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Electronic Polarizabilities of Ions*

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The dipole polarizability α_d has been calculated for several ions by solving the Schrödinger equation for the first-order perturbation of the wave functions of the core electrons. General results have been obtained for the number of nodes of the various types of perturbed wave functions ($nl \rightarrow l'$) in terms of the principal quantum number n. Tables of the perturbed wave functions for the Na^+ and Cl^- ions are presented. The results for α_d of Na^+, K^+, Rb^+, and Cs^+ are in reasonable agreement with those obtained in previous work. Calculations have also been carried out for the electric field at the nucleus due to the charge distribution induced in the ion by an external charge. Values of the quadrupole shielding constant γ_∞ have been obtained for several helium-like ions.

I. INTRODUCTION

THE electronic dipole polarizability α_d of several ions has been previously calculated by means of the Hartree and Hartree-Fock wave functions for the ions.[1,2] In this work, the inhomogeneous Schrödinger equation for the first-order perturbation of the wave functions was solved directly, without any expansion in terms of the eigenfunctions of the unperturbed Hamiltonian. In the present paper, we give the results of similar calculations for Hg^{++} and U^{6+}, which are the two heaviest ions for which Hartree wave functions are available. The purpose of these calculations was to determine the order of magnitude of the dipole polarizability α_d for large Z. The heaviest ion for which calculations were previously carried out is Cs^+, which gave[1] $\alpha_d = 5.03$ A^3. Hartree wave functions[3] for Cs^+ were used in this calculation, since Hartree-Fock functions are not available. Presumably the result for α_d would be somewhat reduced if Hartree-Fock functions (including exchange) were employed.

Besides the results for Hg^{++} and U^{6+}, we have also recalculated the dipole polarizabilities for the Na^+, Cl^-, K^+, Cu^+, Rb^+, and Cs^+ ions, which have been previously obtained in I. The present calculations are believed to be somewhat more accurate. With a few exceptions, the previous values of the various terms of α_d agree within $\sim 10\%$ with the present results.

The calculation of α_d for F^- given in I was carried out by means of the Hartree functions[4] for this ion, which were at that time the only ones available. In the meantime, Hartree-Fock wave functions for F^- have been obtained by Froese.[5] Since the effect of exchange on the wave functions is very important for negative ions, α_d of F^- was recalculated using the Hartree-Fock wave functions.[5]

The calculations of the perturbed wave functions are described in Sec. II. The resulting values of the polarizability α_d are discussed in Sec. III. In Sec. IV, we present a calculation of the electric field produced at the nucleus by the induced charge distribution, for the cases of F^- and Na^+. Section V gives the results of calculations for the following helium-like ions: H^-, He, Li^+, and Be^{++}. Values of the electric field at the nucleus and the quadrupole shielding constant γ_∞ have been obtained for these ions.

II. CALCULATIONS OF THE PERTURBED WAVE FUNCTIONS

The present calculations were carried out in the same manner as in I and II. α_d is given by

$$\alpha_d = \sum_{ns} \frac{8}{3} I(ns \rightarrow p) + \sum_{np} \left[\frac{8}{3} I(np \rightarrow s) + \frac{16}{3} I(np \rightarrow d) \right] + \sum_{nd} \left[\frac{16}{3} I(nd \rightarrow p) + 8I(nd \rightarrow f) \right], \quad (1)$$

where the sums extend over the filled ns, np, and nd shells, as indicated, and $I(nl \rightarrow l')$ denotes the following integral for each type of excitation:

$$I(nl \rightarrow l') = \int_0^\infty u_0'(nl) u_1'(nl \rightarrow l') r dr, \quad (2)$$

where l and l' are the azimuthal quantum numbers of the unperturbed wave function and the perturbation, respectively; u_0' is r times the radial unperturbed (Hartree or Hartree-Fock) wave function, normalized according to

$$\int_0^\infty u_0'^2 dr = 1. \quad (3)$$

In Eq. (2), u_1' is r times the radial part of the perturbation, and is determined by

$$\left[-\frac{d^2}{dr^2} + \frac{l'(l'+1)}{r^2} + V_0 - E_0 \right] u_1'(nl \rightarrow l') = u_0'(nl) r, \quad (4)$$

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[1] R. M. Sternheimer, Phys. Rev. **96**, 951 (1954). This paper will be referred to as I.

[2] R. M. Sternheimer, Phys. Rev. **107**, 1565 (1957). This paper will be referred to as II.

[3] D. R. Hartree, Proc. Roy. Soc. (London) **A143**, 506 (1934).

[4] D. R. Hartree, Proc. Roy. Soc. (London) **A151**, 96 (1935).

[5] C. Froese, Proc. Cambridge Phil. Soc. **53**, 206 (1957).

where V_0 is the unperturbed (spherically symmetric) potential, and E_0 is the unperturbed energy. In solving Eq. (4), the function V_0-E_0 is so chosen that it reproduces the unperturbed wave function u_0'. Thus V_0-E_0 is obtained from

$$V_0-E_0=\frac{1}{u_0'}\frac{d^2u_0'}{dr^2}-\frac{l(l+1)}{r^2}. \tag{5}$$

Equation (1) gives α_d in units a_H^3 (a_H=Bohr radius), and must be multiplied by $(0.529)^3=0.148$ to obtain α_d in units A^3. The terms of α_d [Eq. (1)] will be denoted by $\alpha_d(nl\rightarrow l')$. As was shown in I, the outermost filled shell (with principal quantum number n_0) makes the predominant contribution to α_d, so that terms with $n<n_0$ can usually be neglected.

For Cl^-, K^+, Cu^+, Rb^+, and Cs^+, the same unperturbed wave functions were used as in I, i.e., the Hartree-Fock functions[6,7] for Cl^-, K^+, and Cu^+, and the Hartree functions[3,4] for Rb^+ and Cs^+. For Na^+, we employed the Hartree-Fock functions obtained by Hartree and Hartree,[8] which are slightly more accurate than the wave functions of Fock and Petrashen[9] which were used in I. For Hg^{++} and U^{6+}, we used the Hartree functions obtained by Hartree and Hartree[10] for Hg^{++} and by Ridley[11] for U^{6+}. Unfortunately, Hartree-Fock wave functions (including exchange) are not available for these ions. As a result of the use of Hartree functions (without exchange), the calculated values of α_d are somewhat too large, since the Hartree-Fock functions are more internal than the Hartree functions. However, for U^{6+}, the overestimate of the present values is not expected to be important, because of the relatively tight binding of the outermost electrons ($6s$,$6p$) which arises from the large net charge Z_0 of the ion ($Z_0=6$).

The procedure of the numerical integration of Eq. (4) was as follows. In each case, the equation was integrated inward starting from a large radius r_1 ($\sim 6-10a_H$), with various assumed values of $u_1'(r_1)$. If δ_1 denotes the interval of integration in this region, the value of $u_1'(r_1+\delta_1)$ was obtained from the following equation [see Eq. (58) of I]:

$$u_1'(r_1+\delta_1)=u_1'(r_1)\exp[-|N(r_1)|^{\frac{1}{2}}\delta_1], \tag{6}$$

where $N(r)$ is defined by

$$N(r)\equiv\frac{l'(l'+1)}{r^2}+V_0-E_0-\frac{u_0'r}{u_1'}. \tag{7}$$

We note that if r_1 is chosen large enough, a small error in the initial slope, $[u_1'(r_1+\delta_1)-u_1'(r_1)]/\delta_1$, will have a negligible effect on the calculated values of u_1' in the region of the principal (outermost) maximum of u_0', which makes the predominant contribution to $\alpha_d(nl\rightarrow l')$.

In the region near the nucleus ($r\lesssim 0.4a_H$), the inhomogeneous term of Eq. (4) makes a negligible contribution. Moreover, the E_0 term on the left-hand side is relatively unimportant, so that small differences such as $E_0(ns)-E_0(np)$ can be neglected. As a result, $u_1'(ns\rightarrow p)$ is proportional to $u_0'(np)$ near $r=0$, and similarly $u_1'(np\rightarrow s)\propto u_0'(ns)$. Thus for the $ns\rightarrow p$ and $np\rightarrow s$ excitations, the unperturbed ns and np wave functions can be used up to $r\sim 0.4a_H$. The correct initial value of $u_1'(r_1)$ is then determined from the condition that the internal and external solutions should join smoothly at a radius $r_0\sim 0.4a_H$. More precisely, it was required that the value of $u_1'(r_0+\delta_0)/u_1'(r_0)$ be the same for the internal and external solutions, where δ_0 is the interval of the numerical integration at r_0.

For F^-, Na^+, K^+, and Cl^-, the d wave function pertaining to the internal solution for $n_0p\rightarrow d$ was obtained by outward numerical integration starting with a power series for $r<0.05a_H$. Similarly, for Hg^{++} $5d\rightarrow f$, the internal solution (up to $r\sim 0.4a_H$) was obtained by numerical integration, using values of the tabulated $4f$ wave function[10] to start the integration at $r=0.12a_H$. For Cs^+, $u_1'(5p\rightarrow d)$ was taken as proportional to the Hartree $4d$ function[3] up to $r=0.4a_H$, and similarly for Hg^{++}, $u_1'(5d\rightarrow p)\propto u_0'(5p)$, and for U^{6+}, $u_1'(6p\rightarrow d)\propto u_0'(5d)$ at the joining radius r_0.

Concerning the number of nodes of the solutions u_1', the following results were obtained. For $ns\rightarrow p$, $u_1'(ns\rightarrow p)$ behaves like an np function (for $n\geqq 2$) having $n-2$ nodes. [Of course, for $1s\rightarrow p$, u_1' behaves like $2p$ and has no node; see Eq. (18) of I.] For $np\rightarrow s$, u_1' has n nodes, like the s wave function with principal quantum number $n+1$. The outermost node of $u_1'(np\rightarrow s)$ was not obtained in the calculations of I, probably because the solution at large r was not obtained by inward integration, as was done in the present work. However, it was found that the outermost maximum of $u_1'(np\rightarrow s)$ generally does not contribute a large amount to the integral for $\alpha_d(np\rightarrow s)$ [Eq. (2)], so that the previous values[1] of $\alpha_d(np\rightarrow s)$ are not changed significantly, except for $3p\rightarrow s$ of Cl^-, as will be discussed below.

For $np\rightarrow d$, $u_1'(np\rightarrow d)$ has $n-3$ nodes (for $n\geqslant 3$), and thus behaves like $u_0'(nd)$. $u_1'(2p\rightarrow d)$ has no node, similarly to $u_1'(3p\rightarrow d)$. The case of $nd\rightarrow p$ is similar to $np\rightarrow s$: $u_1'(nd\rightarrow p)$ has $n-1$ nodes, and behaves like an $(n+1)p$ function. Finally, $u_1'(nd\rightarrow f)$ has $n-4$ nodes like an nf function (for $n\geqslant 4$). Moreover, $u_1'(3d\rightarrow f)$ has no node, similarly to $u_1'(4d\rightarrow f)$. In all cases, u_1' has the same sign as u_0' in the region of the outermost maximum of u_1'.

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[6] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A156**, 45 (1936); **A157**, 490 (1936).

[7] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A166**, 450 (1938).

[8] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A193**, 299 (1948).

[9] V. Fock and M. Petrashen, Physik. Z. Sowjetunion **6**, 368 (1934).

[10] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A149**, 210 (1935).

[11] E. C. Ridley, Proc. Roy. Soc. (London) **A243**, 422 (1957).

TABLE I. Perturbation of the wave functions for the Na^+ ion. The radius r is in units a_H.

r	$u_1'(2s \rightarrow p)$	$u_1'(2p \rightarrow s)$	$u_1'(2p \rightarrow d)$
0.02	−0.004	0.130	0.0000
0.04	−0.016	0.205	0.0001
0.06	−0.032	0.240	0.0003
0.08	−0.051	0.244	0.0007
0.10	−0.072	0.227	0.0013
0.12	−0.094	0.195	0.0021
0.14	−0.116	0.151	0.0032
0.16	−0.138	0.102	0.0045
0.18	−0.159	0.048	0.0061
0.20	−0.179	−0.007	0.0080
0.25	−0.225	−0.142	0.0137
0.30	−0.264	−0.262	0.0207
0.35	−0.296	−0.361	0.0287
0.40	−0.320	−0.435	0.0374
0.45	−0.337	−0.487	0.0466
0.50	−0.350	−0.519	0.0561
0.6	−0.361	−0.538	0.0750
0.7	−0.358	−0.513	0.0929
0.8	−0.347	−0.462	0.1091
0.9	−0.330	−0.398	0.1231
1.0	−0.309	−0.331	0.1346
1.1	−0.287	−0.264	0.1435
1.2	−0.264	−0.203	0.1498
1.4	−0.218	−0.100	0.1556
1.6	−0.176	−0.025	0.1533
1.8	−0.139	0.024	0.1450
2.0	−0.107	0.053	0.1327
2.2	−0.083	0.068	0.1185
2.4	−0.063	0.073	0.1040
2.6	−0.047	0.072	0.0898
2.8	−0.035	0.067	0.0763
3.0	−0.026	0.060	0.0643
3.2	−0.020	0.053	0.0538
3.4	−0.015	0.045	0.0447
3.6	−0.011	0.038	0.0368
3.8	−0.008	0.032	0.0299
4.0	−0.006	0.026	0.0239
4.5	−0.003	0.015	0.0134
5.0	−0.001	0.009	0.0076
5.5		0.005	0.0042
6.0		0.003	0.0023

The values of the perturbed wave functions for Na^+, namely, $u_1'(2s \rightarrow p)$, $u_1'(2p \rightarrow s)$, and $u_1'(2p \rightarrow d)$, are listed in Table I. In accordance with the results given above, the $2s \rightarrow p$ and $2p \rightarrow d$ functions have no node, whereas $u_1'(2p \rightarrow s)$ has two nodes (at $r = 0.20a_H$ and $1.7a_H$). Table I shows that the values of $u_1'(2p \rightarrow s)$ in the region of the outermost maximum are considerably smaller than those in the central maximum at $r \sim 0.6a_H$ (~ 0.07 as compared to ~ -0.5).

Table II gives the perturbed wave functions for Cl^-, namely, $2u_1'(3s \rightarrow p)$, $2u_1'(3p \rightarrow s)$, and $2u_1'(3p \rightarrow d)$. It may be noted that the values listed represent twice the normalized functions, as defined by Eqs. (3) and (4). The numbers of nodes are 1 for $3s \rightarrow p$, 3 for $3p \rightarrow s$, and 0 for $3p \rightarrow d$. In this case, the outermost maximum of $u_1'(3p \rightarrow s)$ is quite prominent, and makes a large contribution to $\alpha_d(3p \rightarrow s)$.[12]

The unperturbed $5s$ function and the $5s \rightarrow p$ perturbation $u_1'(5s \rightarrow p)$ for Cs^+ are shown in Fig. 1. Similarly, Fig. 2 shows the $5p$ function of Cs^+ and the corresponding perturbations, $u_1'(5p \rightarrow s)$ and $u_1'(5p \rightarrow d)$.

III. VALUES OF THE POLARIZABILITY α_d

The resulting values of $\alpha_d(n_0 l \rightarrow l')$ and the total α_d are listed in Table III. Except for the case of Cl^- $3p \rightarrow s$, the present values of $\alpha_d(n_0 l \rightarrow l')$ are in good agreement with those previously obtained[1] for Na^+, Cl^-, K^+, and Cs^+. Thus for Na^+, K^+, and Cs^+, the additional maximum of $u_1'(n_0 p \rightarrow s)$ is relatively weak, so that it has only a small effect on $\alpha_d(n_0 p \rightarrow s)$.

For Cl^- $3p \rightarrow s$, the outermost maximum is very pronounced, and actually changes the sign of $\alpha_d(3p \rightarrow s)$. The contribution of the $3p \rightarrow 3s$ excitation to $\alpha_d(3p \rightarrow s)$ was calculated and found to be -1.35 A^3. Thus the contribution to $\alpha_d(3p \rightarrow s)$ of s states lying above $3s$ is $\sim 1.35 + 0.50 = 1.85$ A^3. It was found that the effective potential $V_{0,3p}$ [Eq. (5)] of the $3p$ electrons of Cl^- does not have any bound s states above $3s$. This result is actually not surprising, since the valence electrons are very weakly bound in a negative ion. Thus the positive contribution to $\alpha_d(3p \rightarrow s)$ [which arises from the outermost maximum of $u_1'(3p \rightarrow s)$] is probably due to excitation to low-lying continuum s states.

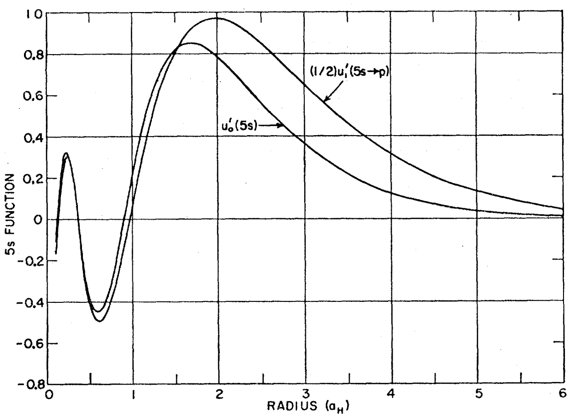

FIG. 1. The $5s$ function $u_0'(5s)$ and the $5s \rightarrow p$ perturbation $u_1'(5s \rightarrow p)$ for Cs^+. The wave functions are not shown for $r < 0.1a_H$.

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[12] Similar tables of the perturbed wave functions for the other ions considered in the present work (F^-, K^+, Cu^+, Rb^+, Cs^+, Hg^{++}, and U^{6+}) are given in a supplementary paper, "Wave Functions for Electronic Polarizabilities of Ions and Quadrupole Antishielding Factors." This paper also contains tables of the perturbed wave functions used to calculate the quadrupole polarizabilities of various ions [R. M. Sternheimer, Phys. Rev. **107**, 1565 (1957)], and the wave functions which determine the effect of the atomic core on the nuclear quadrupole coupling in ions and for atomic ground states and excited states [as obtained by R. M. Sternheimer and H. M. Foley, Phys. Rev. **102**, 731 (1956), and R. M. Sternheimer, Phys. Rev. **105**, 158 (1957)]. This supplementary paper has been deposited as Document No. 6044 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $8.75 for photoprints or $3.00 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

For Cs^+, we have calculated only the $5s \rightarrow p$, $5p \rightarrow s$, and $5p \rightarrow d$ terms. The small term $\alpha_d(4d \rightarrow f) = 0.16$ A^3 was taken from previous work.[1] For U^{6+}, the term $\alpha_d(5d \rightarrow f)$ was calculated, in order to verify that it is indeed small (0.14 A^3) compared to the effect of the $n_0 = 6$ terms (sum $= 1.20$ A^3).

Concerning $\alpha_d(2p \rightarrow d)$ for F^-, it may be noted that because the Hartree-Fock $2p$ function[5] is appreciably more internal than the Hartree $2p$ function used in I, this term is considerably reduced as compared to the result obtained in I (1.234 A^3 instead of the Hartree value[1] 3.11 A^3). The present result $\alpha_d(2p \rightarrow d) = 1.234$ A^3 is in very good agreement with the value 1.237 A^3 obtained by Burns[13] using a variational method. Similarly for Na^+ $2p \rightarrow d$, Burns' value is also in close agreement with our result: 0.132 A^3 as compared to 0.133 A^3. The good agreement with the result of the variational calculation is to be expected for the $2p \rightarrow d$ terms, since Burns assumes that $u_1'(np \rightarrow d)$ is given by $u_1' = u_0' f(r)$, where $f(r)$ is a polynomial in r. Thus u_1' has nodes at the same radii as u_0'. For $2p \rightarrow d$, where neither u_0' nor u_1' has any nodes, this procedure is fully justified. On the other hand, for the heavier ions with $3p \rightarrow d$, $4p \rightarrow d$, $\cdots$ modes of excitation, the assumption $u_1' = u_0' f(r)$ introduces an artificial node into the solution u_1'. The actual solution $u_1'(np \rightarrow d)$ has $n-3$ nodes (for $n \geqslant 3$), whereas $u_0'(np)$ has $n-2$ nodes. The existence of the extra node may account for the small discreancy between the variational results and the present values for K^+ $3p \rightarrow d$ (Burns: 0.972; ours: 1.148 A^3), Cl^- $3p \rightarrow d$ (Burns: 5.03; ours: 5.31 A^3), Rb^+ $4p \rightarrow d$ (Burns: 2.775; ours: 2.568 A^3), and Cs^+ $5p \rightarrow d$ (Burns: 5.79; ours: 4.94 A^3).

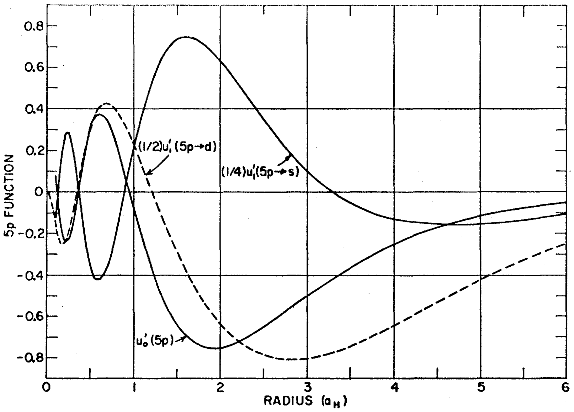

FIG. 2. The $5p$ function $u_0'(5p)$ and the perturbations $u_1'(5p \rightarrow s)$ and $u_1'(5p \rightarrow d)$ for Cs^+. The functions $u_0'(5p)$ and $u_1'(5p \rightarrow s)$ are not shown for $r < 0.1 a_\mathrm{H}$.

The positive sign of $\alpha_d(2p \rightarrow s)$ for F^- (+0.278 A^3) arises from the outermost maximum of u_1', in the same manner as for Cl^- $3p \rightarrow s$. The outer maximum occurs at $r = 3.8 a_\mathrm{H}$ (where $u_1' = 0.858$), whereas the central maximum is located at $r = 0.73 a_\mathrm{H}$ ($u_1' = -1.29$). Presumably, the predominant positive contribution is due to excitation of the $2p$ electrons into s states lying above $2s$.

TABLE II. Perturbation of the wave functions for the Cl^- ion. The radius r is in units a_H.

r	$2u_1'(3s \rightarrow p)$	$2u_1'(3p \rightarrow s)$	$2u_1'(3p \rightarrow d)$
0.01	−0.013	0.659	0.000
0.02	−0.049	1.099	0.000
0.03	−0.100	1.366	−0.001
0.04	−0.165	1.492	−0.002
0.05	−0.239	1.502	−0.003
0.06	−0.316	1.426	−0.005
0.07	−0.396	1.280	−0.008
0.08	−0.477	1.085	−0.012
0.09	−0.558	0.852	−0.016
0.10	−0.638	0.598	−0.021
0.12	−0.782	0.045	−0.033
0.14	−0.909	−0.515	−0.048
0.16	−1.013	−1.047	−0.065
0.18	−1.094	−1.516	−0.085
0.20	−1.149	−1.919	−0.108
0.22	−1.187	−2.246	−0.133
0.24	−1.202	−2.493	−0.160
0.26	−1.194	−2.667	−0.189
0.28	−1.170	−2.768	−0.219
0.30	−1.130	−2.806	−0.250
0.35	−0.969	−2.649	−0.334
0.40	−0.744	−2.225	−0.423
0.45	−0.479	−1.599	−0.514
0.50	−0.193	−0.857	−0.606
0.55	0.098	−0.060	−0.697
0.60	0.387	0.739	−0.786
0.7	0.941	2.205	−0.960
0.8	1.445	3.389	−1.129
0.9	1.867	4.268	−1.295
1.0	2.207	4.848	−1.454
1.1	2.471	5.162	−1.606
1.2	2.660	5.248	−1.748
1.4	2.875	4.954	−2.001
1.6	2.922	4.239	−2.216
1.8	2.855	3.328	−2.394
2.0	2.721	2.369	−2.541
2.2	2.548	1.440	−2.658
2.4	2.355	0.589	−2.749
2.6	2.158	−0.162	−2.815
2.8	1.966	−0.810	−2.862
3.0	1.776	−1.354	−2.890
3.2	1.599	−1.803	−2.896
3.4	1.435	−2.163	−2.889
3.6	1.283	−2.446	−2.864
3.8	1.141	−2.660	−2.827
4.0	1.010	−2.817	−2.781
4.5	0.737	−3.013	−2.626
5.0	0.535	−3.000	−2.433
5.5	0.381	−2.856	−2.221
6.0	0.265	−2.618	−1.983
6.5	0.181	−2.356	−1.758
7.0	0.124	−2.081	−1.539
8	0.055	−1.554	−1.144
9	0.023	−1.123	−0.830
10	0.009	−0.794	−0.591
11		−0.549	−0.413
12		−0.371	−0.282
14		−0.153	−0.121
16		−0.057	−0.048

The term $\alpha_d(5d \rightarrow p)$ of Hg^{++} will now be discussed. This term is positive and relatively large (0.935 A^3). One might have expected that $\alpha_d(5d \rightarrow p)$ would be negative [and of the order of $\alpha_d(5d \rightarrow 5p)$], in simi-

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[13] G. Burns, Phys. Rev. (to be published). See also E. G. Wikner and T. P. Das, Phys. Rev. **107**, 497 (1957); M. Sundbom, Arkiv Fysik **13**, 539 (1958); L. C. Allen (to be published).

TABLE III. Calculated and experimental values of the dipole polarizability α_d. The rows above α_d(calc) give the contributions to α_d of the various modes of excitation of the (outermost) shell with highest principal quantum number n_0. All values are in units A^3.

Ion	F^-	Na^+	Cl^-	K^+	Cu^+	Rb^+	Cs^+	Hg^{++}	U^{6+}
$\alpha_d(n_0s\rightarrow p)$	0.346	0.117	1.38	0.594	0.0737	1.027	2.01	0.202	0.945
$\alpha_d(n_0p\rightarrow s)$	0.278	−0.098	0.50	−0.501	−0.0753	−0.675	−1.51	−0.189	−1.195
$\alpha_d(n_0p\rightarrow d)$	1.234	0.133	5.31	1.148	0.1001	2.568	4.94	0.320	1.452
$\alpha_d(n_0d\rightarrow p)$					0.442			0.935	
$\alpha_d(n_0d\rightarrow f)$					0.441		0.16[a]	1.512[b]	0.142[b]
α_d(calc)	1.858	0.152	7.19	1.241	0.982	2.920	5.60	2.780	1.344
α_d(exp)	0.76-1.04	0.18-0.26	2.97-3.66	0.83-1.20	1.6	1.40-1.81	2.42-3.14		

[a] This term is due to $4d\rightarrow f$.

[b] This term is due to $5d\rightarrow f$.

larity to the $\alpha_d(n_0p\rightarrow s)$ terms of Na^+, K^+, Cs^+, Hg^{++}, and U^{6+}, which are predominantly due to $\alpha_d(n_0p\rightarrow n_0s)$. $\alpha_d(5d\rightarrow 5p)$ is given by

$$\alpha_d(5d\rightarrow 5p)=(0.148\ A^3)(16/3)a_{5p}J_{5p}, \tag{8}$$

where a_{5p} and J_{5p} are defined by

$$a_{5p}\equiv\int_0^\infty u_1'(5d\rightarrow p)u_0'(5p)dr, \tag{9}$$

$$J_{5p}\equiv\int_0^\infty u_0'(5p)u_0'(5d)rdr. \tag{10}$$

It may be noted that a_{5p} is also given by

$$a_{5p}\cong J_{5p}/(E_{5p}-E_{5d}), \tag{11}$$

where E_{5p} and E_{5d} are the unperturbed $5p$ and $5d$ energies. Since $E_{5p}<E_{5d}$, the negative sign of $\alpha_d(5d\rightarrow 5p)$ is obtained directly from Eqs. (8) and (11). From Eqs. (8)–(10), one finds $\alpha_d(5d\rightarrow 5p)=-0.358\ A^3$.

Since the total $\alpha_d(5d\rightarrow p)$ is positive and ~2.6 times $|\alpha_d(5d\rightarrow 5p)|$, it was expected that the $5d\rightarrow 6p$ excitation may make a large contribution. In order to verify this possibility, the $6p$ wave function $u_0'(6p)$ was obtained for the effective potential $V_{0,5d}$ of the $5d$ electrons. It was found that $E_{6p}-E_{5d}=0.813$ ry. The term $\alpha_d(5d\rightarrow 6p)$ is given by

$$\begin{aligned}\alpha_d(5d\rightarrow 6p)&=(0.148\ A^3)(16/3)a_{6p}J_{6p}\\&\cong(0.148\ A^3)(16/3)J_{6p}^2/(E_{6p}-E_{5d}),\end{aligned} \tag{12}$$

where a_{6p} and J_{6p} are obtained from Eqs. (9) and (10) by replacing $5p$ by $6p$. From the first expression of (12), involving $a_{6p}J_{6p}$, one finds $\alpha_d(5d\rightarrow 6p)=1.186\ A^3$. It may be noted that from the second expression which involves $J_{6p}^2/(E_{6p}-E_{5d})$, one obtains $\alpha_d(5d\rightarrow 6p)=1.156\ A^3$, in good agreement with the preceding result ($1.186\ A^3$).

Upon taking the sum $\alpha_d(5d\rightarrow 5p)+\alpha_d(5d\rightarrow 6p)=-0.358+1.186=0.828\ A^3$, one sees that the predominant term is $\alpha_d(5d\rightarrow 6p)$, while the higher excited states above $6p$ make only a small contribution: $0.935-0.828=0.107\ A^3$. The situation for $\alpha_d(5d\rightarrow p)$ of Hg^{++} is similar to that of $\alpha_d(2p\rightarrow s)$ of F^- and $\alpha_d(3p\rightarrow s)$ of Cl^-, where the excited states above n_0s make the predominant contribution, which determines the positive sign of the integral, as discussed above.

The term $\alpha_d(3d\rightarrow p)$ of Cu^+ is very similar to the term $\alpha_d(5d\rightarrow p)$ of Hg^{++}, which has just been discussed. Thus $\alpha_d(3d\rightarrow p)$ is positive and relatively large ($+0.442\ A^3$). This is probably mainly due to excitation of the $3d$ electrons into $4p$ and higher excited p states. In the previous calculation (see Table I of I), the value of $\alpha_d(3d\rightarrow p)$ was found to be small and negative ($-0.084\ A^3$). The other terms of α_d are not changed appreciably, so that the total α_d is increased from $0.470\ A^3$ to $0.982\ A^3$. This value is still somewhat lower than the experimental result $\alpha_d(\text{exp})=1.6\ A^3$, obtained by Tessman, Kahn, and Shockley,[14] but the disagreement is no longer as serious as was believed previously.[1] Unfortunately, the only experimental value of α_d available is that of Tessman *et al.*[14] In this connection, we note that for Ca^{++}, Sr^{++}, and Ba^{++}, where several determinations of α_d exist, the result of Tessman *et al.*[14] (see Table VI of their paper) exceeds other values by the following amounts: for Ca^{++}, $1.1-0.5=0.6\ A^3$; for Sr^{++}, $1.6-0.86=0.74\ A^3$; for Ba^{++}, $2.5-1.6=0.9\ A^3$. Since the discrepancy for Cu^+ is $\sim 0.6\ A^3$, it is quite possible that a major part of the disagreement is due to the uncertainties in the experimental determination of α_d.

On the basis of numerical estimates, it is believed that the accuracy of the various terms of α_d is within ±3%, which is probably also the limit of error of the perturbed wave functions $u_1'(nl\rightarrow l')$ at various radii r, except in the regions of r where u_1' goes through a zero.

The range of the experimental values of α_d is listed in the last row of Table III. This range of α_d was obtained from a consideration of the results of Tessman, Kahn, and Shockley,[14] Pauling,[15] Born and Heisenberg,[16] and Fajans and Joos.[17] Table III shows that for Na^+ and K^+, the calculated α_d lies essentially in the range of the experimental values, whereas for F^-, Cl^-, Rb^+, and Cs^+, the theoretical value is larger than α_d(exp) by a factor of ~2. The agreement for Na^+ and K^+ is probably due to the use of Hartree-Fock wave functions

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[14] Tessman, Kahn, and Shockley, Phys. Rev. **92**, 890 (1953).

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

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

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

in the calculations, and the fact that in positive ions, the outer electrons are relatively tightly bound, and therefore the wave functions are not very sensitive to the effects of electrostatic correlation between the electrons, which are not included in the Hartree-Fock equations. For F^- and Cl^-, although Hartree-Fock wave functions were used, the effects of correlation are expected to be important, because the outermost ($2p$ or $3p$) electrons are very weakly bound. It may be noted that for F^-, the effect of including exchange has reduced the calculated value from 3.20 A^3 (Hartree functions)[1] to 1.86 A^3 (Hartree-Fock), i.e., by a factor 1.7. Thus it is quite possible that the inclusion of correlation, which would make the Hartree-Fock wave functions more internal, would decrease the theoretical value of α_d for F^- by an additional factor of ~ 2, and bring it into agreement with experiment. The same remarks apply to Cl^-. For Rb^+ and Cs^+, the use of the Hartree functions (excluding both exchange and correlation) probably accounts for the overestimate of α_d.

For Hg^{++} and U^{6+}, experimental values of α_d do not seem to be available. The fact that the calculated $\alpha_d(U^{6+})$ is considerably smaller than $\alpha_d(Hg^{++})$ is probably mainly due to the larger net charge of the U^{6+} ion. Upon comparing the calculated values of $\alpha_d(Hg^{++})$ and $\alpha_d(U^{6+})$ with that of $\alpha_d(Cs^+)$ ($=5.60$ A^3), it is seen that α_d does not increase with Z beyond $Z\sim 50$. Instead, there is actually a decrease of α_d in going from Cs^+ to Hg^{++}. This decrease is probably due in part to the increase of the net charge Z_0 of the ion. The effect of a change of Z_0 is very pronounced, as can be seen from a comparison of $\alpha_d(Hg^{++})$ and $\alpha_d(U^{6+})$, or $\alpha_d(Cl^-)$ and $\alpha_d(K^+)$.

TABLE IV. Contributions to the electric field at the nucleus due to the perturbation of the wave functions induced by an external charge. ξ is the induced field in units e/R^2. The last three rows give the total calculated ξ, the actual value of $\xi(=1-Z_0/Z)$, and the ratio $\rho=\xi(\text{calc})/(1-Z_0/Z)$.

Ion	F^-	Na^+
$\xi(1s\rightarrow p)$	0.230	0.187
$\xi(2s\rightarrow p)$	1.374	1.027
$\xi(2p\rightarrow s)$	−1.841	−1.125
$\xi(2p\rightarrow d)$	1.670	1.063
$\xi(\text{calc})$	1.433	1.152
$1-Z_0/Z$	1.111	0.909
ρ	1.290	1.267

IV. ELECTRIC FIELD AT THE NUCLEUS

A sensitive test of the accuracy of the zero-order wave functions u_0' and the perturbed functions u_1' can be obtained by calculating the electric field at the nucleus $\mathbf{E}_{\text{ind}}$ due to the distribution of charge induced in the ion by an external charge placed at a large distance $x=R$ from the nucleus. The quantity $\mathbf{E}_{\text{ind}}$ is of interest, because its exact value is known from an argument first proposed by Feynman.[18] As shown in I [Eq. (113)], from the fact that the net force on the nucleus in the x direction is $-Z_0e^2/R^2$, one finds that the component $E_{\text{ind},x}$ along the x axis is given by

$$E_{\text{ind},x}=\frac{e}{R^2}\left(1-\frac{Z_0}{Z}\right), \tag{13}$$

where Z_0 is the net charge of the ion, and it has been assumed that the external charge is a unit positive charge ($+e$) placed along the positive x axis at a distance R.

In terms of the perturbed wave functions u_1', $E_{\text{ind},x}$ is given by [see Eqs. (119) and (120) of I]

$$E_{\text{ind},x}=\frac{e}{R^2}\Bigg\{\sum_{ns}\frac{8}{3}K(ns\rightarrow p)+\sum_{np}\left[\frac{8}{3}K(np\rightarrow s)+\frac{16}{3}K(np\rightarrow d)\right]+\sum_{nd}\left[\frac{16}{3}K(nd\rightarrow p)+8K(nd\rightarrow f)\right]\Bigg\}, \tag{14}$$

where the sums extend over the filled s, p, and d shells, and $K(nl\rightarrow l')$ denotes the following radial integral:

$$K(nl\rightarrow l')=\int_0^\infty u_0'(nl)u_1'(nl\rightarrow l')r^{-2}dr. \tag{15}$$

It may be noted that, aside from the factor e/R^2, $E_{\text{ind},x}$ differs from the expression for α_d only through the replacement of $I(nl\rightarrow l')$ by $K(nl\rightarrow l')$ [see Eq. (1)].

We denote $E_{\text{ind},x}/(e/R^2)$ by ξ, so that the actual value of ξ is $1-Z_0/Z$. The quantity ξ is given by the curly bracket of Eq. (14). The terms of ξ will be denoted by $\xi(nl\rightarrow l')$. ξ was calculated from the perturbed wave functions for the cases of F^- and Na^+. The results of the calculations are given in Table IV. For $2s\rightarrow p$, $2p\rightarrow s$, and $2p\rightarrow d$, the values of $K(nl\rightarrow l')$ were obtained by numerical integration over the functions u_0' and u_1'. For $1s\rightarrow p$, it was assumed that u_0' can be approximated by a hydrogenic wave function with an appropriate effective Z, obtained by means of Slater's[19] screening constant for $1s$ (0.30). Thus

$$u_0'(1s)=2Z_e^{\frac{3}{2}}r\exp(-Z_er), \tag{16}$$

with $Z_e\equiv Z-0.30$. As shown in I [Eq. (18)], the corresponding u_1' is given by

$$u_1'(1s\rightarrow p)=Z_e^{-\frac{1}{2}}r^2\exp(-Z_er)[1+\tfrac{1}{2}Z_er], \tag{17}$$

whence

$$\xi(1s\rightarrow p)=\frac{8}{3}\int_0^\infty u_0'(1s)u_1'(1s\rightarrow p)r^{-2}dr=\frac{2}{Z_e}. \tag{18}$$

The values of $2/Z_e$ are listed in Table IV. It is seen that both for F^- and Na^+, the calculated ξ exceeds the

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[18] R. P. Feynman, Phys. Rev. **56**, 340 (1939).

[19] J. C. Slater, Phys. Rev. **36**, 57 (1930).

actual value $1-Z_0/Z$. The ratio ρ of the calculated to the actual value, $\rho\equiv\xi(\text{calc})/(1-Z_0/Z)$, is given in the last row of the table. Similar calculations were carried out in I (Table V). The values of ρ obtained in I were 2.05 for F^- and 1.49 for Na^+, as compared to 1.29 and 1.27, respectively, from the present work. It is seen that for F^- in particular, the present value of ξ represents a marked improvement, as was to be expected from the result for α_d. This improvement arises both from the use of Hartree-Fock wave functions, which mainly decreases $\xi(2p\rightarrow d)$, and from the more accurate determination of $u_1'(2p\rightarrow s)$ which leads to a more negative value of $\xi(2p\rightarrow s)$ (present value -1.841, as compared to -1.29 obtained in I).

The use of the hydrogenic approximation for $1s$ introduces some uncertainty in the preceding results. However, even if one assumes an uncertainty of $\pm 20\%$ of the value used $(2/Z_e)$, this leads to a maximum error of only ± 0.04 in ρ for both F^- and Na^+.

For the heavier ions (Cl^-, K^+, $\cdots$), values of ξ have not been obtained, because the required $2s\rightarrow p$, $2p\rightarrow s$, and $2p\rightarrow d$ perturbed wave functions have not been determined for these ions. In contrast to the situation for α_d, the inner shells are expected to make a significant contribution to ξ, essentially because the integrand of K involves the factor r^{-2}, which weights more heavily the region near the nucleus [as compared to the factor r for $I(nl\rightarrow l')$].

It should be pointed out that the calculation of $E_{\text{ind},x}$ may provide a sensitive test for a set of Hartree or Hartree-Fock wave functions for any given ion or neutral atom. (In the latter case, the actual value of ξ is 1.) The value of ρ would then be a criterion for the accuracy of the zero-order wave functions. The calculation of $E_{\text{ind},x}$ probably tests parts of the wave functions which are, on the average, closer to the nucleus than the more external regions which make the predominant contribution to the energy eigenvalue E_0. Thus the value of ρ could be used as an independent criterion, besides the calculation of E_0 for the various electron shells.

V. CALCULATIONS FOR THE HELIUM-LIKE IONS

We have previously obtained solutions[2] for the perturbed wave functions for the following helium-like ions: H^-, He, Li^+, and Be^{++}, for both the dipole polarizability ($1s\rightarrow p$ excitation) and the quadrupole polarizability ($1s\rightarrow d$ excitation). In these calculations, the zero-order $1s$ wave functions u_0' were taken from the work of Löwdin.[20] The dipole perturbation $u_1'(1s\rightarrow p)$ was obtained by means of Eq. (4) (with $l'=1$). The quadrupole perturbation $u_1'(1s\rightarrow d)$ was determined from a numerical solution of the equation

$$\left(-\frac{d^2}{dr^2}+\frac{6}{r^2}+V_0-E_0\right)u_1'(1s\rightarrow d)=u_0'(1s)r^2. \quad (19)$$

The function V_0-E_0 was obtained from the Löwdin wave functions by means of Eq. (5).

The solutions $u_1'(1s\rightarrow p)$ and $u_1'(1s\rightarrow d)$ were used in II to obtain the dipole and quadrupole polarizabilities α_d and α_q (see Table I of II). In connection with the discussion of the preceding section, it is of interest to obtain the electric field at the nucleus $E_{\text{ind},x}$ and the resulting value of ρ. ξ is given by

$$\xi=\frac{8}{3}\int_0^\infty u_0'(1s)u_1'(1s\rightarrow p)r^{-2}dr. \quad (20)$$

The second, third, and fourth columns of Table V list the values of ξ, $1-Z_0/Z$, and $\rho=\xi/(1-Z_0/Z)$. For comparison, we have also given the values of ρ (here denoted by ρ_a) which were obtained in I (see Table V) by means of an analytic approximation to the solutions $u_1'(1s\rightarrow p)$. It is seen that both for H^- and He, the more accurate numerical solution leads to an appreciably lower value of ρ than the approximate analytic solution of I. For Li^+ and Be^{++}, the values of ρ and ρ_a agree within the accuracy of the calculations.

The perturbation $u_1'(1s\rightarrow d)$ can be used to obtain the quadrupole shielding constant[21] γ_∞. For a nucleus with electric quadrupole moment Q, γ_∞ is defined as the ratio of the quadrupole moment induced in the electron core to the nuclear Q. γ_∞ is taken as positive if the induced quadrupole moment tends to shield the nuclear Q, as is the case here. Alternatively, γ_∞ can be defined in terms of the field gradient at the nucleus due to an external charge. For a charge $+e$ placed at $x=R$, the field gradient due to the charge alone is given by $(dE_x/dx)_0=-2e/R^3$. In addition, there will be a contribution due to the charge distribution induced in the ion. This term can be written as $\Delta(dE_x/dx)=+2e\gamma_\infty/R^3$, where γ_∞ is the same quantity as defined above. Thus the total field gradient at the nucleus, dE_x/dx, is given by

$$dE_x/dx=-(2e/R^3)(1-\gamma_\infty). \quad (21)$$

TABLE V. Calculated values of ξ, ρ, and γ_∞ for several helium-like ions. The values of ρ were obtained from the present calculations, using the numerical solutions $u_1'(1s\rightarrow p)$ determined in II. The values of ρ_a were found in I from an analytic approximation to the solutions $u_1'(1s\rightarrow p)$. The shielding constants γ_∞ were obtained in the present work. γ_∞(DB) and γ_∞(S) are the values of γ_∞ previously determined by Das and Bersohn[a] and by Schwartz.[b]

Ion	ξ	$1-Z_0/Z$	ρ	ρ_a	γ_∞	γ_∞(DB)	γ_∞(S)
H^-	3.251	2	1.63	1.91	1.131	1.141	1.080
He	1.261	1	1.26	1.32	0.424	0.416	0.413
Li^+	0.795	0.667	1.19	1.19	0.263	0.256	0.255
Be^{++}	0.569	0.5	1.14	1.13	0.189	0.185	0.185

[a] See reference 23.

[b] See reference 24.

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[20] P. O. Löwdin, Phys. Rev. **90**, 120 (1953).

[21] R. M. Sternheimer, Phys. Rev. **80**, 102 (1950); **84**, 244 (1951); Foley, Sternheimer, and Tycko, Phys. Rev. **93**, 734 (1954); R. M. Sternheimer and H. M. Foley, Phys. Rev. **92**, 1460 (1953); **102**, 731 (1956).

It has been shown[21] that for medium and heavy ions, γ_∞ is negative and very large (of order 10–100). The resulting antishielding of the nuclear quadrupole moment has important effects both for the quadrupole coupling of polar molecules and ionic crystals, and for the relaxation times in nuclear magnetic resonance experiments.[21,22]

For an ion with only a filled 1*s* shell, γ_∞ is given by

$$\gamma_\infty=\frac{8}{5}\int_0^\infty u_0'(1s)u_1'(1s\rightarrow d)r^{-3}dr. \tag{22}$$

The resulting values of γ_∞ are listed in the sixth column of Table V. The last two columns [marked γ_∞(DB) and γ_∞(S)] give the values of γ_∞ previously obtained by Das and Bersohn[23] and by Schwartz.[24] It is seen that the present results for γ_∞ are in good agreement with those of references 23 and 24.

Note Added in Proof.—Additional calculations of polarizabilities and antishielding factors have been carried out for the Na$^+$, K$^+$, and B$^+$ ions. For the case of Na$^+$, the Fock-Petrashen[9] wave functions were used in II to calculate the quadrupole polarizability α_q. Since the Na$^+$ Hartree-Fock wave functions obtained by Hartree and Hartree[8] are believed to be somewhat more accurate than the Fock-Petrashen[9] functions, the perturbed wave functions $u_1'(2s\rightarrow d)$ and $u_1'(2p\rightarrow f)$ were recalculated using $u_0'(2s)$ of reference 8, and $u_0'(2p)$ of Löwdin,[20] which closely approximates the 2*p* function of Hartree and Hartree.[8] The function $u_1'(2p\rightarrow p)$ pertaining to the Löwdin wave function[20] has been obtained previously.[25] The results for the terms of α_q are as follows: $\alpha_q^{(1)}(2s\rightarrow d)=0.0102$ A^5, $\alpha_q^{(1)}(2p\rightarrow p)=0.0218$ A^5, $\alpha_q^{(1)}(2p\rightarrow f)=0.0314$ A^5, giving for the total α_q of Na$^+$: $\alpha_q^{(1)}=0.0634$ A^5. These results may be compared with the corresponding values for the Fock-Petrashen functions, as obtained in II: $\alpha_q^{(2)}(2s\rightarrow d)=0.0133$ A^5, $\alpha_q^{(2)}(2p\rightarrow p)=0.0173$ A^5, $\alpha_q^{(2)}(2p\rightarrow f)=0.0256$ A^5, which give $\alpha_q^{(2)}=0.0562$ A^5. It is seen that $\alpha_q^{(1)}(2s\rightarrow d)$ is smaller than $\alpha_q^{(2)}(2s\rightarrow d)$, whereas $\alpha_q^{(1)}(2p\rightarrow p)$ and $\alpha_q^{(1)}(2p\rightarrow f)$ are larger than the corresponding values $\alpha_q^{(2)}(2p\rightarrow p)$ and $\alpha_q^{(2)}(2p\rightarrow f)$ obtained from the Fock-Petrashen wave functions. These results arise from the fact that the 2*s* function of Hartree and Hartree[8] is slightly more internal than the 2*s* function of Fock and Petrashen,[9] whereas for $u_0'(2p)$, the function of Hartree and Hartree[8] is somewhat more external than that of Fock and Petrashen.[9] The present values for $\alpha_q^{(1)}(nl\rightarrow l')$ are in good agreement with the results obtained by Burns[13] by means of a variational calculation using the wave functions of reference 8: $\alpha_q^B(2s\rightarrow d)=0.0101$ A^5, $\alpha_q^B(2p\rightarrow p)=0.0226$ A^5, $\alpha_q^B(2p\rightarrow f)=0.0322$ A^5.

From the wave functions $u_1'(nl\rightarrow l')$ one can obtain the contributions $\gamma_\infty(nl\rightarrow l')$ to the quadrupole antishielding factor γ_∞. $\gamma_\infty(nl\rightarrow l')$ is given by

$$\gamma_\infty(nl\rightarrow l')=c(nl\rightarrow l')\int_0^\infty u_0'(nl)u_1'(nl\rightarrow l')r^{-3}dr, \tag{23}$$

where $c(nl\rightarrow l')$ is a constant which has the following values: $c(ns\rightarrow d)=8/5$, $c(np\rightarrow p)=48/25$, $c(np\rightarrow f)=72/25$. One thus obtains for Na$^+$, using the wave functions of references 8 and 20: $\gamma_\infty(2s\rightarrow d)=0.234$, $\gamma_\infty(2p\rightarrow p)=-5.16$, $\gamma_\infty(2p\rightarrow f)=0.303$. $\gamma_\infty(1s\rightarrow d)$ is approximately given by[21] $(2/3)Z_e^{-1}=0.062$. Thus the total γ_∞ due to the angular modes of excitation ($ns\rightarrow d$ and $np\rightarrow f$) is: $\gamma_\infty(\text{ang})=0.599$, and the total γ_∞ for Na$^+$ [$=\gamma_\infty(2p\rightarrow p)+\gamma_\infty(\text{ang})$] is -4.56. The present results for $\gamma_\infty(nl\rightarrow l')$ can be compared with the corresponding values of Das and Bersohn[22]: $\gamma_\infty^{DB}(1s\rightarrow d)=0.064$, $\gamma_\infty^{DB}(2s\rightarrow d)=0.326$, $\gamma_\infty^{DB}(2p\rightarrow p)=-5.23$, $\gamma_\infty^{DB}(2p\rightarrow f)=0.304$. It is seen that there is good agreement, except for the term $\gamma_\infty(2s\rightarrow d)$. The reason for the discrepancy in this case may be a shortcoming of the variational method used by Das and Bersohn.[23] Thus the actual perturbed function $u_1'(2s\rightarrow d)$ has no node,[12] whereas the variational function of reference 23 has one node, being proportional to $u_0'(2s)$. Inside the node of $u_0'(2s)$ at $r=0.20a_H$, the functions $u_0'(2s)$ and $u_1'(2s\rightarrow d)$ have therefore opposite sign, so that the actual contribution to the integral of Eq. (23) is negative, whereas the variational calculation gives a positive integrand for all *r*. Thus the absence of a node in the function $u_1'(2s\rightarrow d)$ will act to reduce $\gamma_\infty(2s\rightarrow d)$, in agreement with the results obtained above.

For K$^+$, values of the terms $\gamma_\infty(nl\rightarrow l')$ have been obtained from the wave functions $u_1'(nl\rightarrow l')$ calculated in II, and from the wave functions $v_1'(nl\rightarrow l')$ determined[26] in III, which represent the distortion of the electron core by a nuclear quadrupole moment *Q*. [These functions were called $u_1'(nl\rightarrow l')$ in III, but we use the notation v_1' here in order to avoid confusion with the present functions u_1' which pertain to the perturbation due to an external charge.] In the calculation of v_1' in III, the Hartree-Fock functions for K$^+$ were used[7] for u_0'. In terms of v_1', $\gamma_\infty(nl\rightarrow l')$ is given by

$$\gamma_\infty(nl\rightarrow l')=c(nl\rightarrow l')\int_0^\infty u_0'(nl)v_1'(nl\rightarrow l')r^2dr. \tag{24}$$

From Eq. (24), the following results were obtained: $\gamma_\infty(1s\rightarrow d)=0.0368$, $\gamma_\infty(2s\rightarrow d)=0.1016$, $\gamma_\infty(2p\rightarrow p)=-1.219$, $\gamma_\infty(2p\rightarrow f)=0.1366$, $\gamma_\infty(3s\rightarrow d)=0.298$, $\gamma_\infty(3p\rightarrow p)=-17.15$, $\gamma_\infty(3p\rightarrow f)=0.478$. Thus the total γ_∞ due to the angular modes is: $\gamma_\infty(\text{ang})=1.051$. The total γ_∞ for K$^+$ is given by

$$\gamma_\infty(\text{K}^+)=\gamma_\infty(\text{ang})+\gamma_\infty(2p\rightarrow p)+\gamma_\infty(3p\rightarrow p)=-17.32. \tag{25}$$

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[22] E. G. Wikner and T. P. Das, Phys. Rev. **109**, 360 (1958).

[23] T. P. Das and R. Bersohn, Phys. Rev. **102**, 733 (1956).

[24] C. Schwartz, Ann. Phys. **6**, 170 (1959).

[25] R. M. Sternheimer and H. M. Foley, Phys. Rev. **102**, 731 (1956).

[26] R. M. Sternheimer, Phys. Rev. **105**, 158 (1957). This paper will be referred to as III.

As a check on some of the terms, values of $\gamma_\infty(nl \to l')$ were also obtained by means of Eq. (23) from the functions u_1' determined in II. The results are as follows: $\gamma_\infty(2p \to p) = -1.230$, $\gamma_\infty(3s \to d) = 0.303$, $\gamma_\infty(3p \to p) = -17.83$, $\gamma_\infty(3p \to f) = 0.485$. It is seen that these values are in good agreement with those obtained from v_1'. The maximum deviation occurs for $\gamma_\infty(3p \to p)$, where the difference amounts to 4%. The present results for the terms due to the radial $(np \to p)$ modes can be compared with those of Wikner and Das[22] who used a variational method and obtain: $\gamma_\infty{}^{WD}(2p \to p) = -1.22$, $\gamma_\infty{}^{WD}(3p \to p) = -13.03$. The agreement is very good for $\gamma_\infty(2p \to p)$, but for $3p \to p$, $\gamma_\infty{}^{WD}(3p \to p)$ is lower by 24% than the value obtained from the present work.

We have also calculated γ_∞ for the $(1s)^2(2s)^2$ core of the boron atom, using the wave functions $v_1'(1s \to d)$ and $v_1'(2s \to d)$ determined in III. These perturbed wave functions are based on the Hartree wave functions for boron obtained by Brown, Bartlett, and Dunn.[27] The results are: $\gamma_\infty(1s \to d) = 0.148$, $\gamma_\infty(2s \to d) = 0.620$, giving $\gamma_\infty(\mathrm{B}^+) = 0.768$.

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[27] Brown, Bartlett, and Dunn, Phys. Rev. 44, 296 (1933).

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Application of Wave Functions Containing Interelectron Coordinates. I. The Ground-State Energy of Lithium*

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Several years ago, Pluvinage made a substantial advance in the use of interelectron coordinates in atomic systems by illustrating how the Schrödinger equation can be partially separated in such a way that the interelectron potential no longer appears as the perturbing term. His method gave excellent results when used to obtain variational energies of helium-like systems. In this paper, the Pluvinage method is modified in such a way that it can be applied with a reasonable amount of labor to more complex systems. In this modification, the nuclear coordinates act like Fermi-Dirac "particles" filling the energy levels pairwise, while the interelectron coordinates act like Bose "particles," all of which pile into the lowest energy continuum state. An accurate approximation technique is also developed for use in integrating functions containing three or more interelectron coordinates over the space of the nuclear coordinates. The modified Pluvinage approach is used in conjunction with the approximation technique to calculate the ground-state energy of neutral lithium. Internal evidence indicates that the approximation technique is better than 99% accurate in evaluating the individual integrals which appear. Although the wave function used here has no adjustable parameters, it yields an energy value for lithium which is slightly better than the two-parameter value of Wilson.

1. INTRODUCTION

THE problem of suitably describing atomic systems has been attacked since the advent of Quantum Theory. The statistical theory of Thomas[1] and Fermi,[2] the self-consistent method of Hartree[3] and the methods of Slater[4] and Morse[5] are among the oldest and have been widely investigated. All of these methods deal, in essence, with the nuclear coordinates of the individual electrons. Although it has long been recognized that the interelectron potential within the atom is of comparable magnitude to the nuclear potential, little work was done originally in using interelectron coordinates explicitly. The well-known variational method of Hylleraas[6] does introduce the interelectron coordinates. However, the wave function is specified only after a variational calculation of the energy, and the method is consequently difficult to apply to excited states and to atoms much heavier than lithium. The method of configuration interaction as generalized by Löwdin[7] and applied by Tycko, Thomas, and King[8] shows excellent promise in treating the interelectron effects although the interelectron coordinates are not introduced in a direct manner. The recent approaches of Brueckner[9] and of Bohm and Pines[10] which also treat

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[1] L. H. Thomas, Proc. Cambridge Phil. Soc. 23, 542 (1927).

[2] E. Fermi, Z. Physik 48, 73 (1928).

[3] D. R. Hartree, Proc. Cambridge Phil. Soc. 24, 111 (1928).

[4] J. C. Slater, Phys. Rev. 34, 1293 (1929).

[5] P. M. Morse *et al.*, Phys. Rev. 48, 948 (1935).

[6] E. A. Hylleraas, Z. Physik 54, 374 (1929).

[7] P. O. Löwdin, Phys. Rev. 97, 1474 (1955).

[8] Tycko, Thomas, and King, Phys. Rev. 109, 369 (1958).

[9] K. A. Brueckner and C. A. Levinson, Phys. Rev. 97, 1344 (1955).

[10] D. Bohm and D. Pines, Phys. Rev. 82, 625 (1951).