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Electronic Polarizabilities of the Alkali Atoms. II*

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The electronic dipole polarizabilities α_d of the alkali atoms have been recalculated with the inclusion of the shielding effect of the ion core in the perturbation equations. The resulting values of α_d are close to those obtained in a previous calculation, and are also in very good agreement with the recent experimental values of Hall and Zorn. The dipole polarizabilities α_d of the Rb^+ and Cs^+ ions have been recalculated, using the appropriate Hartree-Fock wave functions (including exchange), which have recently become available. The resulting values of $\alpha_d(\mathrm{Rb}^+)$ and $\alpha_d(\mathrm{Cs}^+)$ are in much better agreement with experiment than those obtained in a previous calculation using Hartree wave functions (without exchange).

I. INTRODUCTION

The purpose of this paper is to present a recalculation of the electronic (dipole) polarizabilities α_d of the alkali atoms.[1] The calculation includes the effect of the shielding by the core of the external potential $\mathcal{E}_0 r\cos\theta$ ($\mathcal{E}_0$ = external electric field), which is seen by the valence electron. This effect, which was neglected in our previous work,[2] has been recently pointed out by Sandars.[3] It turns out that the shielding effect is relatively unimportant in all cases, ranging from a reduction of α_d of 0.4% for Li to a reduction of 8.2% for Cs. The resulting calculated values of α_d for Na, K, Rb, and Cs are in very good agreement with the recently determined experimental α_d values of Hall and Zorn.[4]

An additional purpose of the present calculations was to obtain values of the electric dipole enhancement factor (to be denoted by S), which was first introduced by Sandars.[3] The enhancement factor S represents the ratio d_A/d_e, where d_e is a hypothetical electric dipole moment of the electron, and d_A is the resulting electric dipole moment induced in the alkali atom. The values of S which we have obtained, using the perturbed valence wave functions $u_1(ns\to p)$ of the present work, are in good agreement with the earlier results of Sandars.[3]

In the course of the calculation of α_d for the alkali atoms, it was noticed that the polarizabilities $\alpha_d(\mathrm{Rb}^+)$ and $\alpha_d(\mathrm{Cs}^+)$ for the Rb^+ and Cs^+ ions had not been previously calculated using Hartree-Fock wave functions. Instead, Hartree wave functions (without exchange) were employed, which were the only wave functions available when the previous calculations were carried out (in 1959).[5] In the meantime, Hartree-Fock wave functions for Rb^+ and Cs^+ have been calculated by several workers. Thus it is of interest to recalculate $\alpha_d(\mathrm{Rb}^+)$ and $\alpha_d(\mathrm{Cs}^+)$ using the now available Hartree-Fock wave functions, and this has been done in Sec. III of the present paper. As expected, the resulting values of α_d are considerably smaller than those obtained previously (by a factor of about 1.5), and are more nearly in agreement with the experimental α_d values.

Section IV contains a brief discussion of the main results obtained in the present work.

II. ELECTRONIC POLARIZABILITIES α_d OF THE ALKALI ATOMS

As discussed in the Introduction, we have recalculated the polarizabilities α_d of the alkali atoms. The present calculation includes in an approximate manner the effect of the shielding by the core of the external potential $\mathcal{E}_0 r\cos\theta$, ($\mathcal{E}_0$ = external electric field) which is seen by the valence electron. For comparison, we have also repeated our previous calculations, in which the unshielded potential $\mathcal{E}_0 r\cos\theta$ was used in the perturbation equation. In the following, the unshielded and the shielded cases will be referred to as case a and case b, respectively, (using the subscript a or b).

The notation is the same as in Ref. 2. Thus for the unshielded case (subscript a), the function $u_1'(ns\to p)_\mathrm{a}$ is the solution of the equation

$$(-d^2/dr^2+2/r^2+V_0-E_0)u_{1\mathrm{a}}' = u_0' r\ , \qquad (1)$$

where $u_0' \equiv u_0'(ns)$ is r times the radial part of the unperturbed valence (ns) wave function, normalized according to

$$\int_0^\infty u_0'^2\,dr = 1\ . \qquad (2)$$

The part of the dipole polarizability due to the valence electron (subscript v) is given by

$$\alpha_{v,\mathrm{a}} = \tfrac{4}{3}\int_0^\infty u_0'(ns)u_1'(ns\to p)_\mathrm{a}\, r\,dr \ , \qquad (3)$$

in units a_H^3.

In Eq. (3), the expression $V_0 - E_0$ (V_0 = unperturbed effective potential, E_0 = unperturbed eigenvalue) is obtained directly from the wave function, as has been discussed in our earlier work,[6] namely,

$$V_0 - E_0 = (u_0')^{-1} d^2u_0'/dr^2 \ . \qquad (4)$$

We employed the same valence wave functions $u_0'(ns)$ as in Ref. 2. These functions were so chosen as to reproduce the observed ionization potentials for the alkali atoms.[7] Thus for Li and Na, we used wave functions obtained from the effective potentials of Seitz[8] and Prokofjew,[9] respectively. For the case of K, a potential derived by the author in Ref. 2 was used to calculate $u_0'(4s)$. This potential was obtained from the effective Hartree-Fock potential[10] for K 4s, plus a small term δV which represents correlation effects not included in the Hartree-Fock method. The term δV was adjusted in such a manner that the experimental energy eigenvalue ($E_{0,\,\mathrm{exp}} = -0.3190$ Ry) is reproduced.[2] For Rb, the 5s wave function given by Callaway and Morgan[11] was employed. Finally, for Cs, we used the 6s wave function obtained by Sternheimer[12] ($E_0 \cong E_{0,\,\mathrm{exp}} = -0.2862$ Ry).

When the shielding of the external electric field by the ion core is included, the inhomogeneous term $u_0'r$ of Eq. (1) is replaced by $u_0'rf(r)$, where $f(r)$ is the function introduced by Sandars[3]:

$$f(r) = \frac{r^3 + [\alpha_c/(Z-1)]}{r^3 + [Z/(Z-1)]\alpha_c} \ , \qquad (5)$$

where α_c is the polarizability of the alkali ion core. The function $f(r)$ was determined from the condition that it should equal[13] $1/Z$ at $r=0$, and that it should approach 1 as $r\to\infty$. Moreover, $f(r)$ varies most rapidly in the region where $f(r) \sim \frac12$. The value $f(r) = \frac12$ is actually attained at $r \equiv r_{1/2}$ given by

$$r_{\frac12} = \alpha_c^{\,1/3}[(Z-2)/(Z-1)]^{1/3} \ , \qquad (6)$$

which is approximately $\alpha_c^{1/3}$, except for Li. The values of the static polarizabilities α_c (for infinite wavelength λ) were taken from the paper of Tessman, Kahn, and Shockley.[14] Thus we used: $\alpha_c = 0.029$ Å^3 for Li, 0.255 Å^3 for Na, 1.20 Å^3 for K, 1.80 Å^3 for Rb, and 3.14 Å^3 for Cs. The corresponding values of $r_{1/2}$ (in units a_H) are as follows: 0.46 for Li, 1.16 for Na, 1.97 for K, 2.28 for Rb, and 2.75 for Cs. The resulting functions $f(r)$ for the five alkali atoms are shown in Fig. 1.

The perturbed wave functions including shielding will be denoted by $u_1'(ns\to p)_\mathrm{b}$ or $u_{1\mathrm{b}}'$. Thus $u_{1\mathrm{b}}'$ is determined by the following equation:

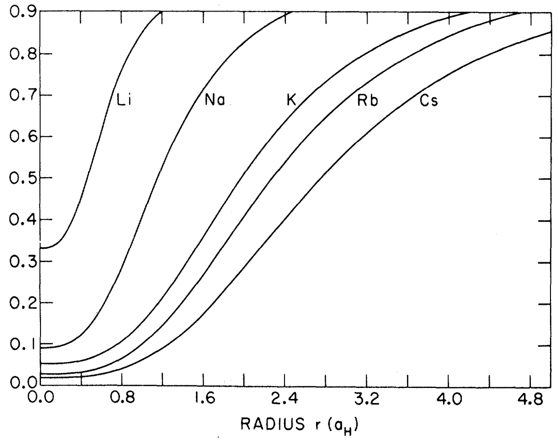

FIG. 1. The Sandars functions $f(r)$ [Eq. (5)] for the electric dipole shielding by the core for the five alkali atoms.

$$(-d^2/dr^2 + 2/r^2 + V_0 - E_0)u_{1\mathrm{b}}' = u_0' rf(r), \qquad (7)$$

and the corresponding valence electron polarizability is given by

$$\alpha_{v,\mathrm{b}} = \tfrac{4}{3}\int_0^\infty u_0'(ns)u_1'(ns\to p)_\mathrm{b}\, r\,dr \ , \qquad (8)$$

in units a_H^3.

As discussed in Ref. 2, we are also interested in the values of the electric field at the nucleus produced by the perturbation $u_{1\mathrm{a}}'$ or $u_{1\mathrm{b}}'$ of the valence electron wave function. This induced field at the nucleus can be written as follows:

$$\vec{\mathcal{E}}_{\mathrm{ind},v} = -\xi_v \vec{\mathcal{E}}_0 \ , \qquad (9)$$

where $\vec{\mathcal{E}}_0$ is the external field, and ξ_v (denoted by ξ_{val} in Ref. 2) is given by

$$\xi_{v,\gamma} = \tfrac{4}{3}\int_0^\infty u_0'(ns)u_1'(ns\to p)_\gamma\, r^{-2}dr \ , \qquad (10)$$

where γ = a or b.

The present calculations of $u_{1\mathrm{a}}'$ and $u_{1\mathrm{b}}'$ from Eqs. (1) and (7), respectively, were carried out by means of a CDC-6600 computer program written by Dr. R. F. Peierls.[15] This program has been described in Ref. 15.

The functions $u_{1\mathrm{a}}'$ and $u_{1\mathrm{b}}'$ obtained in the present work, together with the unperturbed functions $u_0'(ns)$, have been tabulated in a separate paper.[16] The tables of this paper also contain a listing of the effective potentials V_0 [Eq. (4)] and their derivatives dV_0/dr. As will be discussed below, the functions V_0 and dV_0/dr enter into the expression for the Sandars[3] enhancement factor S.

After the functions u'_{1a} and u'_{1b} were determined from Eqs. (1) and (7), respectively, the integrals involved for $\alpha_{v,\mathrm{a}}$, $\alpha_{v,\mathrm{b}}$, $\xi_{v,\mathrm{a}}$ and $\xi_{v,\mathrm{b}}$ [Eqs. (3), (8), and (10)] were calculated using a second computer program also written by Dr. R. F. Peierls, which has been described in Ref. 15. The resulting values of $\alpha_{v,\gamma}$ and $\xi_{v,\gamma}$ ($\gamma = \mathrm{a,b}$) are presented in Table I.

The functions $u'_1(6s\to p)_\mathrm{b}$ and $u'_0(6s)$ for the cesium atom are shown in Fig. 2. For simplicity of notation, the primes have been omitted in this figure, and $u'_1(6s\to p)_\mathrm{b}$ has been written as $u_{1\mathrm{b}}(6s\to p)$. It is seen that at large r, $u'_1(6s\to p)_\mathrm{b}$ and $u'_0(6s)$ have the same sign, which is expected, of course, since the polarizability $\alpha_{v,\mathrm{b}}$ [Eq. (8)] must be positive. We may also note the large values of $u'_1(6s\to p)_\mathrm{b}$ at large r (see the left-hand ordinate scale). The outermost maximum of $u'_1(6s\to p)_\mathrm{b}$ equals -23.2, and occurs at $r = 6.4a_\mathrm{H}$. The large magnitude of $u'_1(6s\to p)_\mathrm{b}$ is directly responsible for the large resulting value of the valence electron polarizability $\alpha_{v,\mathrm{b}}$ (= 65.02 Å^3; see Table I).

The calculations of $\alpha_{v,\mathrm{a}}$ (unshielded case) can be regarded as a check on our previous calculations of $\alpha_d(n_0s\to p)$ in Ref. 2 (see Table III), which were carried out on a desk computer. By comparing the two sets of values, it is seen that the agreement is to within 1%, except for the case of K, where the potentials V_0 used in the two calculations are slightly different. Even in this case, the discrepancy is only ~3%.

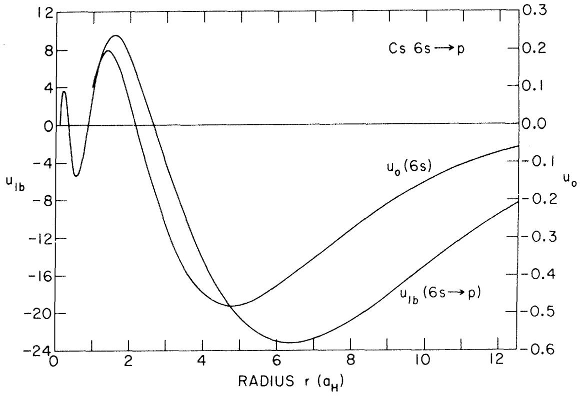

FIG. 2. The perturbed wave function $u_{1\mathrm{b}}(6s\to p)$ and the unperturbed $6s$ function $u_0(6s)$ for the cesium atom.

As mentioned in the Introduction, we have also obtained the values of the electric dipole moment enhancement factor S. According to Sandars,[3] S is given by

$$S = -\tfrac{2}{3}\alpha^2 F_\gamma \int_0^\infty R^S(r) R^p(r) \frac{d}{dr}[V(r)]^2\, dr\,, \quad (11)$$

where $\alpha = e^2/\hbar c$, F_γ is a relativistic correction factor, $R^S = u'_0$, and $R^p(r) = -2u'_1(ns\to p)$. The factor -2 between Sandars's perturbed wave functions and ours can be derived by comparing his Eq. (3) with the Eq. (1) of the present paper. We note that Sandars used atomic units of energy e^2/a_H instead of Rydbergs, so that his $V(r)$ equals one-half of our $V_0(r)$. Upon combining all of these factors, we find that Eq. (11) can be rewritten in terms of our functions u'_0, u'_1, and V_0 as follows:

$$S = +\tfrac{2}{3}\alpha^2 F_\gamma \int_0^\infty u'_0(ns)u'_1(ns\to p)V_0\frac{dV_0}{dr}\, dr. \quad (12)$$

The relativistic factor F_γ is given by[17]

$$F_\gamma = 3/\rho(4\rho^2-1)\,, \quad (13)$$

where $\rho = (1-\alpha^2Z^2)^{1/2}$.

In the same manner as for α_v and ξ_v, we have calculated two values of S for each alkali atom, namely S_a and S_b, pertaining to $u'_1(ns\to p)_\mathrm{a}$ and $u'_1(ns\to p)_\mathrm{b}$, respectively. The potentials V_0 (and the corresponding derivatives dV_0/dr) are those which pertain to the valence wave functions described above [Eq. (4)]. Thus the V_0 have the property that they reproduce the observed ionization potential[7] of the valence electron in each case.

The derivative dV_0/dr was obtained by numerical differentiation of the potential V_0 over most of the range. However, near the nucleus, where

TABLE I. The valence electron polarizabilities ($\alpha_{v,\mathrm{a}}, \alpha_{v,\mathrm{b}}$), the electric dipole shielding factors ($\xi_{v,\mathrm{a}}, \xi_{v,\mathrm{b}}$) and the Sandars electric dipole enhancement factors ($S_\mathrm{a}, S_\mathrm{b}$) for the alkali atoms. For each quantity, subscript a pertains to the unshielded case, while subscript b pertains to the shielded case. The values of $\alpha_{v,\mathrm{a}}$ and $\alpha_{v,\mathrm{b}}$ are in units Å^3. The quantities $\alpha_{v,\mathrm{a}}, \alpha_{v,\mathrm{b}}, \xi_{v,\gamma}$, and S_γ (γ = a or b) are given by Eqs. (3), (8), (10), and (12), respectively.

Atom	$\alpha_{v,\mathrm{a}}$	$\alpha_{v,\mathrm{b}}$	$\xi_{v,\mathrm{a}}$	$\xi_{v,\mathrm{b}}$	S_a	S_b
Li	24.92	24.82	2.567	2.551	4.19×10^{-3}	4.17×10^{-3}
Na	23.18	22.64	2.667	2.568	0.330	0.314
K	47.36	44.74	3.292	3.037	3.04	2.76
Rb	51.06	47.60	3.33	3.00	27.7	24.6
Cs	71.31	65.02	3.70	3.27	159	138

V_0 is rapidly varying, dV_0/dr was obtained analytically as follows. We write

$$V_0 = -2Z_p(r)/r , \tag{14}$$

where $Z_p(r)$ is a slowly varying function of r, which equals Z at $r=0$. Thus we have

$$dV_0/dr = 2Z_p/r^2 - (2/r)\,dZ_p(r)/dr . \tag{15}$$

dZ_p/dr can be obtained numerically. Since this derivative is negative, dV_0/dr is somewhat larger than $2Z_p/r^2$.

At large distances r from the nucleus, we have $Z_p = 1$, so that,

$$V_0 = -2/r; \quad dV_0/dr = +2/r^2 \quad (\text{large } r). \tag{16}$$

However, we note that the predominant contributions to the integral (12) for S come from the region close to the nucleus (e.g., $r \lesssim 0.2a_{\rm H}$ for Cs; $r \lesssim 1a_{\rm H}$ for Li). Near the nucleus, we have

$$u_0' \propto r; \quad u_1' \propto r^2; \quad V_0(dV_0/dr) \propto r^{-3} , \tag{17}$$

so that the integrand approaches a constant value. Actually the maximum of the integrand occurs at $r=0$.

The results of the calculations of $S_{\rm a}$ and $S_{\rm b}$ are listed in the last two columns of Table I. The present results are in very good agreement with those of Sandars,[3] especially for Li, Na, and Rb. For K and Cs, our values are slightly larger than those of Ref. 3, but the differences (a factor of 1.20 for Cs case a, and 1.16 for Cs case b) are probably not very important, in view of the limited accuracy of the experiments which place an upper limit on the electric dipole moment of the cesium atom.[18] The differences between the two results for S (for K and Cs) may well arise from the use of slightly different zero-order potentials V_0 and zero-order wave functions $u_0'(ns)$ in the two calculations.

As was discussed in Ref. 2, the total polarizability of an alkali atom contains a contribution of the ion core, and is thus given by

$$\alpha_{\text{total},\gamma} = \alpha_{v,\gamma} + \alpha_{\text{ion, eff}} , \tag{18}$$

where $\alpha_{\text{ion, eff}}$ is the effective contribution of the ion core, and $\gamma = \text{a}$ or b.

As discussed in Ref. 2, $\alpha_{\text{ion, eff}}$ would be simply equal to α_c, the ion core polarizability, if it were not for the field produced by the valence electron, which tends to shield (and actually overshields) the external field $\mathcal{E}_0$, i.e., ξ_v is larger than 1 in all cases. Thus $\alpha_{\text{ion, eff}}$ represents the response of the ion core to the total potential, namely,

$$V_{\text{total}} = V_{\text{ext}} + V_{\text{ind}} , \tag{19}$$

where $V_{\text{ext}} = \mathcal{E}_0 r\cos\theta$, and the induced potential due to the valence electron V_{ind} will be written as follows:

$$V_{\text{ind}} = -\,\xi(ns\rightarrow p; r)_\gamma \, V_{\text{ext}} . \tag{20}$$

As indicated, $\xi(ns\rightarrow p; r)_\gamma$ is a function of r which depends on $u_0'(ns)$ and $u_1'(ns\rightarrow p)$ of the valence electron. In particular, at the nucleus, we have

$$\xi(ns\rightarrow p; r=0)_\gamma = \xi_{v,\gamma} , \tag{21}$$

where $\xi_{v,\gamma}$ is the dipole shielding factor as given by Eq. (10), and $\gamma = \text{a}$ or b.

As a straightforward generalization of Eq. (10) to $r \neq 0$, we find that $\xi(ns\rightarrow p; r)_\gamma$ is given by

$$\xi(ns\rightarrow p; r)_\gamma = \tfrac{4}{3}\left[\int_r^\infty u_0' u_{1\gamma}' r'^{-2}\,dr' + r^{-3}\int_0^r u_0' u_{1\gamma}' r'\,dr'\right], \tag{22}$$

where $u_0' = u_0'(ns)$ and $u_{1\gamma}' = u_1'(ns\rightarrow p)_\gamma$. The first integral in the square bracket of (22) represents the effect of the perturbed valence density outside the distance r (i.e., $r' > r$), whereas the second integral represents the effect of the dipole moment induced in the valence electron distribution at smaller distances, $r' < r$. We note that $\xi(ns\rightarrow p; r)_\gamma$ represents a *ratio* of two potentials, as shown by Eq. (20). The actual induced potential V_{ind} contains an additional factor $\mathcal{E}_0 r\cos\theta$.

The function $\xi(ns\rightarrow p; r)_\gamma$ for each alkali atom was obtained from the same computer program[15] as was employed in the calculation of $\alpha_{v,\gamma}$ and $\xi_{v,\gamma}$. As an example of the results obtained, Fig. 3 shows the function $\frac{3}{4}\xi(6s\rightarrow p; r)_{\rm a}$ for the cesium atom. The rapid increase of $\frac{3}{4}\xi$ near $r=0$ from 2.776 to a maximum of 5.13 at $r = 0.045a_{\rm H}$ and the subsequent decrease at larger r arise from the fact that near the nucleus, u_0' and u_1' have opposite sign, which leads to a negative contribution to the integrals for $\xi(6s\rightarrow p; r)_{\rm a}$ very close to the nucleus [see Eq. (22)]. On the other hand, for $r \gtrsim 0.035a_{\rm H}$, u_0' and u_1' have generally the same sign, and $\xi(6s\rightarrow p; r)$ decreases rather smoothly to zero at large r [e.g., $\xi(6s\rightarrow p; r)_{\rm a} \cong 0.10$ at $r = 7.4a_{\rm H}$].

For the present purpose of calculating $\alpha_{\text{ion, eff}}$, we must obtain $\xi(ns\rightarrow p; r_1)$ at the radius r_1, where the principal perturbation $u_1'[(n-1)p\rightarrow d]$ of the ion core has its outermost maximum. The values of r_1 thus obtained from a consideration of the $[(n-1)p\rightarrow d]$ wave functions[19] are: $r_1 = 1.0a_{\rm H}$ for Li; $1.4a_{\rm H}$ for Na; $1.6a_{\rm H}$ for K; $2.0a_{\rm H}$ for Rb, and $2.4a_{\rm H}$ for Cs.

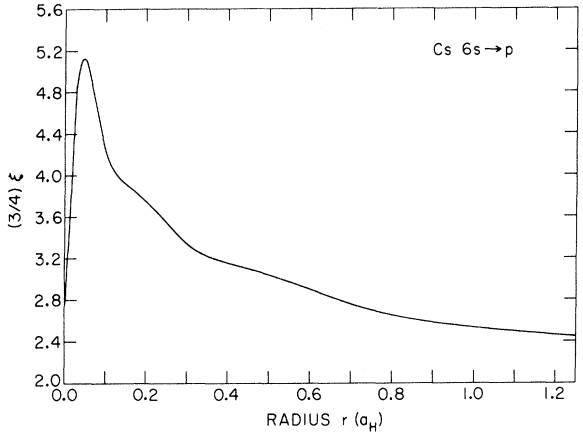

FIG. 3. The dipole shielding function $\frac{3}{4}\xi(6s\to p; r)$ for the cesium atom.

The values of $\xi(ns\to p; r_1)_b$ will be simply denoted by $\xi_{v,b}(r_1)$. Thus the effective perturbing potential at the location of the $[(n-1)p\to d]$ maximum is given by

$$V_{eff} = e\mathcal{E}_0 r\cos\theta[1-\xi_{v,b}(r_1)] , \qquad (23)$$

and hence the contribution of the ion core $\alpha_{ion,eff}$ is approximately given by

$$\alpha_{ion,eff} = \alpha_c[1-\xi_{v,b}(r_1)] , \qquad (24)$$

where α_c is the ion core polarizability, which will be obtained from Ref. 14.

Equation (24) is completely equivalent to Eq. (12) of Ref. 2, in which $\beta\xi_{val} = \xi_{v,b}(r_1)$, i.e., β was defined as

$$\beta \equiv \xi_{v,b}(r_1)/\xi_{v,b}(0) , \qquad (25)$$

where $\xi_{v,b}(0)$ is the value of $\xi_{v,b}(r)$ at the nucleus; thus $\xi_{v,b}(0) = \xi_{v,b}$ of Table I.

The values of $\xi_{v,b}(r_1)$ as obtained from Eq. (22) are as follows: 3.59 for Li; 2.21 for Na; 2.48 for K; 2.17 for Rb; and 2.22 for Cs. Upon inserting these results together with the α_c values[14] into Eq. (24), we obtain the following values for $\alpha_{ion,eff}$ (in units Å^3): -0.075 for Li; -0.31 for Na; -1.77 for K; -2.11 for Rb; and -3.83 for Cs. These core corrections are negative, evidently because the $\xi_{v,b}(r_1)$ values are larger than 1 in all cases. A similar result was already obtained in Ref. 2.

For comparison with Ref. 2, we may note that the β values, as obtained from Eq. (25), are as follows: $\beta = 1.41$ for Li; 0.86 for Na; 0.82 for K; 0.72 for Rb; and 0.68 for Cs. Except for Li, where we had used[2] $\beta \sim 1.0$, the present values are quite close to those of Ref. 2, as was of course expected, since the values of β were obtained here in the same manner as in Ref. 2. For Li, β is actually larger than 1. This result can be understood easily by referring to Fig. 3 for Cs $6s\to p$. As shown in this figure, and as discussed after Eq. (22), $\xi_v(r)$ increases rapidly to a maximum for increasing r near the nucleus, before its subsequent decrease for larger r. Whereas for Cs, the maximum occurs at $r = 0.045a_H$, for Li, the maximum is attained only at $r = 1.10a_H$, i.e., in the same region of $r_1(\sim 1.0a_H)$ in which $\xi_{v,b}(r_1)$ is evaluated. Thus $\xi_{v,b}(r_1)/\xi_{v,b}(0)$ is larger than 1 for Li. On the other hand, for the heavier alkalis, the radius r_{max} of the maximum of $\xi_{v,b}$ is well inside r_1, so that $\beta < 1$. As an example, for Na $3s\to p$, we have $r_{max} = 0.24a_H$, and at $r = 0.76a_H$, $\xi_{v,b}(r)$ has again decreased to its value at $r = 0$, namely, $\xi_{v,b}(0) = 2.57$. Hence $\xi_{v,b}(r_1 = 1.4a_H) < \xi_{v,b}(0)$ and β is less than 1 ($\beta = 0.86$), as mentioned above.

By means of the values of $\alpha_{ion,eff}$ listed above, and the valence electron polarizabilities $\alpha_{v,\gamma}$ ($\gamma = $a,b) of Table I, we obtain the values of the total polarizability $\alpha_{t,a}$ and $\alpha_{t,b}$ which have been listed in Table II. The fourth column of this table gives the experimental values α_{exp} of Hall and Zorn,[4] with which the theoretical values $\alpha_{t,b}$ can be directly compared. It is seen that the agreement is good and is generally within the experimental uncertainties. In particular, the calculations reproduce the observed near-equality of α_d(K) and α_d(Rb), and the jump for higher Z to a much larger α_d for the cesium atom. (It may be noted that the calculations of Ref. 2 also gave agreement with this trend of the experimental values.)

In the next column of the table, we have listed the values of $\alpha_{t,b}/\alpha_{t,a}$, namely the reduction of α_t as a result of the use of the Sandars cutoff function $f(r)$ [Eq. (5)] in determining the perturbations $u_1'(ns\to p)_b$ from Eq. (7). It is seen that the decrease of α_t is a relatively small effect (a maximum of 8.2% for Cs). The relatively small reduction of α_t arises from the fact that in the region of the outermost maxima of $u_0'(ns)$ and $u_1'(ns\to p)$ (see Fig. 2), the values of $f(r)$ are already very close to 1.

The last three columns of Table II give the values of r_1, $\xi_{v,b}(r_1)$, and α_c which were used in the calculation of the core contribution $\alpha_{ion,eff}$ from Eq. (24). It should be noted that although our treatment of $\alpha_{ion,eff}$ is approximate, this does not introduce any appreciable uncertainty into the total $\alpha_{t,a}$ or $\alpha_{t,b}$, because the term $\alpha_{ion,eff}$ represents only a small fraction of $\alpha_{t,\gamma}$ [see Eq. (18)]. The maximum relative contribution occurs for Cs, and in this case $-\alpha_{ion,eff}/\alpha_{t,b}$ is only $3.83/61.19 = 0.063$. For Na, the corresponding ratio has decreased to $0.31/22.33 = 0.014$.

TABLE II. The total (valence electron + core) dipole polarizabilities $\alpha_{t,\mathrm{a}}$ and $\alpha_{t,\mathrm{b}}$, the corresponding experimental values α_{exp} of Hall and Zorn (Ref. 4), and the ratios $\alpha_{t,\mathrm{b}}/\alpha_{t,\mathrm{a}}$ for the alkali atoms. The values of α are in units Å^3. The last three columns of the table give: (1) the distance r_1 (units a_{H}) at which $\xi_{v\mathrm{b}}$ is evaluated in Eq. (24); (2) the ion core polarizability α_c (units Å^3) used in Eq. (24) for the ionic term $\alpha_{\mathrm{ion,\,eff}}$; (3) the value of $\xi_{v,\mathrm{b}}(r_1)$ as obtained from Eq. (22).

Atom	$\alpha_{t,\mathrm{a}}$ (Å^3)	$\alpha_{t,\mathrm{b}}$ (Å^3)	α_{exp} (Å^3)$^{\mathrm{a}}$	$\alpha_{t,\mathrm{b}}/\alpha_{t,\mathrm{a}}$	r_1 (a_{H})	α_c (Å^3)	$\xi_{\mathrm{v,b}}(r_1)$
Li	24.84	24.74	•••	0.996	1.0	0.029	3.59
Na	22.85	22.33	24.4 ± 1.7	0.977	1.4	0.255	2.21
K	45.36	42.97	45.2 ± 3.2	0.947	1.6	1.20	2.48
Rb	48.54	45.49	48.7 ± 3.4	0.937	2.0	1.80	2.17
Cs	66.67	61.19	63.3 ± 4.6	0.918	2.4	3.14	2.22

[a] For comparison, the earlier experimental values of Salop, Pollack, and Bederson (Ref. 4) are as follows: 20 ± 3 for Li; 20 ± 2.5 for Na; 36 ± 4.5 for K; 40 ± 5 for Rb; and 52.5 ± 6.5 for Cs.

The final values of $\alpha_{t,\mathrm{b}}$ as given in Table II are as follows (in units Å^3):

$$\alpha_{t,\mathrm{b}}(\mathrm{Li})=24.74;\quad \alpha_{t,\mathrm{b}}(\mathrm{Na})=22.33;$$
$$\alpha_{t,\mathrm{b}}(\mathrm{K})=42.97;\quad \alpha_{t,\mathrm{b}}(\mathrm{Rb})=45.49;$$
$$\alpha_{t,\mathrm{b}}(\mathrm{Cs})=61.19. \tag{26}$$

As discussed above, these values are in essential agreement with experiment.[4]

As will be shown in the next section (Sec. III). there is some evidence that the choice of Sandars for $f(r)$ [Eq. (5)] underestimates the actual $f(r)$ in the region of r_1, i.e., of the outermost maximum of the principal perturbation ($np\to d$) of the alkali ion core. In other words, the actual $f(r)$ may be closer to 1 in this region than is given by Eq. (5). Thus the values of $\alpha_{t,\mathrm{b}}$ given above would represent a lower limit to the actual theoretical alkali polarizabilities.

An alternative set of values can be obtained by taking the averages of $\alpha_{t,\mathrm{a}}$ (unshielded case) and $\alpha_{t,\mathrm{b}}$. The resulting values will be denoted by $\alpha_{t,\mathrm{ab}}$. Thus

$$\alpha_{t,\mathrm{ab}}\equiv\tfrac{1}{2}(\alpha_{t,\mathrm{a}}+\alpha_{t,\mathrm{b}}). \tag{27}$$

The results for $\alpha_{t,\mathrm{ab}}$ are as follows (in units Å^3):

$$\alpha_{t,\mathrm{ab}}(\mathrm{Li})=24.79;\quad \alpha_{t,\mathrm{ab}}(\mathrm{Na})=22.59;$$
$$\alpha_{t,\mathrm{ab}}(\mathrm{K})=44.17;\quad \alpha_{t,\mathrm{ab}}(\mathrm{Rb})=47.02;$$
$$\alpha_{t,\mathrm{ab}}(\mathrm{Cs})=63.93\ . \tag{28}$$

It should be pointed out that to within the experimental uncertainties of Ref. 4, there is no essential difference between the values $\alpha_{t,\mathrm{b}}$ [Eq. (26)] and $\alpha_{t,\mathrm{ab}}$ [Eq. (28)] for the alkali atoms, i.e., both sets of values are in equally good agreement with the experimental observations. However, if the above mentioned conjecture about the actual $f(r)$ should turn out to be correct, then the results for $\alpha_{t,\mathrm{ab}}$ give a better approximation to the rigorous theoretical values for α_d of the alkali atoms.

III. ELECTRONIC POLARIZABILITIES α_d OF THE Rb$^+$ AND Cs$^+$ IONS

As mentioned in the Introduction, one of the purposes of the present work has been to obtain more accurate values of the dipole polarizabilities $\alpha_d(\mathrm{Rb}^+)$ and $\alpha_d(\mathrm{Cs}^+)$ of the Rb$^+$ and Cs$^+$ ions, using the newly available Hartree-Fock wave functions for these ions. In this section, we shall report the results of this calculation, and its bearing on the determination of the cutoff function $f(r)$.

We will begin with the calculations of α_d for Cs$^+$. The corresponding Hartree-Fock wave functions have been obtained by Freeman and Watson.[20]

The calculations of $u_1'(nl\to l')_{\mathrm{a}}$ and $u_1'(nl\to l')_{\mathrm{b}}$ were carried out, using essentially the same equations [Eqs. (1) and (7)], as in the work of Sec. II. Thus

$$\left(-\frac{d^2}{dr^2}+\frac{l'(l'+1)}{r^2}+V_0-E_0\right)u_1'(nl\to l')_{\mathrm{a}}=u_0'(nl)r. \tag{29}$$

For each case, the effective values of (V_0-E_0) were obtained from an equation similar to Eq. (4), namely,

$$V_0-E_0=(u_0')^{-1}\,d^2u_0'/dr^2-l(l+1)/r^2. \tag{29a}$$

The CDC-6600 computer program was again used to integrate the differential equations. After the functions $u_1'(nl\to l')$ have been determined, the contribution of $(nl\to l')$ to the dipole polarizability is obtained from the following equation[5,13]:

$$\alpha_d(nl \to l')_\gamma = c(l \to l') \int_0^\infty u_0'(nl) u_1'(nl \to l')_\gamma \, r dr \, , \quad (30)$$

where γ = a or b, $l' = l \pm 1$, and the angular coefficients $c(l \to l')$ for the closed shells have the following values: $c(s \to p) = c(p \to s) = \frac{8}{3}$; $c(p \to d) = c(d \to p) = \frac{16}{3}$; $c(d \to f) = 8$. Obviously, the coefficient $\frac{4}{3}$ of Eqs. (3) and (8) pertaining to a single valence electron is just $\frac{1}{2}$ of the coefficient $c(s \to p) = \frac{8}{3}$ pertaining to a filled ns shell.

The results for $\alpha_d(nl \to l')$ of Cs$^+$ are as follows:

(a) For the wave functions $u_{1\text{a}}'$ [i.e., those derived without the factor $f(r)$]:

$$\alpha_d(5s \to p) = 1.84 \text{ Å}^3; \quad \alpha_d(5p \to s) = -1.87 \text{ Å}^3;$$
$$\alpha_d(5p \to d) = 3.66 \text{ Å}^3; \quad \alpha_d(4d \to f) = 0.13 \text{ Å}^3; \quad (31)$$

giving a total $\alpha_d(\text{Cs}^+)_\text{a} = 3.76$ Å^3, which, as expected, is somewhat larger than the experimental result $\alpha_{d,\text{exp}}(\text{Cs}^+) = 3.14$ Å^3, but is also considerably better than the value 5.60 Å^3 obtained from the Hartree wave functions (excluding exchange); see Ref. 5, Table III.

(b) For the wave functions $u_{1\text{b}}'$ [i.e., those derived including $f(r)$][21]:

$$\alpha_d(5s \to p) = 0.669 \text{ Å}^3; \quad \alpha_d(5p \to s) = -0.460 \text{ Å}^3 \cdot$$
$$\alpha_d(5p \to d) = 1.79 \text{ Å}^3; \quad \alpha_d(4d \to f) \cong 0.05 \text{ Å}^3, \quad (32)$$

giving a total $\alpha_d(\text{Cs}^+) = 2.05$ Å^3. This value is smaller than the range of the experimental results[14,22–25] for Cs$^+$, namely, 2.42 to 3.14 Å^3, thus indicating that the function $f(r)$ of Sandars[3] probably tends to underestimate the actual $f(r)$. In this connection, we note that the $\alpha_d(\text{Cs}^+)$ calculated with the present Hartree-Fock wave functions and with the actual (correct) $f(r)$ should be somewhat larger than the experimental value, since the Hartree-Fock method ignores correlation $(1/r_{ij})$ effects, whose inclusion would decrease the theoretical value of α_d. However, on account of the rather large range of experimental values[14,22–25] (2.42 to 3.14 Å^3), such a criterion would be difficult to apply precisely.

The above mentioned results for cases (a) and (b) have been presented in Table III. Besides the values of $\alpha_{d,\text{a}}(nl \to l')$ and $\alpha_{d,\text{b}}(nl \to l')$, this table includes the ratios $\alpha_{d,\text{b}}/\alpha_{d,\text{a}}$, and, in the last two columns, the Hartree-type results of Ref. 5 (see Table III), here denoted by $\alpha_{d,\text{H}}(nl \to l')$, as well as the ratios $\alpha_{d,\text{a}}/\alpha_{d,\text{H}}$, i.e., the reduction arising from the use of the Hartree-Fock (HF) wave functions (as compared to the Hartree wave functions) for $u_0'(nl)$. It is seen that the reduction produced by the use of HF functions is a factor of 0.671. Such a value seems to be reasonable for a moderately tightly bound ion such as Cs$^+$. By contrast, the reduction factor of

$$0.545 = \alpha_{d,\text{b}}(\text{Cs}^+)/\alpha_{d,\text{a}}(\text{Cs}^+) \, ,$$

arising from the Sandars cutoff function [see Eq. (5) and Fig. 1], seems to be excessively small. Of course, such a result could have been expected, given the form of Eq. (5), which yields $f(r) = 0.5$ at $r = 2.75a_\text{H}$, i.e., in the region of the outermost maximum of $u_1'(5p \to d)$.

The perturbed wave functions $u_1'(nl')_\text{a}$ and $u_1'(nl \to l')_\text{b}$ for Cs$^+$, as well as the functions $u_1'(nl \to l')_\text{a}$ for Rb$^+$, have been presented in a separate paper.[26]

We will now discuss the calculation of $\alpha_d(\text{Rb}^+)$ using Hartree-Fock wave functions. In the same manner as for Cs$^+$, this polarizability had been previously calculated using Hartree wave functions, which were the only functions available at that time (in 1959); see Ref. 5, Table III. In the present work, we used the Hartree-Fock (HF) wave functions of Watson and Freeman[20] for Rb$^+$ $3d$ and $4p$, and the Hartree-Fock-Slater wave function of Herman and Skillman[27] for Rb$^+$ $4s$. In contrast to the work on Cs$^+$, we have obtained

TABLE III. The terms $\alpha_{d,\text{a}}(nl \to l')$ and $\alpha_{d,\text{b}}(nl \to l')$ and the ratios $\alpha_{d,\text{b}}/\alpha_{d,\text{a}}$ for the polarizability of the Cs$^+$ ion, as calculated from the appropriate Hartree-Fock wave functions (Ref. 20). In the same manner as in Tables I and II, the subscript a pertains to the unshielded case, while the subscript b pertains to the shielded case. The last two columns of the table give $\alpha_{d,\text{H}}(nl \to l')$, and the ratios $\alpha_{d,\text{a}}/\alpha_{d,\text{H}}$, where $\alpha_{d,\text{H}}(nl \to l')$ is the value previously obtained using Hartree wave functions (see Ref. 5, Table III). All values of α_d are in units Å^3.

$\alpha_d(nl \to l')$	$\alpha_{d,\text{a}}$	$\alpha_{d,\text{b}}$	$\alpha_{d,\text{b}}/\alpha_{d,\text{a}}$	$\alpha_{d,\text{H}}$	$\alpha_{d,\text{a}}/\alpha_{d,\text{H}}$
$\alpha_d(5s \to p)$	1.84	0.669	0.364	2.01	0.915
$\alpha_d(5p \to s)$	−1.87	−0.460	0.246	−1.51	1.238
$\alpha_d(5p \to d)$	3.66	1.790	0.489	4.94	0.741
$\alpha_d(4d \to f)$	0.13	0.05	0.385	0.16	0.813
Sum	3.76	2.05	0.545	5.60	0.671

only the wave functions $u_1'(nl\rightarrow l')_{\mathrm{a}}$ as calculated from Eq. (1), i.e., without the factor $f(r)$.

The resulting values of $\alpha_d(nl\rightarrow l')_{\mathrm{a}}$ are as follows:

$$\alpha_d(4s\rightarrow p)=0.749\ \text{Å}^3;\quad \alpha_d(4p\rightarrow s)=-0.667\ \text{Å}^3;\quad \alpha_d(4p\rightarrow d)=1.915\ \text{Å}^3;\quad \alpha_d(3d\rightarrow f)=0.023\ \text{Å}^3; \tag{33}$$

giving a total $\alpha_d(\mathrm{Rb}^+)=2.020$ Å^3. As expected, this value is somewhat larger than the experimental range of values,[14,22–25] namely from 1.40 to 1.81 Å^3, but represents also a considerable improvement over the Hartree function result of 2.92 Å^3 (see Ref. 5, Table III).[28]

The present results for Rb$^+$ have been given in Table IV (values of $\alpha_{d,\mathrm{a}}$ in column 2), together with the previous Hartree function results (denoted by $\alpha_{d,\mathrm{H}}$) and the ratios $\alpha_{d,\mathrm{a}}/\alpha_{d,\mathrm{H}}$. It is seen that for the total $\alpha_d(\mathrm{Rb}^+)$ [excluding the small $(3d\rightarrow f)$ term], the reduction factor $\alpha_{d,\mathrm{a}}/\alpha_{d,\mathrm{H}}$ is 0.684, which, as expected, is close to the corresponding value for Cs$^+$, namely 0.671.

IV. SUMMARY AND DISCUSSION

We have recalculated the dipole polarizabilities α_d of the alkali atoms with the inclusion of the shielding function $f_0(r)$ of Sandars[3] in the perturbation equation.[29] The resulting values denoted by $\alpha_{t,\mathrm{b}}$ are somewhat smaller than those obtained in a previous calculation,[2] in which the effect of $f_0(r)$ was neglected. The maximum reduction of α_d occurs for Cs and amounts to 9.6% for $\alpha_{t,\mathrm{b}}$ [i.e., $\alpha_{t,\mathrm{b}}=61.19$ Å^3, α_t (Ref. 2) $=67.7$ Å^3; $61.19/67.7=0.904$]. Since there exists some evidence that the choice $f_0(r)$ may underestimate the actual $f(r)$, it seems more reasonable to choose the average $\alpha_{t,\mathrm{ab}}$ of the unshielded values $(\alpha_{t,\mathrm{a}})$ and the shielded values $(\alpha_{t,\mathrm{b}})$, as an approximation to the "true" theoretical values of α_d. The resulting values of $\alpha_{t,\mathrm{ab}}$ for the five alkali atoms are given in Eq. (28), and they are in very good agreement with the experimental results of Hall and Zorn,[4] which are listed in Table II. In particular, the theoretical results reproduce the experimental facts that: (a) There is a large increase in α_d in going from Na to K (from ~24 Å^3 to ~45 Å^3); (b) The value of α_d increases by less than 10% in going from K to Rb (~45 Å^3 for K; ~49 Å^3 for Rb); (c) There is a second noticeable increase of α_d in going from Rb to Cs (from ~49 Å^3 for Rb to ~ 63 Å^3 for Cs).

TABLE IV. The terms $\alpha_{d,\mathrm{a}}(nl\rightarrow l')$ and $\alpha_{d,\mathrm{H}}(nl\rightarrow l')$, and the ratios $\alpha_{d,\mathrm{a}}/\alpha_{d,\mathrm{H}}$ for the polarizability of the Rb$^+$ ion. The values of $\alpha_{d,\mathrm{a}}$ were obtained using the appropriate Hartree-Fock wave functions (Refs. 20 and 27) and pertain to the unshielded case. The values of $\alpha_{d,\mathrm{H}}(nl\rightarrow l')$ were obtained in a previous calculation using Hartree wave functions (see Ref. 5, Table III). All values of α_d are in units Å^3.

$\alpha_d(nl\rightarrow l')$	$\alpha_{d,\mathrm{a}}$	$\alpha_{d,\mathrm{H}}$	$\alpha_{d,\mathrm{a}}/\alpha_{d,\mathrm{H}}$
$\alpha_d(4s\rightarrow p)$	0.749	1.027	0.729
$\alpha_d(4p\rightarrow s)$	−0.667	−0.675	0.988
$\alpha_d(4p\rightarrow d)$	1.915	2.568	0.746
Sum	1.997	2.920	0.684

As indicated by the subscript t (for "total"), the calculated values of α_d include the contribution of the ion core (besides the dominant term due to the valence electron). The ion core term of α_d is given by Eq. (24) for $\alpha_{\mathrm{ion,eff}}$.

In Sec. III, we have recalculated α_d for the Rb$^+$ and Cs$^+$ ions, using the Hartree-Fock wave functions for Rb$^+$ and Cs$^+$, which had not been previously available, i.e., at the time when our previous calculations of Ref. 5 were performed. The use of the Hartree-Fock functions brings the calculated values into closer agreement with experiment. Thus $\alpha_{d,\mathrm{a}}(\mathrm{Cs}^+)=3.76$ Å^3, as compared to the experimental value $\alpha_{d,\mathrm{exp}}(\mathrm{Cs}^+)=3.14$ Å^3. [The previous result, using Hartree wave functions, was $\alpha_{d,\mathrm{H}}(\mathrm{Cs}^+)=5.60$ Å^3.] A similar improvement was obtained for Rb$^+$, in which case, $\alpha_{d,\mathrm{a}}=2.02$ Å^3, as compared to[14] $\alpha_{d,\mathrm{exp}}=1.80$ Å^3 and $\alpha_{\mathrm{d,H}}=2.92$ Å^3 (previous value).[30]

In the case of Cs$^+$, we also carried out the calculation of α_d using the shielding function $f_0(r)$ in the perturbation equations. The resulting α_d value, denoted by $\alpha_{d,\mathrm{b}}$, was found to be *smaller* than the range of the experimental values, namely $\alpha_{d,\mathrm{b}}(\mathrm{Cs}^+)=2.05$ Å^3, as compared to $\alpha_{d,\mathrm{exp}}$ in the range[14,22–25] from 2.42 to 3.14 Å^3. This discrepancy gives an indication that the function $f_0(r)$ of Sandars[3] probably underestimates the actual $f(r)$, as discussed above.

It should be noted that in recent years, calculations of the polarizabilities have been carried out by two methods which are, in principle, more accurate than the effective potential procedure[30] used in the present work. One of these methods is the fully coupled Hartree-Fock method, which has already been mentioned in Ref. 28. This procedure was originated by the work of Dalgarno,[31] Allen,[32] and Kaneko.[33] A comprehensive description of the various aspects of the coupled Hartree-Fock method has been given in the paper of Langhoff, Karplus, and Hurst.[34] The second procedure, which is based on the Brueckner-Goldstone technique,[35] was originated by Kelly,[36] and has been further elaborated by Chang, Pu, and Das.[37] The work of Lahiri and Mukherji[38] follows along the same lines as the coupled Hartree-Fock method.[31–33]

In connection with the calculations of the present work which pertain to all of the alkali atoms, it should be mentioned that the two methods discussed above are considerably more complicated than the procedure introduced by the author,[30] which has been used here. For essentially this reason, the fully coupled Hartree-Fock calculations of Lahiri and Mukherji[38] extend only to 10-electron systems with closed shells (e.g., F^-, Ne, and Na^+), and 18-electron systems (e.g., Cl^-, Ar, and K^+). Similarly, concerning the Brueckner-Goldstone technique, to our knowledge, this method has been used so far only for lithium,[37] beryllium,[36] and oxygen.[39]

Our value of $\alpha_d(\mathrm{Li}) = 24.84$ Å^3 is in excellent agreement with that of Lahiri and Mukherji[38] (coupled Hartree-Fock method; $\alpha_d = 25.2$ Å^3) and with that of Chang *et al.*[37] (Brueckner-Goldstone technique; $\alpha_d = 24.84$ Å^3). The paper of Chang *et al.*[37] discusses specifically the separate 1*s* and 2*s* contributions for lithium, as well as the intershell and intrashell consistency effects (see Table I). The consistency effects are found to be unimportant for the polarizability α_d, and in fact the intershell consistency term (-0.156 Å^3) has been taken into account in an approximate manner in the present calculations. Thus in the present context, this term corresponds to the term $-\alpha_c \xi_{v,\mathrm{b}}(r_1)$ in Eq. (24), which represents the moment induced in the 1*s* shell by the $2s \rightarrow p$ perturbation of the 2*s* electrons. With $\alpha_c = 0.029$ Å^3 and $\xi_{v,\mathrm{b}}(r_1) = 3.59$ (see Table II), we have $-\alpha_c \xi_{v,\mathrm{b}}(r_1) = -0.104$ Å^3, which is of the same order as the more accurate value (-0.156 Å^3) calculated by the diagrammatic approach in Ref. 37. In any case, this correction is very small compared to the total polarizability ($\sim 0.6\%$). This effect might be more important for the heavy alkali atoms, but, as discussed above, the corresponding ratio $-\alpha_{\mathrm{ion,eff}}/\alpha_{t,\mathrm{b}}$ is always small, reaching a maximum of 0.063 for Cs.

We can also compare the results obtained for the dipole shielding factor[13] ξ for the lithium atom (denoted by γ_d in Ref. 37) with those implied by the present work. The value $\xi_{v,\mathrm{a}} = 2.567$ obtained here (see Table I) is in good agreement with the result $\gamma_d = 2.752$ of Chang *et al.*,[37] considering that the 2*s* wave functions used in the two calculations are slightly different. The value $\gamma_d(1s) = 0.845$ (Ref. 37) is close to that expected from the hydrogenic result, $2/Z_e = 2/2.69 = 0.743$, assuming an effective charge $Z_e = 2.69$ for the 1*s* electrons of lithium.[40] Finally the "intershell consistency term" $\gamma_d = -2.508$ appears to correspond directly to the effect first pointed out by the present author in Ref. 2 (see p. 1223), namely the shielding term $\xi_{\mathrm{core,val}}$ produced by the dipole moment which is induced in the ion core by the induced dipole moment of the valence electron (2*s*). An approximate estimate of $\xi_{\mathrm{core,val}}$ is given by $-\xi_{v,\mathrm{b}}(r_1)\gamma_d(1s)$, or $-\xi_{v,\mathrm{b}}(r_1)(2/Z_e)$ using the hydrogenic approximation. With $\xi_{v,\mathrm{b}}(r_1) = 3.59$ (see Table II), these two estimates amount to -3.03 and -2.67, respectively. Both values are in reasonable agreement with the result -2.508 calculated in Ref. 37. Concerning the correlation effects, which were shown by Chang *et al.*[37] to be quite small for both α_d and γ_d, it should be noted that since our 2*s* wave function reproduces the experimental ionization potential, it already includes a large part of the effect of correlation with the 1*s* electrons, which is obtained in the diagrammatic approach of Chang, Pu, and Das.[37] A similar comment applies, of course, to the *ns* valence wave functions of the other alkalis, which also include to some extent the correlation effects with the corresponding ion cores.

In summary, we believe that the intershell consistency terms for α_d will be small in all cases, and are already approximately taken into account by the term $-\xi_{v,\mathrm{b}}(r_1)\alpha_c$ in Eq. (24) for $\alpha_{\mathrm{ion,eff}}$. This conclusion is also borne out by the results obtained by Lahiri and Mukherji[38] (first paper of Ref. 38; see Table IV), in which it is shown that the result of using the coupled Hartree-Fock method for the beryllium atom has a negligible effect on α_d (change from $44.40 a_{\mathrm{H}}^3$ to $44.46 a_{\mathrm{H}}^3$). [On the other hand, the effect on the dipole shielding factor β_∞ is very important, essentially because of the term $\xi_{\mathrm{core,val}}$, which changes the 1*s* contribution from a positive to a negative quantity, i.e., from $+0.501$ to -0.784.]

Besides the work of Refs. 34 and 38, we also note that similar calculations using the coupled Hartree-Fock method have been carried out by Dalgarno and co-workers,[41] by Cohen and Roothaan,[42] and by Kaneko and Arai.[43] As pointed out in Ref. 38, the values of the quadrupole antishielding factor[44] γ_∞ and of the quadrupole polarizability[6,25] α_q obtained by the author's method[6] (Sternheimer procedure) are generally in good agreement with those obtained by the more accurate coupled Hartree-Fock method. For the dipole polarizability α_d, the discrepancy between the two types of results is larger in some cases,[43] and for the dipole shielding factor,[13] it is essential to use the coupled Hartree-Fock method.[28] However, both in the quadrupole case and for the outer shells in the dipole case, the perturbed wave functions[16,26] obtained by the author's method[6] are expected to be quite accurate, and could be used as a first approximation in obtaining the corresponding solutions for the coupled Hartree-Fock method.

It is, of course, realized that the Sandars function $f_0(r)$ [Eq. (5)] represents a semi-empirical description of the shielding by the ion core. However, in the absence of calculations of the dipole shielding factor and the corresponding function $f(r)$ for atoms with $Z > 18$, such a choice seems to be the best that one can do, and moreover, the form of $f_0(r)$ is reasonable, since it has the correct value[13] at $r=0$, and slowly approaches 1 at radii $r \gtrsim \alpha_c^{1/3}$ [Eq. (6)]. The essential result of the present calculations is that the perturbed wave functions $u'_{1b}(ns \to p)$ [see Fig. 2] have their outermost maxima at such large radii that $f(r)$ is approximately 1 in this region, and hence the calculated polarizability α_d is reduced by a relatively small amount (< 10% in all cases). Thus the good agreement with the experimental values of α_d, which was previously found in Ref. 2, is maintained upon including the effect of $f(r)$. It is believed that the uncertainty of the theoretical values $\alpha_{t,\mathrm{b}}$ of Table II is probably smaller than the uncertainties of the experimental values of the alkali atom polarizabilities.

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[1] A preliminary account of this work has been presented at the February 1969 Meeting of the American Physical Society in New York. See Bull. Am. Phys. Soc. 14, 82 (1969).

[2] R. M. Sternheimer, Phys. Rev. 127, 1220 (1962).

[3] P. G. H. Sandars, Physics Letters 22, 290 (1966).

[4] W. D. Hall, University of Michigan Ph. D. thesis, 1967 (unpublished), p. 101; J. C. Zorn, private communication. See also W. D. Hall and J. C. Zorn, Bull. Am. Phys. Soc. 12, 131 (1967). Experimental values of the alkali atom polarizabilities α_d have been previously determined by H. Scheffers and J. Stark, Z. Physik 35, 625 (1934); A. Salop, E. Pollack, and B. Bederson, Phys. Rev. 124, 1431 (1961); G. E. Chamberlain and J. C. Zorn. Phys. Rev. 129, 677 (1963). Previous theoretical determinations of α_d for the alkali atoms (besides Ref. 2) have been reported in the following papers: D. R. Bates and A. Damgaard, Phil. Trans. Roy. Soc. (London) A242, 101 (1949); A. Dalgarno and A. E. Kingston, Proc. Phys. Soc. (London) A73, 455 (1959); P. M. Stone and J. R. Reitz, Phys. Rev. 131, 2101 (1963); M. Mizushima, J. D. Feichtner, and M. E. Hoover, Phys. Rev. 137, A702 (1965); A. Dalgarno and R. M. Pengelly, Proc. Phys. Soc. (London) 89, 503 (1966); K. Murakawa and M. Yamamoto, J. Phys. Soc. Japan 21, 821 (1966); P. W. Langhoff, M. Karplus, and R. P. Hurst, J. Chem. Phys. 44, 505 (1966); E. S. Chang, R. T. Pu and T. P. Das, Phys. Rev. 174, 16 (1968). For a review of measurements and calculations of atomic polarizabilities, see the article of B. Bederson and E. J. Robinson, in Advances in Chemical Physics, edited by J. Ross (Academic Press Inc., New York 1966), Vol. 10, p. 1.

[5] R. M. Sternheimer, Phys. Rev. 115, 1198 (1959). See Table III.

[6] R. M. Sternheimer, Phys. Rev. 86, 316 (1952); 95, 736 (1954); 105, 158 (1957); 107, 1565 (1957).

[7] R. F. Bacher and S. A. Goudsmit, Atomic Energy States (McGraw-Hill Book Company, Inc., New York, 1932).

[8] F. Seitz, Phys. Rev. 47, 400 (1935); W. Kohn and N. Rostoker, *ibid.* 94, 1111 (1954).

[9] W. Prokofjew, Z. Physik 48, 255 (1929).

[10] D. R. Hartree and W. Hartree, Proc. Cambridge Phil. Soc. 34, 550 (1938).

[11] J. Callaway and D. F. Morgan, Phys. Rev. 112, 334 (1958).

[12] R. M. Sternheimer, Phys. Rev. 78, 235 (1950).

[13] H. M. Foley, private communication; R. M. Sternheimer, Phys. Rev. 96, 951 (1954), see p. 963–965.

[14] J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. 92, 890 (1953).

[15] R. M. Sternheimer, M. Blume, and R. F. Peierls, Phys. Rev. 173, 376 (1968); R. M. Sternheimer, Phys. Rev. 164, 10 (1967); see the discussion on pages 13 and 15.

[16] Tables of the functions $u'_{1a}(ns \to p)$, $u'_{1b}(ns \to p)$, $u'_0(ns)$, and of the effective potentials V_0 and dV_0/dr are given in a supplementary paper (unpublished). For this supplementary material, order NAPS Document No. 00457 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th Street, New York, New York 10001; remitting $1.00 for microfiche or $3.00 for photocopies.

[17] H. Kopfermann, Nuclear Moments (Academic Press Inc., New York, 1958).

[18] P. G. H. Sandars and E. Lipworth, Phys. Rev. Letters 13, 718 (1964); J. P. Carrico, E. Lipworth, P. G. H. Sandars, T. S. Stein, and M. C. Weisskopf, Phys. Rev. 174, 125 (1968).

[19] R. M. Sternheimer, ADI Auxiliary Publications Project Document No. 6044, 1959, Library of Congress, Washington, D. C., (unpublished).

[20] R. E. Watson and A. J. Freeman, Phys. Rev. 124, 1117 (1961), and private communication.

[21] The value of $\alpha_d(4d \to f)$ for case b [perturbation $rf(r)$; cf. Eq. (5)] represents an estimate based on the value (0.13 Å^3) calculated without $f(r)$, and on the reduction expected from the results for $\alpha_d(5s \to p)$.

[22] K. Fajans and G. Joos, Z. Physik 23, 1 (1924).

[23] M. Born and W. Heisenberg, Z. Physik 23, 388 (1924).

[24] L. Pauling, Proc. Roy. Soc. (London) A114, 191 (1927).

[25] J. E. Mayer and M. G. Mayer, Phys. Rev. 43, 605 (1933).

[26] Tables of the perturbed wave functions $u_1'(nl \to l')$ as well as the unperturbed functions $u_0'(nl)$ pertaining to the calculations of Sec. III are given in a supplementary paper (unpublished). For this supplementary material, order NAPS Document No. 00457 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th Street, New York, New York 10001; remitting $1.00 for microfiche or $3.00 for photocopies.

[27] F. Herman and S. Skillman, Atomic Structure Calculations (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

[28] In addition to the perturbed wave functions $u_1'(nl \to l')$ for the Rb^+ and Cs^+ ions, the paper of Ref. 26 also contains tables of the corresponding perturbed functions $u_1'(nl \to l')_a$ [solutions of Eq. (29)] for the following four ions: Li^+, Na^+, K^+, and Cu^+. These wave functions had been used in an attempt to calculate the function $f(r)$ directly from the $u_1'(nl \to l')_a$, in order to compare with the semi-empirical Sandars function of Eq. (5). Since Eq. (29) was used to obtain the u_1', this procedure corresponds to the use of the uncoupled Hartree-Fock method, in the terminology of A. Dalgarno, Advan. Phys. 11, 281 (1962). After these calculations were completed, it was realized that only the so-called coupled Hartree-Fock method (in which the perturbation is made self-consistent) is adequate to give reliable values of $f(r)$, and, in particular, of $f(0) = 1 - \xi$, where ξ is the dipole shielding factor (introduced in reference 13), also denoted by β_∞. For an accurate calculation of $f(r)$, the most practical procedure appears to be that of J. Lahiri and A. Mukherji, J. Phys. Soc. Japan 21, 1178 (1966); Phys. Rev. 153, 386 (1967); 155, 24 (1967). An extensive review of the coupled Hartree-Fock perturbation scheme has been given by Dalgarno in the aforementioned reference.

[29] In this section (Sec. IV), we denote the semi-empirical Sandars approximation to the shielding function [Eq. (5)] by $f_0(r)$, to distinguish it from the actual shielding function [as obtained from the $u_1'(nl \to l')$], which is denoted by $f(r)$ (see also footnote 28).

[30] The method of the effective one-electron potential used in this paper [Eq. (29a)], which was introduced by the author (see Ref. 6), has been extensively used in calculations of atomic and molecular wave functions. See, for example, T. P. Das and R. Bersohn, Phys. Rev. 102, 733 (1956); K. J. Duff and T. P. Das, Phys. Rev. 168, 43 (1968); M. Karplus and H. J. Kolker, J. Chem. Phys. 38, 1263 (1963); J. I. Musher, Rev. Mod. Phys. 39, 203 (1967); J. I. Musher and R. Silbey, Phys. Rev. 174, 94 (1968); S. T. Epstein and J. H. Karl, J. Chem. Phys. 44, 4347 (1966).

[31] A. Dalgarno, Proc. Roy. Soc. (London) A251, 282 (1959).

[32] L. C. Allen, Phys. Rev. 118, 167 (1960).

[33] S. Kaneko, J. Phys. Soc. Japan 14, 1600 (1959).

[34] P. W. Langhoff, M. Karplus, and R. P. Hurst, J. Chem. Phys. 44, 505 (1966).

[35] K. A. Brueckner, Phys. Rev. 97, 1353 (1955); 100, 36 (1955); J. Goldstone, Proc. Roy. Soc. (London) A239, 267 (1957).

[36] H. P. Kelly, Phys. Rev. 131, 684 (1963); 136, B896 (1964); H. P. Kelly and H. S. Taylor, J. Chem. Phys. 40, 1478 (1964).

[37] E. S. Chang, R. T. Pu, and T. P. Das, Phys. Rev. 174, 16 (1968).

[38] J. Lahiri and A. Mukherji, J. Phys. Soc. Japan 21, 1178 (1966); Phys. Rev. 153, 386 (1967); 155, 24 (1967).

[39] H. P. Kelly, Phys. Rev. 144, 39 (1966).

[40] H. James, J. Chem. Phys. 2, 794 (1934).

[41] A. Dalgarno, Advan. Phys. 11, 281 (1962); A. Dalgarno and J. M. McNamee, Proc. Phys. Soc. (London) 77, 673 (1961); A. Dalgarno and H. A. J. McIntyre, *ibid.* 85, 47 (1965).

[42] H. D. Cohen and C. C. J. Roothaan, J. Chem. Phys. 43, S34 (1965); H. D. Cohen, *ibid.* 43, 3558 (1965); 45, 10 (1966).

[43] S. Kaneko and S. Arai, J. Phys. Soc. Japan 26, 170 (1969).

[44] R. M. Sternheimer, Phys. Rev. 84, 244 (1951); 105, 158 (1957); 146, 140 (1966); 159, 266 (1967); H. M. Foley, R. M. Sternheimer, and D. Tycko, *ibid.* 93, 734 (1954); R. M. Sternheimer and H. M. Foley, *ibid.* 102, 731 (1956).