0, 4s} dr \right] / (E_{4s} - E_{3d}). \quad (15)$$

The  $4s$  eigenfunction  $u'_{0, 4s}$  has been calculated for the same effective potential  $V_0$  in which the  $3d$  electrons move, and it was found that  $E_{4s} - E_{3d} = 0.334 \text{ ry}$ . (The Hartree-Fock eigenvalue<sup>10</sup>  $E_{3d}$  is  $-1.613 \text{ ry}$ , so that  $E_{4s} = -1.279 \text{ ry}$  in the effective-field approximation.) The integral  $\int_0^\infty u'_{0, 3d} r^2 u'_{0, 4s} dr$  was found to be  $-2.020$ , so that the  $4s$  term of  $u'_{1, 2 \rightarrow 0}$  is  $(-2.020/0.334)u'_{0, 4s} = -6.048u'_{0, 4s}$ . A comparison of  $a_{4s}u'_{0, 4s}$  with the complete perturbation  $u'_{1, 2 \rightarrow 0}$  shows clearly that the  $4s$  term almost completely accounts for the total  $u'_{1, 2 \rightarrow 0}$ , as was expected from the smallness of the energy denominator. Thus  $a_{4s}u'_{0, 4s}$  is very close to  $u'_{1, 2 \rightarrow 0}$  for all values of  $r$ . The ratio  $\rho \equiv a_{4s}u'_{0, 4s}/u'_{1, 2 \rightarrow 0}$  is  $0.984$  at the outermost

(fourth) maximum of  $u'_{0,4s}$  at  $r=2.0a_H$ ;  $\rho$  is 0.964 at the third maximum of  $u'_{0,4s}$  at  $r=0.55a_H$ , and  $\rho=0.912$  at  $r=4a_H$ . Another way of showing the predominance of the 4s term consists in evaluating the  $3d \rightarrow 4s$  contribution to  $\alpha_q$ , which is equal to

$$\alpha_q(3d \rightarrow 4s) = (8/5)(0.0415)(2.020)^2/0.334 = 0.811 A^5. \quad (16)$$

Here  $0.0415 = (0.529)^5$  is a factor needed to convert to units  $A^5$ . Comparison with Table II shows that  $\alpha_q(3d \rightarrow 4s)$  accounts for  $0.811/0.840 = 0.965$  of the complete  $3d \rightarrow s$  term.

The large magnitude of the  $3d \rightarrow 4s$  excitation raises the question as to the applicability of the first-order perturbation theory which has been used here. In particular, the difference  $E_{4s} - E_{3d}$  depends sensitively on the effective potential  $V_0$  used in the calculations, and one may inquire about the magnitude of the induced quadrupole moment  $Q_{\text{ind}}$  for the case that the  $3d$  and  $4s$  states are exactly degenerate ( $E_{3d} = E_{4s}$ ).<sup>14</sup> In this case, following the usual methods of perturbation theory, one must solve the secular determinant<sup>15</sup>:

$$\begin{vmatrix} H_{1,aa} - E_1 & H_{1,ab} \\ H_{1,ba} & H_{1,bb} - E_1 \end{vmatrix} = 0. \quad (17)$$

Here  $H_{1,aa}$ ,  $H_{1,ab}$ ,  $\dots$  are matrix elements of the perturbation  $H_1$ , and  $E_1$  is the first-order change of the energy due to  $H_1$ . For a unit point charge placed along the positive  $x$  axis at  $x=R$ ,  $H_1$  is given by<sup>1</sup>

$$H_1 = -(\gamma^2/R^3)(3 \cos^2\theta - 1), \quad (18)$$

where  $\theta$  is the angle between the radius vector (of length  $r$ ) and the  $x$  axis. In Eq. (18),  $H_1$  is given in Rydberg units, if  $r$  and  $R$  are in units  $a_H$ . We denote the  $3d$  state by  $a$  and the  $4s$  state by  $b$ . It may be noted that the only  $3d$  state of interest here is the state with magnetic quantum number  $m=0$ . One obtains

$$H_{1,aa} = -(4/7)R^{-3} \int_0^\infty u'^2_{0,3d} r^2 dr = -0.734R^{-3} \text{rydberg}, \quad (19)$$

$$H_{1,ab} = H_{1,ba} = -(2/5^{\frac{1}{2}})R^{-3} \int_0^\infty u'_{0,3d} r^2 u'_{0,4s} dr = 1.806R^{-3} \text{rydberg}, \quad (20)$$

$$H_{1,bb} = 0. \quad (21)$$

In Eqs. (19) and (20), the factors  $4/7$  and  $2/5^{\frac{1}{2}}$  arise from the integration over the angular wave functions. The integral  $\int_0^\infty u'^2_{0,3d} r^2 dr$  over the Hartree-Fock func-

tion<sup>10</sup> has the value  $1.285a_H^2$ . Upon solving Eq. (17), one obtains two roots:  $E_{1\alpha} = -2.210R^{-3}$ ,  $E_{1\beta} = 1.476R^{-3}$  rydbergs. The wave function  $\psi_\alpha$  corresponding to the lower energy  $E_{1\alpha}$  is found to be<sup>15</sup>:

$$\psi_\alpha = 0.775\psi_{3d,0} - 0.633\psi_{4s}, \quad (22)$$

where  $\psi_{3d,0}$  and  $\psi_{4s}$  are the unperturbed  $3d$  function (with  $m=0$ ) and the  $4s$  function, respectively. In order to obtain the induced quadrupole moment  $Q_{\text{ind}}$ , we note that if the  $3d$  electrons with  $m=0$  had the wave function  $\psi_{3d,0}$ , the total quadrupole moment of the ion would be zero, because of the equal population of the  $3d$ ,  $m=0$ ,  $\pm 1$ , and  $\pm 2$  states which results in spherical symmetry. Thus the replacement of  $\psi_{3d,0}$  by  $\psi_\alpha$  leads to a quadrupole moment:

$$Q_{\text{ind}} = 2 \int (\psi_\alpha^2 - \psi_{3d,0}^2) r^2 (3 \cos^2\theta - 1) dV = 2.96a_H^2, \quad (23)$$

where the factor 2 arises from the presence of the two electrons with  $m=0$ . The numerical result  $2.96a_H^2$  for  $Q_{\text{ind}}$  is obtained in a straightforward manner, using the values of  $\int_0^\infty u'^2_{0,3d} r^2 dr = 1.285a_H^2$  and  $\int_0^\infty u'_{0,3d} r^2 u'_{0,4s} dr = -2.020a_H^2$ .

Equation (23) gives the maximum value of  $Q_{\text{ind}}$  due to the  $3d \rightarrow 4s$  excitation. In order to determine whether the first-order perturbation result for  $\alpha_q(3d \rightarrow 4s) = 0.811 A^5$  is adequate in a typical case, we will obtain the corresponding value of  $Q_{\text{ind}}$  and compare it with (23). It will be assumed that the external charge (e.g., the neighboring ion in a polar molecule) is at a distance  $R = 5a_H = 2.65 A$ . By virtue of Eq. (8),  $Q_{\text{ind}}$  is given by

$$Q_{\text{ind}} = \frac{2\alpha_q}{R^3} (2)(0.811) = \frac{2.65}{2.65^3} = 0.0871 A^2 = 0.311a_H^2, \quad (24)$$

which is a factor of  $\sim 10$  smaller than the maximum value  $2.96a_H^2$ . Another way of making the comparison is to obtain the  $4s$  admixture coefficient  $b_{4s}$  which is found to be

$$b_{4s} = -\frac{H_{1,ab}}{E_{4s} - E_{3d}} = -\frac{1.806}{(125)(0.334)} = -0.0431, \quad (25)$$

where Eq. (20) has been used. It may be noted that  $b_{4s}$  differs from  $a_{4s}$  of Eq. (15) by a factor  $(2/5^{\frac{1}{2}})R^{-3}$ , which comes from the integration over the angular wave functions and the definition of  $H_1$  [Eq. (18)].

The results of Eqs. (24) and (25) show that  $Q_{\text{ind}}$  and  $b_{4s}$  are sufficiently small that the first-order perturbation value  $\alpha_q(3d \rightarrow 4s) = 0.811 A^5$  is expected to be quite accurate. Actually, one can carry out an exact treatment of the  $3d-4s$  admixture also when the zero-order energies  $E_{3d}$  and  $E_{4s}$  are different. One obtains a secular determinant similar to (17). Upon taking the next higher order term in the admixture, one finds that  $b_{4s}$  is

<sup>14</sup> I wish to thank Professor R. H. Dalitz for suggesting to me a consideration of the case of degenerate  $3d$  and  $4s$  levels.

<sup>15</sup> See, for example, Eyring, Walter, and Kimball, *Quantum Chemistry* (John Wiley and Sons, Inc., New York and London, 1944), p. 96.

changed by an amount

$$\delta b_{4s} = \frac{(H_{1,bb} - H_{1,aa})H_{1,ab}}{(E_{4s} - E_{3d})^2} = 7.5 \times 10^{-4}. \quad (26)$$

Upon including  $\delta b_{4s}$  and a term ( $\propto b_{4s}^2$ ) due to the normalization of the perturbed wave function, one obtains  $Q_{\text{ind}} = 0.303a_H^2$ , so that the correction to (24) is less than 3%. This conclusion depends, of course, on the value of  $E_{4s} - E_{3d}$ . If this energy difference were substantially less than 0.3 ry, the actual  $Q_{\text{ind}}$  would be appreciably smaller than the first-order result and would have to be obtained from an exact calculation of the 4s admixture.

As has been discussed in I, the induced quadrupole

moment contributes to the spectral term defects of the alkalis, for which it gives of the order of 10 to 30% of the amount contributed by the induced dipole moment.<sup>6</sup> The perturbed wave functions obtained in the present work may also be of interest in the construction of appropriate wave functions for polar molecules.<sup>16</sup>

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<sup>16</sup> L. C. Allen, *Bull. Am. Phys. Soc. Ser. II*, **2**, 43 (1957).

## Inelastic Scattering of 20-kev Electrons in Metal Vapors\*

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The low-energy losses of 20-kev electrons passing through the vapors of Zn, Cd, Hg, Na, K, Mg, Ca, Sb, Pb, and KCl, have been measured by using an electrostatic analyzer previously used for measuring electron energy losses in thin metal films. The atomic transitions corresponding to the measured energy losses are in many cases fairly easily established. However, there remain some which are questionable due to the fact that there is more than one feasible transition with energy differences of the order of the given energy loss. It is established that the principal interaction results in the excitation from the ground state of the neutral atom to the first excited level—the resonance excitation. It is also found that dipole excitations predominate

### INTRODUCTION

FROM the time that Franck and Hertz<sup>1</sup> first demonstrated in 1914 the existence of quantized inelastic collisions between electrons and gas atoms, many experiments were performed to measure such quanta of energy loss. This work was summarized up to 1925 by Compton and Mohler.<sup>2</sup> Brode,<sup>3</sup> in 1933, reviewed the study of the collisions of electrons with atoms, and more recently Massey and Burhop<sup>4</sup> have brought this information up to date. The energy losses have been called resonance losses and critical potentials. Most of the measurements were made for the permanent gases although a few were made for the metal vapors. All of these measurements were made at very low primary-electron energies, generally not extending beyond the value of the first ionization potential of the atom.

The measurements to be described were performed with primary electrons of 20-kev energy, principally because we were interested in obtaining the energy losses in metal vapors under the same conditions as our measurements previously reported<sup>5</sup> for the energy losses of 20–30 kev electrons in thin metal films.<sup>6</sup> With high-energy electrons one is not limited, in principle, to exciting only dipole and higher multipole transitions as is the case with electromagnetic radiation; it should be possible to excite monopole transitions as well.<sup>7</sup> However, the Born approximation predicts that dipole excitations of the atomic electrons should predominate. Fano<sup>8</sup> has described the relative probabilities of excitation and ionization when a high-energy electron (1–100 kev) interacts with hydrogen atoms. In Fig.

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<sup>1</sup> J. Franck and G. Hertz, *Verhandl. deut. physik. Ges.* **16**, 457 (1914).

<sup>2</sup> K. T. Compton and F. L. Mohler, *National Research Council (U.S.) Bull.* **48**, Vol. 9 (1924–1925).

<sup>3</sup> R. B. Brode, *Revs. Modern Phys.* **5**, 257 (1933).

<sup>4</sup> H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, England, 1952).

<sup>5</sup> Marton, Leder, and Mendlowitz in *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press, Inc., New York, 1955), Vol. 7, p. 183.

<sup>6</sup> E. J. Sternglass, *Nature* **178**, 1387 (1956), has stated that measurement of the energy losses of electrons in metal vapors may provide a test for distinguishing between individual atomic and collective losses of electrons in thin solid films.

<sup>7</sup> In what follows, all transitions other than dipole will be referred to as optically forbidden or forbidden transitions.

<sup>8</sup> U. Fano in *Radiation Biology*, edited by A. Hollaender (McGraw-Hill Book Company, Inc., New York, 1954), Vol. 1, p. 56.