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Effect of the Atomic Core on the Nuclear Quadrupole Coupling*

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The effect of the electron core on the nuclear electric quadrupole coupling has been evaluated for several atomic ground states and first excited states. The antishielding produced by the $np\rightarrow p$ and $nd\rightarrow d$ excitations of the core is taken into account in all cases. For the ground states, the effect of the angular modes of excitation predominates, and gives a net shielding of the same order as that predicted by the Thomas-Fermi model, except for two cases of heavy atoms (Cs,W) where the antishielding predominates. For the first excited (p) states of the alkalis (except Li) there is a net antishielding which ranges from 10 percent for Na to 24 percent for Cs. Approximate values of the quadrupole correction factor are given for 9 atomic states.

I. INTRODUCTION

IT has been previously shown[1–3] that the effect of the atomic core on the nuclear quadrupole coupling can be represented as the interaction of the valence electron with the quadrupole moment induced in the core by the nuclear quadrupole moment Q. The Thomas-Fermi model was used to calculate this effect,[1,2] and gives a shielding of Q of the order of 10 percent, i.e., the quadrupole coupling is decreased in absolute magnitude by this amount. This effect corresponds to an angular rearrangement of the electronic charge. For a positive Q, the electrons tend to concentrate along the axis of Q where the potential energy is a minimum. This angular rearrangement is due to an excitation of s electrons into higher d states, and of p electrons into f states. It was also shown that, in addition, the perturbation by the nuclear Q gives rise to an excitation of p electrons into higher p states, and a similar effect takes place for d electrons which are excited into higher d states. This effect corresponds to a radial redistribution of the charge of the electron core. If $Q>0$, then along the axis of Q, the electrons tend to be closer to the nucleus than in the unperturbed state, while at right angles to the axis of Q the electrons are on the average farther from the nucleus than without the perturbation. The radial redistribution tends to reinforce the effect of the nuclear Q if the valence electron is sufficiently far outside the core, and for this reason has been referred to as an antishielding. This effect depends sensitively on the principal and azimuthal quantum numbers of the external shells of the core, and cannot be obtained from the Thomas-Fermi model. The effect of the radial modes was shown to be small for the case of Cl previously discussed. However, in a recent investigation of the nuclear quadrupole coupling in polar molecules,[2] it was found that the total induced quadrupole moment due to the antishielding is very large for heavy atoms such as Rb and Cs. Accordingly the effect of the core for the atomic ground states has been calculated for some atoms heavier than those previously investigated. It was found that for Cs and W there is a net antishielding due to the effect of the radial modes, although for light atoms the shielding due to the angular modes generally predominates.

The radial rearrangement of the electron distribution affects most strongly the outer parts of the atomic core, so that the antishielding effect increases rapidly with increasing distance from the nucleus in this region. Thus one may expect that for excited atomic states there will be a net antishielding, even though the shielding due to the angular modes predominates for the ground state. This expectation was borne out by calculations for the first excited (p) states of the alkalis, for which one finds a net antishielding varying from 10 percent for Na to 24 percent for Cs.

In order to check the accuracy of the Thomas-Fermi model, wave function calculations of the shielding due to the angular modes ($ns\rightarrow d$, $np\rightarrow f$) have been previously carried out[2] for Li, Al, and Cl. It was found that the interaction of the valence electron with the induced moment obtained from the wave-function calculations is $\sim$1.5 times smaller than the interaction with the Thomas-Fermi induced moment. It seemed of interest to check the Thomas-Fermi model for a heavy atom. For this purpose, the perturbed wave functions for the angular modes were calculated for the case of Cs. Similarly to the result for light atoms, it was found that the interaction of a $6p$ electron with the induced moment based on the perturbed wave functions is 1.4 times smaller than the interaction with the Thomas-Fermi induced moment. Thus the Thomas-Fermi values divided by 1.5 should give the order of magnitude of the shielding throughout the range of Z.

The present calculations of the effect of the distortion of the atomic core cannot be checked directly by experimental values. In order to obtain some information on the expected accuracy of the calculations, the same method as used here was applied to calculate the electronic polarizability α of several ions. It was

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[1] R. M. Sternheimer, Phys. Rev. **80**, 102 (1950).

[2] R. M. Sternheimer, Phys. Rev. **84**, 244 (1951); **86**, 316 (1952); Foley, Sternheimer, and Tycko, Phys. Rev. **93**, 734 (1954). These papers will be referred to as I, II, and III respectively.

[3] R. M. Sternheimer and H. M. Foley, Phys. Rev. **92**, 1460 (1953). In Eqs. (42) and (43) of this paper, L should be replaced by $\tilde{L}$.

found that the calculated values of α lie between 1 and 1.5 times the experimental values in most cases. It may be expected that the accuracy of the calculation of the quadrupole coupling will be of the same order as for α. Thus the values of the quadrupole correction as obtained from the Hartree-Fock wave functions should be accurate, in general, within a factor of 1.5 and may tend to be somewhat larger than the actual values. The calculations of α will be reported in a forthcoming paper.

II. QUADRUPOLE CORRECTION FOR ATOMIC GROUND STATES AND EXCITED STATES

This section is devoted to obtaining values of the quadrupole correction R for several atomic ground states and excited states. Here R is the ratio of minus the interaction energy due to the induced moment to the energy of interaction with the nuclear Q. R is given by

$$R=\frac{\int_0^\infty \gamma v'^2 r^{-3}dr}{\int_0^\infty v'^2 r^{-3}dr}, \tag{1}$$

where r is the distance from the nucleus, v' is the radial part of the valence wave function times r, normalized according to

$$\int_0^\infty v'^2 dr=1, \tag{1a}$$

and

$$\gamma(r)=(1/Q)\left[\int_0^r Q_i dr'+r^5\int_r^\infty Q_i r'^{-5}dr'\right], \tag{2}$$

where $Q_i(r)dr$ is the induced quadrupole moment between r and $r+dr$. Q_i consists of two terms, $Q_{i,\,\mathrm{ang}}$ and $Q_{i,\,\mathrm{rad}}$ which are, respectively, the induced moment density due to the angular and radial excitations of the core. The angular term will be discussed first. For B, Na, Cl, and Cs, this term was obtained from wave-function calculations. The expression for $Q_{i,\,\mathrm{ang}}$ is

$$Q_{i,\,\mathrm{ang}}(r)=Qr^2\left[\frac{8}{5}\sum_n (u_0'u'_{1,\,0\to2})_{ns}+\frac{72}{25}\sum_n (u_0'u'_{1,\,1\to3})_{np}+\frac{8}{5}\sum_n (u_0'u'_{1,\,2\to0})_{nd}+\frac{144}{35}\sum_n (u_0'u'_{1,\,2\to4})_{nd}\right]. \tag{3}$$

Here each sum over the principal quantum number n extends over the occupied s, p, d shells, respectively; the u'_0 are the corresponding unperturbed radial functions times r, normalized according to (1a); $u'_{1,\,l\to l'}$ is r times the radial part of the excitation of nl to l', where l and l' are the azimuthal quantum numbers of the unperturbed function and the perturbation, respectively. The numerical coefficients of Eq. (3) arise from the summation over the magnetic substates of nl and integration over the angle θ between the radius vector of the electron and the axis of Q. The first two coefficients pertaining to the s and p shells have been given previously in I. The remaining ones, which pertain to the excitation of d shells, are derived below (see Sec. IV). As shown in I, the $u'_{1,\,l\to l'}$ are determined by the equation

$$\left[-\frac{d^2}{dr^2}+\frac{l'(l'+1)}{r^2}+V_0-E_0\right]u'_{1,\,l\to l'}=\frac{u_0'}{r^3}, \tag{4}$$

where V_0 and E_0 are the unperturbed potential and energy, respectively. The details of the solution of Eq. (4) are given in Sec. III. For the unperturbed functions u'_0 we used the Hartree or Hartree-Fock functions for the elements considered. For B, the Hartree wave functions of Brown, Bartlett, and Dunn[4] were employed. For Na, the Hartree-Fock wave functions of Fock and Petrashen[5] were used. The u'_0 for Cl^- and Cs^+ were taken from Hartree's work.[6,7]

For the cases of Cu, Rb, and W, $Q_{i,\,\mathrm{ang}}$ was obtained from the Thomas-Fermi model, which gives

$$Q_{i,\,\mathrm{ang}}=0.2998Q(\chi x)^{\frac{1}{2}}(x/r), \tag{5}$$

where χ and x are the Thomas-Fermi function and variable, respectively; $x=(Z^{\frac{1}{3}}/0.8853)r$, where r is in units a_H (Bohr radius). For large r, the Thomas-Fermi model gives a $1/r$ dependence for $Q_{i,\,\mathrm{ang}}$ instead of an exponential decrease as required by the wave functions. For this reason, Eq. (5) was modified at large r so as to agree with the total induced moment $Q_{iT,\,\mathrm{ang}}$ obtained from the wave-function calculations. The values obtained for Cl and Cs (see Sec. III) were interpolated to give $Q_{iT,\,\mathrm{ang}}(\mathrm{Cu})\cong2.0Q$, $Q_{iT,\,\mathrm{ang}}(\mathrm{Rb})\cong2.2Q$, and Eq. (5) was replaced by an exponential for large x ($x\gtrsim9$) so adjusted that $\int_0^\infty Q_{i,\,\mathrm{ang}}dr$ has the appropriate value. For W, a value $Q_{iT,\,\mathrm{ang}}=3.5Q$ was used. We note that the treatment of $Q_{i,\,\mathrm{ang}}$ at large r is not critical, because most of the quadrupole coupling takes place near the nucleus.

The term $Q_{i,\,\mathrm{rad}}$ due to the radial modes is obtained from the corresponding excited wave functions. As shown in I, these functions are determined by the equation

$$\left[-\frac{d^2}{dr^2}+\frac{l(l+1)}{r^2}+V_0-E_0\right]u'_{1,\,l\to l}=u_0'\left(\frac{1}{r^3}-\left\langle\frac{1}{r^3}\right\rangle_{nl}\right). \tag{6}$$

Here $u'_{1,\,l\to l}$ is r times the radial part of the perturbation; $\langle 1/r^3\rangle_{nl}$ is the average of $1/r^3$ for the unperturbed function u'_0 whose principal and azimuthal quantum

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[4] Brown, Bartlett, and Dunn, Phys. Rev. **44**, 296 (1953).

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

[6] D. R. Hartree, Proc. Roy. Soc. (London) **156**, 45 (1936).

[7] D. R. Hartree, Proc. Roy. Soc. (London) **143**, 506 (1934).

numbers are n and l, respectively. That solution of (6) must be chosen which is orthogonal to u'_0. $Q_{i,\,\mathrm{rad}}$ is given by

$$Q_{i,\,\mathrm{rad}}(r)=Qr^2\biggl[\frac{48}{25}\sum_n(u'_0u'_{1,\,1\to1})_{np}+\frac{16}{7}\sum_n(u'_0u'_{1,\,2\to2})_{nd}+\frac{224}{75}\sum_n(u'_0u'_{1,\,3\to3})_{nf}\biggr],\tag{7}$$

where the sums extend over the occupied p, d, and f shells, respectively. The numerical coefficients of (7) are obtained from the summation over the magnetic substates and the integration over θ. The coefficient for $np\to p$ has been derived in I. The coefficients for $nd\to d$ and $nf\to f$ are obtained below.

Except for the case of W, the wave functions $u'_{1,\,l\to l}$ have been obtained previously, in connection with the work on the quadrupole coupling in polar molecules.[2] The same procedure was employed for W, using the Hartree wave functions obtained by Manning and Millman.[8] The method of calculation will be briefly described. The left-hand side of Eq. (6) involves the function

$$P(r)\equiv[l(l+1)/r^2]+V_0-E_0.\tag{8}$$

In view of the equation satisfied by u'_0, P can be obtained directly from the tabulated Hartree wave functions, as follows,

$$P(r_n)=[u'_0(r_n+\delta)-2u'_0(r_n)+u'_0(r_n-\delta)]/\delta^2u'_0(r_n),\tag{9}$$

where r_n is a selected point, and δ is the interval of integration. The solution is started near $r=0$ by means of a power series, as shown in I. By subtracting a suitable multiple of u'_0 from the resulting function $u'_{1,\,l\to l}$ one obtains a function orthogonal to u'_0, which is the desired perturbation. The zero-order core wave functions used in these calculations are those mentioned above in connection with $Q_{i,\,\mathrm{ang}}$, as well as the Hartree-Fock functions[9] for Cu$^+$ and the Hartree functions for[10] Rb$^+$.

After $Q_{i,\,\mathrm{ang}}$ and $Q_{i,\,\mathrm{rad}}$ are determined, the function $\gamma(r)$ of Eq. (2) can be obtained by numerical integration. In practice, in order to separate the effects of the angular and radial modes, two functions were calculated, $\gamma_{\mathrm{ang}}(r)$ and $\gamma_{\mathrm{rad}}(r)$, defined by

$$\gamma_{\mathrm{ang}}(r)\equiv(1/Q)\biggl[\int_0^r Q_{i,\,\mathrm{ang}}dr'+r^5\int_r^\infty Q_{i,\,\mathrm{ang}}r'^{-5}dr'\biggr],\tag{10}$$

$$\gamma_{\mathrm{rad}}(r)\equiv(1/Q)\biggl[\int_0^r Q_{i,\,\mathrm{rad}}dr'+r^5\int_r^\infty Q_{i,\,\mathrm{rad}}r'^{-5}dr'\biggr].\tag{11}$$

The corresponding contributions to the quadrupole coupling are proportional to

$$\langle\gamma_{\mathrm{ang}}/r^3\rangle=\int_0^\infty \gamma_{\mathrm{ang}}v'^2r^{-3}dr,\tag{12}$$

$$\langle\gamma_{\mathrm{rad}}/r^3\rangle=\int_0^\infty \gamma_{\mathrm{rad}}v'^2r^{-3}dr.\tag{13}$$

The values of $\langle\gamma_{\mathrm{ang}}/r^3\rangle$, $\langle\gamma_{\mathrm{rad}}/r^3\rangle$, together with their sum $\langle\gamma/r^3\rangle$ are given in Table I. The valence wave functions v' used in the calculations were obtained from the above-mentioned references, except for Rb $5p$ and Cs $6p$. These two functions were obtained by numerical integration of the Schroedinger equation using an appropriate potential V_0. Table I lists the values of the average $\langle1/r^3\rangle$ for the valence wave functions and of the resulting ratio R, as well as $1/(1-R)$. We note that the $4p$ state of Rb, and $5p$ of Cs are filled in the normal state of the atom. The values of R were calculated for these states only because they show the dependence of R on the principal quantum number of v'. A check on the accuracy of the valence wave functions can be obtained by comparing the calculated values of $\langle1/r^3\rangle$ with those obtained by Barnes and Smith[11] from the observed fine structure of these levels. These values are 0.608, 0.244, 7.16, 0.845, $1.29a_{\mathrm{H}}^{-3}$ for B $2p$, Na $3p$, Cl $3p^5$, Rb $5p$, and Cs $6p$, respectively. Comparison with the values of Table I shows that the agreement is reasonably good, the calculated values being somewhat smaller than the fine-structure results, as would be expected since the Hartree wave functions are probably more external than the actual wave functions. It should be stressed that both $\langle\gamma/r^3\rangle$ and $\langle1/r^3\rangle$ are very sensitive to the detailed behavior of the wave functions. A part of this dependence on the wave function is eliminated in the calculation of the ratio R, since $\langle\gamma/r^3\rangle$ and $\langle1/r^3\rangle$ generally vary with the wave function v' in the same manner. Thus if v' is too external, both $\langle1/r^3\rangle$ and $\langle\gamma/r^3\rangle$ are generally decreased.

TABLE I. Values of quadrupole interaction $\langle\gamma/r^3\rangle$ due to induced moment, values of $\langle1/r^3\rangle$, and of correction term R for several atomic ground states and excited states. These values are calculated from the Hartree-Fock wave functions, and disregard the exchange terms. $\langle\gamma_{\mathrm{ang}}/r^3\rangle$ and $\langle\gamma_{\mathrm{rad}}/r^3\rangle$ are the contributions of the angular and radial modes to $\langle\gamma/r^3\rangle\cdot\langle\gamma/r^3\rangle$ and $\langle1/r^3\rangle$ are in units a_{H}^{-3}.

Element	State	$\langle\gamma_{\mathrm{ang}}/r^3\rangle$	$\langle\gamma_{\mathrm{rad}}/r^3\rangle$	$\langle\gamma/r^3\rangle$	$\langle1/r^3\rangle$	R	$1/(1-R)$
B	$2p$	0.0757	0	0.0757	0.535	0.142	1.165
Na	$3p$	0.0151	−0.0291	−0.0140	0.145	−0.097	0.912
Cl	$3p^5$	0.333	0.104	0.437	5.73	0.076	1.081
Cu	$3d^94s^2$	1.95	−0.699	1.25	7.52	0.166	1.20
Rb	$4p$	0.844	−0.229	0.615	19.6	0.031	1.031
Rb	$5p$	0.0341	−0.190	−0.156	0.647	−0.241	0.806
Cs	$5p$	0.58	−0.974	−0.394	22.3	−0.018	0.984
Cs	$6p$	0.0343	−0.304	−0.270	1.11	−0.244	0.804
W	$5d^4$	0.678	−3.10	−2.43	4.76	−0.510	0.663

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[8] M. F. Manning and J. Millman, Phys. Rev. **49**, 848 (1936).

[9] D. R. Hartree, Proc. Roy. Soc. (London) **157**, 490 (1936).

[10] D. R. Hartree, Proc. Roy. Soc. (London) **151**, 96 (1935).

[11] R. G. Barnes and W. V. Smith, Phys. Rev. **93**, 95 (1954).

Table I shows that for all of the ground states considered, except for W, R is positive, meaning that the shielding due to the angular modes predominates. The preponderance of the antishielding for the case of W is partly due to the fact that the $5p$ shell has a very large total induced moment ($\sim -27Q$). As was pointed out in III, the function γ_{rad} increases very rapidly with increasing r (see Fig. 2 of III). Since the electronic distribution of $5d$ is rather external, the antishielding is quite pronounced and predominates over the effect of the angular modes. It should be mentioned that the detailed vector coupling for W was not calculated, but the contribution of the $5d$ electrons to the radial modes was taken as $\frac{3}{10}$ of that which would be produced by a complete $5d$ shell. This approximation is probably adequate since the $5d\rightarrow d$ term is small compared to the contribution of the core.

For the first excited states of Na, Rb, and Cs, R is in all three cases negative, because the antishielding predominates on account of the external distribution of the excited-state wave functions. The result for the $3p$ state of Na ($R=-0.10$) may be of interest, because the hfs of this state has been recently measured.[12]

The values of R of Table I do not include the exchange terms due to the induced quadrupole moment. The exchange terms have been derived in I for the interaction of a p valence electron with a core of closed s and p shells. This derivation is extended in Sec. IV to d shells of the core. From these results one obtains the following expression for the ratio of minus the exchange energy to the main term in the quadrupole coupling, for an external p electron:

$$\delta R_e=-\frac{1}{\langle r^{-3}\rangle}\left\{\sum_n\left[\frac{4}{3}K(ns\rightarrow d,P_1)\right]_{ns}+\sum_n\left[4K(np\rightarrow p,P_0)+\frac{4}{25}K(np\rightarrow p,P_2)+\frac{36}{25}K(np\rightarrow f,P_2)\right]_{np}+\sum_n\left[\frac{4}{3}K(nd\rightarrow s,P_1)+\frac{4}{3}K(nd\rightarrow d,P_1)+\frac{12}{49}K(nd\rightarrow d,P_3)+\frac{72}{49}K(nd\rightarrow g,P_3)\right]_{nd}\right\}. \quad (14)$$

Here the sums extend over all occupied s, p, and d shells of the core. K is defined by

$$K(nl\rightarrow l',P_L)\equiv\int_0^\infty u'_0 v' f_L dr, \quad (15)$$

where u'_0 is the appropriate unperturbed radial function (nl), and $f_L(r)$ is given by

$$f_L(r)=r^{-L-1}\int_0^r u'_{1,\,l\rightarrow l'}v'r'^L dr'+r^L\int_r^\infty u'_{1,\,l\rightarrow l'}v'r'^{-L-1}dr', \quad (16)$$

where $u'_{1,\,l\rightarrow l'}$ is the perturbation which corresponds to the excitation considered. In the following, the ratio of the induced effects including exchange will be denoted by R_e, so that

$$R_e=R+\delta R_e. \quad (17)$$

The exchange terms of Eq. (14) fall into two classes: (a) the terms of type $-4K(np\rightarrow p,P_0)/\langle r^{-3}\rangle$ whose sum will be denoted by $\delta R_{e,\,0}$; (b) all other terms, whose sum will be called $\delta R'_e$. Thus

$$\delta R_e=\delta R_{e,\,0}+\delta R'_e. \quad (18)$$

The reason for this separation will now be shown. The $\delta R_{e,\,0}$ term arises not only in the quadrupole coupling, but also in the hfs due to the nuclear magnetic moment and in the fine structure. The origin of this term can best be seen by considering the perturbation of the core by the valence electron. As shown in II [see Eqs. (39) and (40)] the exchange between the core and the valence electron gives rise to an excitation of each p shell of the core into higher p states having the same magnetic quantum number m as the valence electron. If $\tilde{u}'_1$ denotes the radial wave function (times r) for excitation of the p shell, the quadrupole coupling is given by

$$q'=c\int_0^\infty\left[v'^2+4\sum_n(u'_0\tilde{u}'_1)_{np}\right]r^{-3}dr, \quad (19)$$

where u'_0 and v' are r times the radial part of the wave function of the core and the valence electron, respectively; $c=-\frac{2}{5}$ for $m=0$, and $+\frac{1}{5}$ for $m=\pm 1$. Equation (19) does not include other first-order induced effects besides the $np\rightarrow p$ exchange terms. $\tilde{u}'_1$ is determined by

$$\left(-\frac{d^2}{dr^2}+\frac{2}{r^2}+V_0-E_0\right)\tilde{u}'_1=\left[r^{-1}\int_0^r u'_0v'dr'+\int_r^\infty u'_0v'r'^{-1}dr'\right]v'(r). \quad (20)$$

The appearance of $4\sum_n(u'_0\tilde{u}'_1)_{np}$ along with v'^2 in Eq. (19) is a result of the fact that the induced density has the same m as the valence electron. As shown previously[2,3] the contribution of $4u'_0\tilde{u}'_1$ to the quadrupole coupling is equal to the $4K(np\rightarrow p,\ P_0)$ term obtained above. The fact that the induced density has the same m as the valence electron is also responsible for the appearance of this term in the magnetic hfs and in the fine structure.

It was shown in I that when $\langle 1/r^3\rangle$ is obtained from the magnetic hfs interval a and the nuclear magnetic moment μ, the correction factor C by which a/μ is multiplied is given by

$$C=(1-\delta R_m)/(1-R_e). \quad (21)$$

Here δR_m is defined as minus the interaction energy due to the core for the magnetic hfs divided by the inter-

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[12] I. I. Rabi (private communication).

action energy for the valence electron. Thus δR_m corresponds to $-R_m$ as defined in I and II. δR_m is given by

$$\delta R_m = \delta R_{e,0} + \delta R'_m, \tag{22}$$

where $\delta R'_m$ is a term of the same type as $\delta R'_e$. As shown in II [see Eqs. (56) and (56a)], $\delta R'_m$ is a sum of terms containing the integrals $K(nl \rightarrow l', P_L)$ $(L > 0)$ but with coefficients which differ from those of (14). Moreover, these coefficients are different for the $^2P_{\frac{1}{2}}$ and $^2P_{\frac{3}{2}}$ states of the atom.

In view of (21) and (22) the quadrupole correction factor C is given by

$$C = \frac{1 - \delta R_{e,0} - \delta R'_m}{1 - R - \delta R_{e,0} - \delta R'_e} = \left[1 - \frac{\delta R'_m}{1 - \delta R_{e,0}}\right] \Bigg/ \left[1 - \frac{R + \delta R'_e}{1 - \delta R_{e,0}}\right]. \tag{23}$$

As will be shown, $\delta R'_m$ and $\delta R'_e$ are generally small compared to $\delta R_{e,0}$. If these terms could be entirely neglected, C would be given by

$$C = 1 \Bigg/ \left[1 - \frac{R}{1 - \delta R_{e,0}}\right]. \tag{23a}$$

Since $\delta R_{e,0} < 0$, R is effectively decreased. $\delta R_{e,0}$ has been calculated in I for Al $3p$ and Cl $3p^5$; the values are -0.174 and -0.472, respectively. In the present work the calculation of the exchange terms has been extended to B $2p$, Na $3p$, and Cs $6p$. Since B has no filled p shells, $\delta R_{e,0}$ is zero. For Na and Cs, $\delta R_{e,0}$ is -0.180 and -0.152, respectively. Thus the factor $1 - \delta R_{e,0}$ in (23a) is of order 1.15–1.5.

The term $\delta R_e'$ in the quadrupole coupling will now be considered. $\delta R_e'$ has been evaluated in I for Li $2p$, Al $3p$, and Cl $3p^5$, and was found to be -0.061, -0.033, and -0.037, respectively, for these states. In the present work, calculations carried out for B $2p$, Na $3p$, and Cs $6p$ gave the values -0.086, -0.015, and -0.009, respectively.

Equation (23) shows that C involves $\delta R'_m$ besides $\delta R_{e,0}$ and $\delta R'_e$. An experimental indication about the values of $\delta R'_m$ is provided by the ratio of the magnetic hfs intervals a for the $^2P_{\frac{1}{2}}$ and $^2P_{\frac{3}{2}}$ states. This ratio is given by

$$\frac{a(^2P_{\frac{3}{2}})}{a(^2P_{\frac{1}{2}})} = \frac{F(3/2)[1 - \delta R_m(^2P_{\frac{3}{2}})]}{5F(1/2)[1 - \delta R_m(^2P_{\frac{1}{2}})]}, \tag{24}$$

where $F(j)$ is a relativistic correction obtained by Casimir.[13] Equation (24) will be applied to the case of boron-11 for which measurements of a have been carried out recently by Wessel.[14] From the experimental values $a(^2P_{\frac{3}{2}}) = 73.347$ Mc/sec and $a(^2P_{\frac{1}{2}}) = 366.2$ Mc/sec, together with[13] $F(3/2) = 1.0006$ and $F(1/2) = 1.0025$, one obtains $[1 - \delta R_m(^2P_{\frac{3}{2}})]/[1 - \delta R_m(^2P_{\frac{1}{2}})] = 1.0034$. The calculated values[15] of the δR_m are $\delta R_m(^2P_{\frac{3}{2}}) = -0.0485$ and $\delta R_m(^2P_{\frac{1}{2}}) = -0.0290$, so that $[1 - \delta R_m(^2P_{\frac{3}{2}})]/[1 - \delta R_m(^2P_{\frac{1}{2}})] = 1.0190$. Thus the calculated deviation from 1 is too large by a factor ∼6. A similar discrepancy[16] was found in II for the $^2P_{\frac{3}{2}}$ and $^2P_{\frac{1}{2}}$ states of Cl. Since the same integrals $K(nl \rightarrow l')$ are involved in the quadrupole term $\delta R'_e$ as in $\delta R'_m$, the calculated values of $\delta R'_e$ cannot be considered as completely reliable. However, there seems to be no reason to believe that the actual value of $\delta R'_e$ will be of a larger order of magnitude than is given by the calculations, and it may well be smaller, as is indicated by the magnetic hfs.

Values of C will be given in Sec. V. In obtaining C we will use Eq. (23) except that $\delta R'_m$ will be taken as zero, since $\delta R'_m$ appears to be small (∼0.01) from the experimental values of the intervals a. This procedure is probably adequate, except perhaps for the heavy atoms Rb, Cs, and W, where the effect of the core on the magnetic hfs is pronounced.[17] Thus C is obtained from

$$C = 1 \Bigg/ \left[1 - \frac{R + \delta R'_e}{1 - \delta R_{e,0}}\right]. \tag{25}$$

The uncertainty of the values of $\delta R'_e$ will be taken into account.

Besides the exchange terms, it should be noted that three effects contribute uncertainties of the order 0.01–0.02 in R_e. (1) The second-order quadrupole effect, previously described in III, is evaluated in the Appendix for the ground state of Cl, and adds a term $+0.005$ to R_e. This effect arises from the perturbation of the core wave functions by the external valence electron (or hole) taken in second order. In first order the perturbation gives rise to an added term in the electric field gradient at the nucleus which corresponds to the first-order induced effect described above (angular, radial, and exchange terms).[3] In second order, the perturbation of the core wave functions gives rise to additional terms in the quadrupole coupling. These terms arise both from the square of the first-order perturbed wave functions, and from the overlap of the unperturbed functions with the second-order perturbed

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[13] H. B. G. Casimir, *On the Interaction between Atomic Nuclei and Electrons* (Teyler's Tweede Genootschap, Haarlem, 1936).

[14] G. Wessel, Phys. Rev. **92**, 1581 (1953).

[15] As shown in II, besides the excited $nl \rightarrow l'$ waves which contribute to the quadrupole coupling, δR_m involves also the excitation of s states of the core into higher s states by virtue of exchange with the valence electron. These $ns \rightarrow s$ terms were calculated for B $2p$, and are included in the values of δR_m given here.

[16] The reason for the discrepancy of the magnetic hfs correction factor is difficult to determine. As pointed out in II, a relatively small inaccuracy of the radial wave functions used in the calculations could be responsible for the disagreement. Another possible reason is that the electrostatic correlation of the valence electron with the core electrons of antiparallel spin is not taken into account, whereas the correlation of the core electrons of parallel spin is represented to some extent by the exchange terms which give rise to δR_m. It is possible that inclusion of the correlation for antiparallel spin would being the values of $[1 - \delta R_m(^2P_{\frac{3}{2}})]/[1 - \delta R_m(^2P_{\frac{1}{2}})]$ closer to 1.

[17] G. F. Koster, Phys. Rev. **86**, 148 (1952).

wave functions obtained by applying twice the perturbation due to the external valence electron.

(2) The Hartree-Fock functions which have been used in the calculations do not give as much binding as the actual wave functions which would be obtained from an exact solution of the Schroedinger equation for the core. As a result, the actual induced quadrupole moment is probably smaller than the Hartree-Fock value because an increase of the binding is expected to lead to a decrease of the polarizability. Such an effect was found in calculating the electronic polarizabilities α of various ions using the Hartree-Fock wave functions. As an example, for K^+, the calculated value of α is 1.26A^3 as compared to experimental values ranging from 0.87A^3 to 1.20A^3. For Cl^-, the calculated $\alpha = 5.6A^3$ is a factor 1.7 larger than the experimental value ($\sim$3.3A^3). From these results it is expected that the calculated values of R tend to be somewhat larger than the actual values, possibly by as much as a factor of 1.5. The quadrupole correction R is probably less sensitive to the exact amount of binding than the polarizability α, since R depends on the behavior of the core wave functions near the nucleus, whereas α is determined mainly by the behavior of the wave functions in the outer parts of the core which is more sensitive to small changes of the binding.

(3) The numerical integrations introduce some error in the results. The possible errors are due to the interpolation necessary to find a suitably well-behaved function, and the finite size of the intervals used. The corresponding uncertainties were generally found to be small. A detailed check was made for the case of Cl. As shown previously,[3] the contribution of a given mode of excitation to $\langle\gamma_{\text{ang}}/r^3\rangle$ or $\langle\gamma_{\text{rad}}/r^3\rangle$ can be found in two independent ways: (a) by calculating the interaction of the valence electron with the quadrupole moment induced by the nuclear Q which corresponds to the mode of excitation considered (e.g., $1s\rightarrow d$); (b) by finding first the excitation of the same type ($1s\rightarrow d$) produced by the asymmetric potential of the valence electron, and then obtaining the contribution to the quadrupole coupling at the nucleus due to this mode of excitation. In general the contributions calculated by both methods agreed within $\sim$10 percent. Thus for $3s\rightarrow d$ the contribution to $\langle\gamma_{\text{ang}}/r^3\rangle/\langle 1/r^3\rangle$ was obtained as 0.00684 from method (a) and 0.00693 from (b). The only exception is the $3p\rightarrow p$ term of $\langle\gamma_{\text{rad}}/r^3\rangle$ where the value calculated from (b) was found to be $\sim$1.5 times larger than that given by (a). It is believed that this discrepancy is associated with the external charge distribution of $3p$, and could be resolved by taking a larger number of steps in the numerical integration than was used ($\sim$50 intervals δ). However, in view of the other uncertainties it did not seem worthwhile to carry out this refinement of the calculation.

III. WAVE-FUNCTION CALCULATIONS OF SHIELDING

Calculations of the perturbed wave functions for the angular modes were previously carried out[2] for Li, Al, and Cl, in order to check the prediction of the Thomas-Fermi model. It was found that the perturbed wave functions lead to values of $\langle\gamma_{\text{ang}}/r^3\rangle$ which are $\sim$1.5 times smaller than those obtained from the Thomas-Fermi density of the induced moment. This result shows that the statistical model tends to overestimate the shielding for light atoms. In order to check the accuracy of the Thomas-Fermi model for a heavy atom, the excited waves due to the perturbation by the nuclear Q were calculated for the case of Cs^+, using the Hartree functions[7] for the unperturbed functions u'_0.

The angular part of the induced moment $Q_{i,\text{ang}}$ is given by Eq. (3). The radial parts $u'_{1,l\rightarrow l'}$ of the excited wave functions are determined by Eq. (4). The function in the square bracket of (4), which will be called P', was calculated as follows,

$$P' \equiv \frac{l'(l'+1)}{r^2} + V_0 - E_0 = P + \frac{l'(l'+1) - l(l+1)}{r^2}, \quad (26)$$

where P is obtained from u'_0 [see Eq. (9)]. The integrations of Eq. (4) were performed somewhat differently for the different angular modes. For $ns\rightarrow d$, the integration was started near $r=0$, using the power series [see Eq. (10) of I],

$$u'_{1,0\rightarrow 2} = a_0 + a_1 r + a_2 r^2 + a_3 r^3 + a_4 r^4 + \cdots + b_3 r^3 \log r + b_4 r^4 \log r + \cdots, \quad (27)$$

where a_3 is arbitrary and the remaining coefficients a_i and b_i are determined by Eq. (4), as was shown in I. The integrations were carried out for various a_3, until a value of a_3 was found for which the resulting $u'_{1,0\rightarrow 2}$ is well-behaved for large r. In practice, the numerical solutions obtained for two neighboring values of a_3 which enclose the correct value diverge slowly, the one to positive, the other to negative values, for $r\rightarrow\infty$. However, they agree closely (in general, within 10 percent) in the region near the nucleus which is of importance for the quadrupole coupling. For $nd\rightarrow s$, the integration was started at $r=0$ by means of a power series $a_1 r + a_2 r^2 \cdots$. In this case, a_1 is arbitrary, and its value is varied until the resulting $u'_{1,2\rightarrow 0}$ is well-behaved at infinity.

For the $np\rightarrow f$ waves, a method of inward integration was used, starting at a large radius r_1, as follows. Equation (4) can be written

$$-d^2u'_{1,1\rightarrow 3}/dr^2 + Nu'_{1,1\rightarrow 3} = 0, \quad (28)$$

where

$$N \equiv P' - u'_0/(r^3 u'_{1,1\rightarrow 3}), \quad (29)$$

and P' is defined by Eq. (26). Note that for sufficiently large r, N approaches the constant value $-E_0$. For the numerical integration it is assumed that N is constant for $r>r_1$. For an assumed value of $u'_{1,1\to3}(r_1)$, N is calculated from Eq. (29), and $u'_{1,1\to3}(r_1+\delta)$ is obtained from

$$u'_{1,1\to3}(r_1+\delta)=u'_{1,1\to3}(r_1)\exp(-N^{\frac{1}{2}}\delta). \qquad (30)$$

The numerical integration is then carried out starting with the two values $u'_{1,1\to3}(r_1)$ and $u'_{1,1\to3}(r_1+\delta)$. This procedure is repeated for several choices of $u'_{1,1\to3}(r_1)$ until a value is found for which the corresponding $u'_{1,1\to3}$ goes to zero at $r=0$. This requirement is appropriate since the actual solution is proportional to r near $r=0$. For the $nd\to g$ waves the same method of inward integration as for $np\to f$ was employed.

After the functions $u'_{1,l\to l'}$ were determined, the distribution of the induced moment $Q_{i,\mathrm{ang}}$ was obtained from Eq. (3). This distribution can be compared with the prediction of the Thomas-Fermi model [Eq. (5)]. Both functions $Q_{i,\mathrm{ang}}/Q$ are shown in Fig. 1. It is seen that the agreement between the wave-function calculations and the Thomas-Fermi model is reasonably good. Of course the Thomas-Fermi model smoothes over the maxima of $Q_{i,\mathrm{ang}}$ as obtained from the wave functions, which correspond to the electronic shells of the ion.

When γ_{ang} is calculated from $Q_{i,\mathrm{ang}}$ as obtained from the wave-function calculations, one finds for the $6p$ state, $\langle\gamma_{\mathrm{ang}}/r^3\rangle=0.0343a_{\mathrm{H}}^{-3}$ (see Table I). The Thomas-Fermi values of $Q_{i,\mathrm{ang}}$ lead to $\langle\gamma_{\mathrm{ang}}/r^3\rangle=0.0492a_{\mathrm{H}}^{-3}$ which is a factor $\sim$1.4 larger than the value obtained from the wave functions. The result that the Thomas-Fermi model gives an overestimate of $\langle\gamma_{\mathrm{ang}}/r^3\rangle$ can be attributed in part to the fact that the Thomas-Fermi density $Q_{i,\mathrm{ang}}$ is too large at small r. As shown in Fig. 1, inside $r=0.7a_{\mathrm{H}}$ $Q_{i,\mathrm{ang}}$ as obtained from the Thomas-Fermi model is appreciably larger than the wave function values, except for a small region near $r=0.3a_{\mathrm{H}}$, which corresponds to the maximum of the M shell. These results for Cs together with those for light atoms indicate that the Thomas-Fermi value of $\langle\gamma_{\mathrm{ang}}/r^3\rangle$ divided by 1.5 should give the correct order of magnitude of the shielding throughout the range of Z.

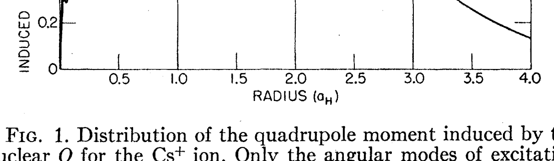

FIG. 1. Distribution of the quadrupole moment induced by the nuclear Q for the Cs$^+$ ion. Only the angular modes of excitation of the core are included. The curve marked WF is obtained from wave function calculations using the Hartree wave functions for Cs$^+$. The curve marked Th-F is calculated from the Thomas-Fermi model [see Eq. (5)].

From the excited core wave functions for Cs it is of interest to calculate the total induced moment due to the various perturbed waves, as obtained by integrating the terms of Eq. (3) over r. The total induced moment due to the angular modes is $Q_{iT,\mathrm{ang}}=2.95Q$. The largest contributions are made by the $5s\to d$ and $5p\to f$ waves, which give $Q_{iT,\mathrm{ang}}(5s\to d)=0.93Q$, and $Q_{iT,\mathrm{ang}}(5p\to f)=0.76Q$, corresponding to the large values of $\langle r^2\rangle$ for these shells. The remaining induced moment of $1.26Q$ is made up of contributions 0.012, 0.064, 0.27, and $0.91Q$ from the $n=1$, 2, 3, and 4 shells, respectively. By comparing $Q_{iT,\mathrm{ang}}/Q$ for Cs with the values for light atoms (0.62 for Na, 1.06 for Al, 1.41 for Cl) it is seen that $Q_{iT,\mathrm{ang}}/Q$ increases slowly with Z.

The present values of $Q_{i,\mathrm{ang}}$ for Cs obtained from the perturbed wave functions have been used in the calculation of the values of $\langle\gamma_{\mathrm{ang}}/r^3\rangle$ for the $5p$ and $6p$ states, which are given in Table I. The values of $\langle\gamma_{\mathrm{rad}}/r^3\rangle$ for these states were obtained by means of the function $Q_{i,\mathrm{rad}}$ for the radial modes obtained in III. The $5p$ state is, of course, occupied so that the corresponding quadrupole correction is only of theoretical interest. The calculations for this state indicate a weak net antishielding. This result is in contrast to the results for the ground states of the light atoms for which the shielding predominates, although for $3p$ of Al, as shown in I, the effect of the angular modes is only slightly larger than the antishielding due to $2p\to p$. It has also been shown above that for the somewhat external $5d$ electron of W, the antishielding predominates strongly. Nevertheless, the correction $\langle\gamma_{\mathrm{rad}}/r^3\rangle/\langle 1/r^3\rangle$ for the radial modes, which is $-3.10/4.76=-0.65$ (see Table I) is small compared to the total induced moment in units of Q which is ~-50. The reason is that the induced moment due to the radial modes is localized considerably outside the region where most of the quadrupole coupling of the $5d$ electron takes place $(\langle r^{-3}\rangle_{5d}^{-\frac{1}{3}}=0.60a_{\mathrm{H}})$.

On the basis of the two examples of Cs $5p$ and W $5d^4$, it is not possible to conclude that the antishielding generally predominates for heavy atoms. To ascertain this point would require more extensive calculations. However, the fact that the antishielding appears to be relatively more important for heavy atoms than for light atoms can be attributed in part to the somewhat different Z dependence of the effect of the angular and the radial modes. As shown in III, the induced moment due to the radial modes $Q_{iT,\mathrm{rad}}$ increases very rapidly with Z, namely from $-2.7Q$ for Na$^+$ to $-90Q$ for Cs$^+$. In comparison, $Q_{iT,\mathrm{ang}}$ increases less rapidly, i.e., from $0.61Q$ for Na$^+$ to $2.95Q$ for Cs$^+$. The tendency for $R>0$ (shielding) for low Z, and $R<0$ for high Z can be correlated with the different Z dependence of the angular and the radial modes.

Besides the calculations for Cs, wave function calculations of the shielding were also carried out for B, Na, and Cl. The resulting values of $\langle\gamma_{\text{ang}}/r^3\rangle$ are given in Table I.

IV. EXCITATION OF *d* SHELLS OF THE CORE

In previous work[2] the calculations of induced effects have been restricted to atoms with closed *s* and *p* shells. In the present section these results will be extended to *d* states of the core.

We consider the excitation of *d* states by the field of the nuclear Q. The perturbation of *d* states to excited *d* states will be treated first. For the state $m=0$, we have for the unperturbed wave function (times r),

$$u_0^{(0)}=(5/8)^{\frac{1}{2}}u'_0(3\cos^2\theta-1)=u'_0\Theta_2^0, \tag{31}$$

where u'_0 is r times the radial function normalized according to

$$\int_0^\infty u'^2_0dr=1. \tag{31a}$$

The angular functions Θ_l^m are normalized according to

$$\int_0^\pi|\Theta_l^m|^2\sin\theta d\theta=1. \tag{31b}$$

In Eq. (31) and in the following a superscript (e.g., for $u_0^{(0)}$) indicates the value of the magnetic quantum number m. The equation for the perturbed wave $u_1^{(0)}$ is

$$(H_0-E_0)u_1^{(0)}=-H_1u_0^{(0)}+E_1u_0^{(0)}, \tag{32}$$

where H_1 is the perturbation of the Hamiltonian, and is given by

$$H_1=-QP_2^0/r^3, \tag{33}$$

where P_l^m is the Legendre polynomial. E_1 is the first-order perturbation of the energy, and has the following value, in view of (31) and (33),

$$E_1=\int_0^\infty\int_0^\pi H_1[u_0^{(0)}]^2dr\sin\theta d\theta=-(2/7)Q\langle r^{-3}\rangle_{nd}. \tag{34}$$

Upon substituting (31), (33), and (34) in Eq. (32) one obtains

$$(H_0-E_0)u_1^{(0)}=\left(\frac{5}{32}\right)^{\frac{1}{2}}Q(3\cos^2\theta-1)^2\frac{u'_0}{r^3}-(2/7)Q\langle r^{-3}\rangle_{nd}u'_0\Theta_2^0. \tag{35}$$

The factor $(5/32)^{\frac{1}{2}}(3\cos^2\theta-1)^2$ in the first term on the right-hand side must now be written as a sum of *s*, *d*, and *g* functions. From these functions arise the $nd\to s$, $nd\to d$, and $nd\to g$ excited waves, respectively. The *d* wave part is given by $c_2\Theta_2^0$, where

$$c_2=(5/32)^{\frac{1}{2}}\int_0^\pi(3\cos^2\theta-1)^2\Theta_2^0\sin\theta d\theta=2/7. \tag{36}$$

One thus obtains the following expression for the *d* wave part of $u_1^{(0)}$ which will be called $u^{(0)}{}_{1,2\to2}$,

$$u^{(0)}{}_{1,2\to2}=(2/7)(5/8)^{\frac{1}{2}}Qu'_{1,2\to2}(3\cos^2\theta-1), \tag{37}$$

where the radial function $u'_{1,2\to2}$ is determined by [see Eq. (6)]

$$M_2u'_{1,2\to2}=u'_0(r^{-3}-\langle r^{-3}\rangle_{nd}). \tag{38}$$

Here and in the following, M_l is defined by

$$M_l\equiv-\frac{d^2}{dr^2}+\frac{l(l+1)}{r^2}+V_0-E_0. \tag{39}$$

By means of Eqs. (31) and (37), one obtains for the induced moment $Q_{iT}{}^{(0)}$ due to the $m=0$ electrons,

$$Q_{iT}{}^{(0)}=4\int_0^\infty\int_0^\pi u_0{}^{(0)}u^{(0)}{}_{1,2\to2}(3\cos^2\theta-1)r^2dr\sin\theta d\theta=\frac{32}{49}Q\int_0^\infty u'_0u'_{1,2\to2}r^2dr, \tag{40}$$

where the factor 4 arises from the fact that the first-order density is $2u_0{}^{(0)}u^{(0)}{}_{1,2\to2}$ for each $m=0$ electron.

In the same manner as in the derivation of (37) one finds for the *d* wave perturbation of the $m=\pm1$ states,

$$u^{(\pm1)}{}_{1,2\to2}=\frac{Qu'_{1,2\to2}\Theta_2^{\pm1}}{7}=\mp\frac{15^{\frac{1}{2}}}{14}Qu'_{1,2\to2}\sin\theta\cos\theta. \tag{41}$$

The $\mp$ sign in the last expression corresponds to the choice of phases of Condon and Shortley,[18] and, of course, does not affect the final result. The induced moment due to the four electrons with $m=\pm1$ is given by

$$Q_{iT}{}^{(\pm1)}=8\int_0^\infty\int_0^\pi u'_0\Theta_2{}^{\pm1}u^{(\pm1)}{}_{1,2\to2}(3\cos^2\theta-1)r^2dr\sin\theta d\theta=\frac{16}{49}Q\int_0^\infty u'_0u'_{1,2\to2}r^2dr. \tag{42}$$

In a similar manner, one obtains for the *d* wave perturbation of the $m=\pm2$ states,

$$u^{(\pm2)}{}_{1,2\to2}=-\frac{2}{7}Qu'_{1,2\to2}\Theta_2{}^{\pm2}=-\frac{15^{\frac{1}{2}}}{14}Qu'_{1,2\to2}\sin^2\theta. \tag{43}$$

The resulting induced moment due to the $m=\pm2$ electrons is

$$Q_{iT}{}^{(\pm2)}=8\int_0^\infty\int_0^\pi u'_0\Theta_2{}^{\pm2}u^{(\pm2)}{}_{1,2\to2}(3\cos^2\theta-1)r^2dr\times\sin\theta d\theta=\frac{64}{49}Q\int_0^\infty u'_0u'_{1,2\to2}r^2dr. \tag{44}$$

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[18] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Macmillan Company, New York, 1935), p. 52.

From Eqs. (40), (42), and (44) one obtains for the total induced moment due to $nd\rightarrow d$ for the complete d shell,

$$Q_{iT}(nd\rightarrow d)=(16/7)Q\int_0^\infty u'_0u'_{1,2\rightarrow 2}r^2dr. \tag{45}$$

The induced moment due to the $nd\rightarrow s$ waves can be found in the same manner. Only the $m=0$ electrons contribute. In Eq. (35) the s wave part of $(5/32)^{\frac{1}{2}}\times(3\cos^2\theta-1)^2$ can be written $c_0\Theta_0{}^0$ where

$$c_0=(5/32)^{\frac{1}{2}}\int_0^\pi(3\cos^2\theta-1)^2\Theta_0{}^0\sin\theta d\theta=5^{-\frac{1}{2}}. \tag{46}$$

Therefore one obtains for the s wave part of the perturbation,

$$u^{(0)}{}_{1,2\rightarrow 0}=10^{-\frac{1}{2}}Qu'_{1,2\rightarrow 0}, \tag{47}$$

where the radial function $u'_{1,2\rightarrow 0}$ is determined by [see Eq. (4)]

$$M_0u'_{1,2\rightarrow 0}=u'_0/r^3. \tag{48}$$

Note that the E_1 term of (32) does not contribute, since it gives only a d function. The resulting term in the induced moment is

$$Q_{iT}(nd\rightarrow s)=4\int_0^\infty\int_0^\pi u'_0\Theta_2{}^0u^{(0)}{}_{1,2\rightarrow 0}(3\cos^2\theta-1)r^2dr\times\sin\theta d\theta=\frac{8}{5}Q\int_0^\infty u'_0u'_{1,2\rightarrow 0}r^2dr. \tag{49}$$

The derivation of the $nd\rightarrow g$ wave with $m=0$ will now be briefly outlined. If one subtracts from $(5/32)^{\frac{1}{2}}\times(3\cos^2\theta-1)^2$ its s and d wave parts, one is left with the g wave part, which in view of Eqs. (36) and (46) is given by

$$A_g=\left(\frac{5}{32}\right)^{\frac{1}{2}}(3\cos^2\theta-1)^2-\frac{\Theta_0{}^0}{5^{\frac{1}{2}}}-\frac{2\Theta_2{}^0}{7}=\left(\frac{5}{32}\right)^{\frac{1}{2}}\left(9\cos^4\theta-\frac{54}{7}\cos^2\theta+\frac{27}{35}\right). \tag{50}$$

Hence the g wave perturbation $u^{(0)}{}_{1,2\rightarrow 4}$ is given by

$$u^{(0)}{}_{1,2\rightarrow 4}=\frac{9}{2}\left(\frac{5}{8}\right)^{\frac{1}{2}}Qu'_{1,2\rightarrow 4}\left(\cos^4\theta-\frac{6}{7}\cos^2\theta+\frac{3}{35}\right), \tag{51}$$

where the radial function $u'_{1,2\rightarrow 4}$ is determined by

$$M_4u'_{1,2\rightarrow 4}=u'_0/r^3. \tag{52}$$

The $nd\rightarrow g$ wave functions for $m=\pm1$, and ±2 are given by

$$u^{(\pm1)}{}_{1,2\rightarrow 4}=\mp\frac{3}{2}\left(\frac{15}{4}\right)^{\frac{1}{2}}Qu'_{1,2\rightarrow 4}\times(\sin\theta\cos^3\theta-(3/7)\sin\theta\cos\theta), \tag{53}$$

$$u^{(\pm2)}{}_{1,2\rightarrow 4}=\frac{3}{2}\left(\frac{15}{16}\right)^{\frac{1}{2}}Qu'_{1,2\rightarrow 4}\times(\sin^2\theta\cos^2\theta-(1/7)\sin^2\theta). \tag{54}$$

For the total induced moment, one finds

$$Q_{iT}(nd\rightarrow g)=4\sum_{m=-2}^{2}\int_0^\infty\int_0^\pi u_0{}^{(m)}u_{1,2\rightarrow 4}{}^{(m)}(3\cos^2\theta-1)r^2dr\times\sin\theta d\theta=\frac{144}{35}Q\int_0^\infty u'_0u'_{1,2\rightarrow 4}r^2dr. \tag{55}$$

The exchange terms involving the excitation of the d shell will now be obtained. For this purpose, it will be assumed that the valence electron is in a p state with $m_v=0$. Here m_v is the magnetic quantum number of the valence electron while m_u will denote the magnetic quantum number of the nd state. Of course, the choice of m_v is immaterial, since the final result is independent of m_v. The $nd\rightarrow d$ waves will be treated presently. We consider first the electron with $m_u=0$. As was shown in I, the exchange energy can be regarded as due to the interaction of an exchange potential V_e with the overlap density $u_0{}^{(0)}v$ of the unperturbed wave functions of the core and the valence electron. Here v is the wave function (times r) of the valence electron, and is given by

$$v=(3/2)^{\frac{1}{2}}v'\cos\theta, \tag{56}$$

where v' is the radial function, normalized according to (1a). V_e is the potential produced by the overlap of $u_1{}^{(0)}$ with v. Since $u_1{}^{(0)}$ and v are a d wave and a p wave, respectively, V_e has both a P_1 and a P_3 part. The P_1 part will be considered first. It arises from the term $2(r_</r_>{}^2)\sum^1{}_{m=-1}P_1{}^m(\theta_1)P_1{}^{-m}(\theta_2)$ of $2/r_{12}$, where r_{12} is the distance between the two electrons, $r_<$ and $r_>$ are the smaller and the larger, respectively, of the distances r_1 and r_2 of the electrons from the nucleus; $\theta_{1,2}$ is the angle between the radius vector and the axis of Q. For $m_u=0$ we have

$$V_{e,P_1}{}^{(0)}=-4\left[\int_0^\infty\int_0^\pi u^{(0)}{}_{1,2\rightarrow 2}v\cos\theta_2(r_</r_>{}^2)dr_2\times\sin\theta_2d\theta_2\right]\cos\theta_1, \tag{57}$$

where the factor -4 arises from the Rydberg units and from a factor of 2 in the overlap density. Upon inserting Eqs. (37) and (56) in (57), one obtains

$$V_{e,P_1}{}^{(0)}=-[16/7(15)^{\frac{1}{2}}]Qf_1(r_1)\cos\theta_1, \tag{58}$$

where $f_L(r_1)$ is defined by

$$f_L(r_1)=r_1{}^{-L-1}\int_0^{r_1}u'_{1,l\rightarrow l'}v'r_2{}^Ldr_2+r_1{}^L\int_{r_1}^\infty u'_{1,l\rightarrow l'}v'r_2{}^{-L-1}dr_2, \tag{59}$$

and $u'_{1,\,l\to l'}$ is taken as $u'_{1,\,2\to 2}$. The exchange energy is given by

$$\Delta E_{e,P_1}{}^{(0)}=\int_0^\infty\int_0^\pi V_{e,P_1}{}^{(0)}u_0{}^{(0)}vdr_1\sin\theta_1 d\theta_1. \quad (60)$$

Upon inserting (31), (56), and (58) in (60), one obtains

$$\Delta E_{e,P_1}{}^{(0)}=-(32/105)QK(nd\to d,P_1), \quad (61)$$

where $K(nl\to l',P_L)$ is defined by

$$K(nl\to l',P_L)=\int_0^\infty u'_0 v' f_L dr, \quad (62)$$

with f_L given by (59). For the $m_u=\pm 1$ states, $V_{e,P_1}{}^{(\pm 1)}$ for the P_1 interaction is given by

$$V_{e,P_1}{}^{(\pm 1)}=-4\left[\int_0^\infty\int_0^\pi u^{(\pm 1)}{}_{1,\,2\to 2}v\left(\frac{\sin\theta_2}{\sqrt{2}}\right)\frac{r_<}{r_>{}^2}dr_2 \times\sin\theta_2 d\theta_2\right]\frac{\sin\theta_1}{\sqrt{2}}. \quad (63)$$

In view of (41) one finds

$$V_{e,P_1}{}^{(\pm 1)}=\pm(4/35)(5/2)^{\frac{1}{2}}Qf_1(r_1)\sin\theta_1. \quad (64)$$

One obtains for the exchange energy for the two electrons with $m_u=\pm 1$ and spin parallel to the valence electron spin,

$$\Delta E_{e,P_1}{}^{(\pm 1)}=2\int_0^\infty\int_0^\pi V_{e,P_1}{}^{(\pm 1)}u_0{}^{(\pm 1)}vdr_1\sin\theta_1 d\theta_1 =-\frac{8}{35}QK(nd\to d,P_1). \quad (65)$$

As is easily seen, the $m_u=\pm 2$ electrons do not contribute to the P_1 exchange interaction. Thus Eqs. (61) and (65) give for the total P_1 interaction with $nd\to d$,

$$\sum_{m_u=-2}^{2}\Delta E_{e,P_1}{}^{(m_u)}=-(8/15)QK(nd\to d,P_1). \quad (66)$$

The direct interaction of Q with the valence electron is

$$E_Q=-Q\int_0^\infty\int_0^\pi P_2{}^0v^2r^{-3}\sin\theta d\theta dr=-(2/5)Q\langle r^{-3}\rangle_v, \quad (67)$$

where $\langle r^{-3}\rangle_v$ is the average of r^{-3} over the valence wave function. Thus one obtains the following contribution to R_e,

$$\delta R_e(nd\to d,P_1)=-(4/3)K(nd\to d,P_1)/\langle r^{-3}\rangle_v, \quad (68)$$

where the $-$ sign indicates that for $K>0$ the effect is a negative shielding.

The P_3 exchange with $nd\to d$ can be obtained in a similar manner, and gives the result

$$\delta R_e(nd\to d,P_3)=-(12/49)K(nd\to d,P_3)/\langle r^{-3}\rangle_v, \quad (69)$$

where the f_L which appears in Eq. (62) for K is given by f_3 of (59) with $u'_{1,\,l\to l'}$ taken as $u'_{1,\,2\to 2}$.

The exchange of the valence electron with the $nd\to s$ excitation is obtained as follows. Only the electron with $m_u=0$ (and parallel spin) contributes. In view of Eq. (47) for the perturbation $u^{(0)}{}_{1,\,2\to 0}$, we have

$$V_e=-4\left[\int_0^\infty\int_0^\pi u_1v(r_</r_>{}^2)\cos\theta_2 dr_2\sin\theta_2 d\theta_2\right]\cos\theta_1 =-\frac{4}{15^{\frac{1}{2}}}Qf_1\cos\theta_1, \quad (70)$$

where f_1 is obtained from Eq. (59), with $u'_{1,\,l\to l'}$ taken as $u'_{1,\,2\to 0}$. The resulting energy term is

$$\Delta E_e=\int_0^\infty\int_0^\pi V_e u_0{}^{(0)}vdr_1\sin\theta_1 d\theta_1 =-\frac{8}{15}QK(nd\to s,P_1). \quad (71)$$

In view of (67) the contribution to R_e is given by

$$\delta R_e(nd\to s,P_1)=-(4/3)K(nd\to s,P_1)/\langle r^{-3}\rangle_v. \quad (72)$$

The exchange of the valence electron with the $nd\to g$ waves can be treated in the same manner. Since the overlap of the valence function with the excited g wave produces angular terms which vary as P_3 and P_5, while the overlap of p with d produces P_1 and P_3 terms, the interaction involves only the P_3 term of $2/r_{12}$. By summing over the contributions of the m_u states of the d shell, one obtains

$$\delta R_e(nd\to g,P_3)=-(72/49)K(nd\to g,P_3)/\langle r^{-3}\rangle_v, \quad (73)$$

where K is given by (62) with $f_L=f_3$ as obtained from Eq. (59) in which $u'_{1,\,l\to l'}$ is taken as $u'_{1,\,2\to 4}$.

Upon combining the preceding results for the d shells [Eqs. (68), (69), (72), and (73)] with those found in I for the exchange with the closed s and p shells, one obtains Eq. (14) for the contribution of exchange to R_e for the case of an external p electron.

The effect of the $nf\to f$ radial modes induced by the nuclear Q has been given in Eq. (7). The derivation follows the same lines as for the $nd\to d$ terms. Here only the expressions for the perturbed wave functions $u^{(m)}{}_{1,\,3\to 3}$ will be given:

$$u^{(0)}{}_{1,\,3\to 3}=(4/15)(7/8)^{\frac{1}{2}}Q(5\cos^3\theta-3\cos\theta)u'_{1,\,3\to 3}, \quad (74)$$

$$u^{(\pm 1)}{}_{1,\,3\to 3}=\mp(1/5)(21/32)^{\frac{1}{2}} \times Q(5\cos^2\theta\sin\theta-\sin\theta)u'_{1,\,3\to 3}, \quad (75)$$

$$u^{(\pm 3)}{}_{1,\,3\to 3}=\mp(1/3)(35/32)^{\frac{1}{2}}Q\sin^3\theta u'_{1,\,3\to 3}, \quad (76)$$

and $u^{(\pm 2)}{}_{1,\,3\to 3}=0$. We use the same convention of signs for $\Theta_3{}^{\pm 1}$ and $\Theta_3{}^{\pm 3}$ as in Condon and Shortley.[18] The radial function $u'_{1,\,3\to 3}$ is determined by Eq. (6). The resulting induced moment is

$$Q_{iT}(nf\to f)=\sum_{m=-3}^{3}\int_0^\infty\int_0^\pi u_0{}^{(m)}u^{(m)}{}_{1,\,3\to3}(3\cos^2\theta-1)r^2dr \times\sin\theta d\theta=\frac{224}{75}Q\int_0^\infty u'_0u'_{1,\,3\to3}r^2dr,\quad(77)$$

where $u_0{}^{(m)}$ is the unperturbed f function (times r) for magnetic quantum number m.

V. CONCLUSIONS

The atomic core introduces three types of terms into the quadrupole coupling: (1) shielding terms due to angular modes of excitation of the core; (2) terms due to radial modes which are generally antishielding; (3) exchange terms.

(1) The shielding terms have been considered as due to the interaction of the angular part of the induced quadrupole moment with the valence electron. The effect of the angular modes is generally overestimated by a factor ~1.5 by the Thomas-Fermi model. This conclusion can be drawn from the previous wave-function calculations[2] for Li, Al, and Cl, as well as from the present calculations for Cs. Although the total induced moment due to the angular modes is appreciable (e.g., $1.41Q$ for Cl), the contribution to the quadrupole coupling is only of order 10 percent of the direct interaction of Q with the valence electron, because only the induced moment near the nucleus contributes appreciably on account of the penetration of the valence electron.

(2) The effect of the radial modes generally produces an antishielding i.e., it reinforces the effect of the nuclear Q, and increases the magnitude of the quadrupole coupling. As was shown in III, the total induced moment due to the radial modes, $Q_{iT,\,\mathrm{rad}}$, is very large, with values ranging from $-2.7Q$ for Na^+ to $-90Q$ for Cs^+. However, the induced moment distribution is quite external, and for this reason, the antishielding due to the radial modes is, in general, unimportant for the atomic ground states (except for heavy atoms) but becomes rapidly more effective as more external distributions of the valence electron are being considered. Thus for the first excited (p) states of the alkalis the antishielding predominates and gives effects ranging from 10 percent for Na to 24 percent for Cs.

The radial modes vanish for s states, and depend sensitively on the azimuthal quantum number. $Q_{iT,\,\mathrm{rad}}$ increases very rapidly with increasing principal quantum number n, and is generally larger for the $np\to p$ wave than for the $nd\to d$ wave of the same shell. By far the largest term of $Q_{iT,\,\mathrm{rad}}$ is due to the outermost shell. The Thomas-Fermi model appears not to include the effect of the radial modes. This result is not surprising in view of the sensitive dependence on l, and the fact that the effect concerns mostly the outermost shell of the core.

(3) The exchange terms are discussed in Secs. II and IV. In the present work values have been obtained for B $2p$, Na $3p$, and Cs $6p$, besides previous calculations[2] for Li $2p$, Al $3p$, and Cl $3p^5$.

For light atoms where the effect of the core on the magnetic hfs is small the correction factor C is given by

$$C=1\bigg/\left[1-\frac{R+\delta R'_e}{1-\delta R_{e,\,0}}\right].\quad(25)$$

The values of R are listed in Table I. The exchange terms $\delta R_{e,\,0}$ and $\delta R'_e$ are given in Sec. II. For the cases of Cu, Rb, and W, these terms were obtained by interpolation of the values calculated for the other elements. The resulting values of C are: 1.12 ± 0.08 for Li $2p$, 1.06 ± 0.11 for B $2p$, 0.92 ± 0.02 for Na $3p$, 0.97 ± 0.03 for Al $3p$, 1.03 ± 0.05 for Cl $3p^5$, 1.10 ± 0.10 for Cu $3d^94s^2$, 0.82 ± 0.02 for Rb $4p$, 0.83 ± 0.02 for Cs $6p$, 0.68 ± 0.10 for W $5d^4$. The upper and lower limits correspond to the uncertainty of $\delta R'_e$. The upper limit of C is obtained by assuming that $\delta R'_e$ is actually zero, while the lower limit corresponds to a value of $\delta R'_e$ which is twice that calculated from the perturbed wave functions. For Cu and W, the uncertainty ±0.10 is somewhat larger than that obtained from $\delta R'_e$ alone. It is seen from Table I that for all cases the values $C=1/(1-R)$ which would be obtained without exchange are inside the range of C given above, so that the inclusion of exchange does not materially affect the results. The contribution of exchange for excited states (Na, Rb, Cs) is very small, so that the values of C are most probably less than 1 for these states (net antishielding), even allowing for a considerable uncertainty of the exchange terms.

The present values of C for B, Al, Cl, and Cu may be compared with those given in Table III of II. The values of II (e.g., $C=1.068$ for Cl) are close to the upper limit of the range of C given above, corresponding to the fact that $\delta R'_e$ was assumed very small in the calculations of II. The calculations for the first excited (p) states of Na, Rb, and Cs have not been previously carried out. The present values for Li $2p$ and Al $3p$ are based on I. We note that since there are no filled p shells for Li, there is no antishielding, and hence C exceeds 1 for all excited states of the valence electron. Calculations for W have not been carried out previously. However, in Table III of II, Thomas-Fermi values of C were given for the neighboring elements Lu and Ta, for which the valence electron is also in the $5d$ state. The present calculations for $5d$ of W show that these values are probably incorrect because of the neglect of antishielding. In general, the values of C given in II cannot be considered as reliable, except for the four cases B, Al, Cl, and Cu which are supported by the present calculations, if one assumes that the exchange term $\delta R'_e$ is, in fact, very small. In order to obtain accurate values of C for the other atomic states of Table III of II, it would be necessary to carry out a calculation of the antishielding and exchange for each element. However, it may be expected from the present work that the shielding predominates for light atoms, and that the actual correction factors are in many cases close to those given in II. For the ground states of heavy atoms ($Z \gtrsim 55$) there is an indication that the antishielding predominates. For all cases, the correction factors listed in II give a rough upper limit, since both the radial and the exchange terms tend to decrease C.

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APPENDIX. SECOND-ORDER QUADRUPOLE EFFECT

It has been pointed out in III, in connection with the quadrupole coupling in polar molecules, that the quadrupole distortion induced in the core by an external charge gives rise in second order to a further contribution to the quadrupole coupling. In the present case, the external charge corresponds to the valence electron. As has been shown previously,[3] the distortion of the core by the valence electron taken in first order is equivalent to the interaction of the valence electron with the quadrupole moment induced in the core by the nuclear Q. The second-order quadrupole effect involves the perturbation of the core by the external valence electron taken in second order. In as much as the first-order quadrupole correction is small for atoms, (of the order of 10 percent), it was expected that the second-order quadrupole effect would be even smaller, of the order of 1 percent of the main term in the quadrupole coupling. This expectation was borne out by a calculation of the second-order quadrupole effect for the $3p^5$ state of Cl.

In the following we will first give a derivation of the second-order quadrupole effect for s states of the core. The valence electron (or hole) is assumed in a p state with magnetic quantum number $m=1$; the p state will be taken as $3p$ (Cl). The various perturbations which arise in first and second order have been given in Fig. 3 of III. In first order, one obtains a d wave, d_{ns}. In second order, d_{ns} is excited into an s wave, a d wave d'_{ns}, and a g wave. The first-order perturbation Ψ_1 is determined by

$$(H_0-E_0)\Psi_1=[(-2/r_{12})+E_1]\Psi_0, \tag{1A}$$

where $\Psi_0=\psi_{ns}(1)\psi_{3p,1}(2)$ is the zero-order wave function, H_0 and E_0 are the unperturbed Hamiltonian and energy, respectively, E_1 is the first-order perturbation energy, and vanishes for s states. Ψ_1 can be written,

$$\Psi_1=\sum_{mm'} a_{mm'}\psi_{d,m}(1)\psi_{3p,m'}(2), \tag{2A}$$

where $a_{mm'}$ is a coefficient, $\psi_{d,m}$ is the perturbed d wave, $\psi_{3p,m'}$ is a $3p$ function, m and m' are the magnetic quantum numbers of the d wave and of $3p$, respectively. Upon inserting (2A) in (1A) one obtains

$$(H_0-E_0)\sum_{mm'} a_{mm'}\psi_{d,m}(1)\psi_{3p,m'}(2) \\ =[(-2/r_{12})+E_1]\psi_{1s}(1)\psi_{3p,1}(2). \tag{3A}$$

Since we are interested in the P_2 perturbation, the term of $-2/r_{12}$ which will be used is

$$-2(r^2_{<}/r^3_{>})\sum_{m=-2}^{2} P_2^m(\theta_1)P_2^{-m}(\theta_2).$$

The values of $a_{mm'}$ are obtained in the same manner as shown in II for the magnetic hfs. These values depend on the normalization of $\psi_{d,m}$ which will be chosen as follows. $\psi_{d,m}$ will be written

$$\psi_{d,m}=[w_1'(d_{ns})/r]\Theta_2^m, \tag{4A}$$

where Θ_2^m is the normalized angular function [Eq. (31b)], and the radial function $w_1'(d_{ns})$ is determined by

$$M_2 w_1'(d_{ns})=fu'_0, \tag{5A}$$

where u'_0 is r times the radial ns function, M_2 is defined by Eq. (39), and $f(r)$ is given by

$$f(r)=r^{-3}\int_0^r v'^2 r'^2 dr' + r^2\int_r^\infty v'^2 r'^{-3} dr', \tag{6A}$$

with $v'=r$ times the radial $3p$ function, normalized according to (1a). Equation (5A) and the values of $a_{mm'}$ are obtained by multiplying both sides of (3A) by $\Theta_2^{m*}(1)\psi^*_{3p,m'}(2)$ and integrating over $\sin\theta_1 d\theta_1$ and $d\mathbf{r}_2$, where θ_1 is the polar angle of electron 1, and $d\mathbf{r}_2$ denotes the volume element of electron 2. Throughout this discussion we use wave functions normalized to a volume element $\sin\theta_i d\theta_i dr_i$. The resulting equation for $a_{mm'}$ is

$$a_{mm'}=-2\int_0^\pi \Theta_1^1\Theta_1^{m'*}P_2^{m'-1} \\ \times\sin\theta_2 d\theta_2\int_0^\pi P_2^{1-m'}\Theta_2^0\Theta_2^{m*}\sin\theta_1 d\theta_1. \tag{7A}$$

From (2A) and (7A) one obtains

$$\Psi_1=(2/5^{\frac{3}{2}})[\psi_{d,0}(1)\psi_{3p,1}(2)-3^{\frac{1}{2}}\psi_{d,1}(1)\psi_{3p,0}(2) \\ +6^{\frac{1}{2}}\psi_{d,2}(1)\psi_{3p,-1}(2)]. \tag{8A}$$

It will now be verified that the overlap of Ψ_0 and Ψ_1 gives the previous result[2] for the first-order induced effect [Eq. (3)]. The quadrupole coupling q' will be defined by

$$q'=-\int[\rho(3\cos^2\theta-1)/(2r^3)]dV, \tag{9A}$$

where ρ is the electronic probability density and dV is the volume element. The main term of q' which is due to the valence electron density is given by

$$q'_0=-\int_0^\infty v'^2r^{-3}dr\int_0^\pi |\Theta_1{}^1|^2P_2{}^0\sin\theta d\theta =(1/5)\langle r^{-3}\rangle_v. \quad (10A)$$

The term of q' due to the overlap of Ψ_0 and Ψ_1 is

$$\Delta q'=-4\int\Psi_0\Psi_1P_2{}^0(1)r_1{}^{-3}dV_1dV_2$$

$$=-\frac{8}{5^{3/2}}\int_0^\pi \Theta_0{}^0\Theta_2{}^0P_2{}^0\sin\theta_1d\theta_1\int_0^\infty\frac{u'_0w_1'(d_{ns})}{r^3}dr, \quad (11A)$$

where dV_i is the volume element of electron i, and the factor 4 in the first equation arises from the presence of two terms in the overlap for each s electron. Upon evaluating (11A) one finds in view of (10A)

$$\Delta q'=-(8/5)\left[\int_0^\infty u'_0w_1'r^{-3}dr\right]q'_0/\langle r^{-3}\rangle_v. \quad (12A)$$

Equation (12A) gives the same result as the induced moment density $(8/5)Qu'_0u'_{1,0\rightarrow2}r^2$ since the radial integral over $u'_0u'_{1,0\rightarrow2}$ and v'^2 is equal to $\int_0^\infty[u'_0w'_1/r^3]dr$ of (12A), as shown in reference 3.

The second-order terms arise from two sources. The square of the first-order perturbation $\Psi_1{}^2$ contributes a term. We have

$$\Psi_1{}^2=(4/125)[\psi^2{}_{d,0}(1)\psi^2{}_{3p,1}(2)+3\psi^2{}_{d,1}(1)\psi^2{}_{3p,0}(2) +6\psi^2{}_{d,2}(1)\psi^2{}_{3p,-1}(2)+\cdots], \quad (13A)$$

where cross terms have not been written down since they do not contribute to q'. The contribution to q' is

$$\Delta q'_1=-2\int\Psi_1{}^2P_2{}^0(1)r_1{}^{-3}dV_1dV_2$$

$$=-\frac{8}{125}[I_2{}^0+3I_2{}^1+6I_2{}^2]J(d_{ns},d_{ns}), \quad (14A)$$

where $I_l{}^m$ is defined by

$$I_l{}^m\equiv\int_0^\pi|\Theta_l{}^m|^2P_2{}^0\sin\theta d\theta, \quad (15A)$$

and

$$J(a,b)\equiv\int_0^\infty w'_i(a)w'_j(b)r^{-3}dr, \quad (16A)$$

where $w'_i(a)$ and $w'_j(b)$ are the radial parts of the perturbed wave functions whose subscript (i,j) indicates the order of the perturbation. One finds $I_2{}^0=2/7$, $I_2{}^1=1/7$, $I_2{}^2=-2/7$. Thus Eq. (14A) gives

$$\Delta q'_1/q'_0=(8/25)J'(d_{ns},d_{ns}), \quad (17A)$$

where $J'(a,b)$ is defined by

$$J'(a,b)\equiv J(a,b)/\langle r^{-3}\rangle_v. \quad (18A)$$

The other second-order term is contributed by the overlap of Ψ_0 with the second-order perturbation of the wave function, which will be called Ψ_2. Ψ_2 is determined by

$$(H_0-E_0)\Psi_2=(-2/r_{12})\Psi_1+E_2\Psi_0+E_1\Psi_1, \quad (19A)$$

where E_1 and E_2 are the first- and second-order perturbations of the energy, respectively. Ψ_2 consists of s, d, and g waves, but only the d wave, which will be called d'_{ns}, is of interest since the overlap of ns with excited s or g waves does not contribute to the quadrupole coupling. The term $E_2\Psi_0$ enters only into the equation for the s wave, so that it will not be considered here. Moreover, $E_1=0$ for s states. Ψ_2 will be written

$$\Psi_2=\sum_{mm'}b_{mm'}\chi_{d,m}(1)\psi_{3p,m'}(2), \quad (20A)$$

where $b_{mm'}$ is a coefficient, $\chi_{d,m}$ is the d'_{ns} wave, m and m' are the magnetic quantum numbers of d'_{ns} and $3p$, respectively. Upon inserting (8A) and (20A) into (19A), one obtains

$$(H_0-E_0)\sum_{mm'}b_{mm'}\chi_{d,m}(1)\psi_{3p,m'}(2)$$

$$=-\frac{4}{5^{3/2}r_{12}}[\psi_{d,0}(1)\psi_{3p,1}(2)-3^{1/2}\psi_{d,1}(1)\psi_{3p,0}(2) +6^{1/2}\psi_{d,2}(1)\psi_{3p,-1}(2)]. \quad (21A)$$

A given $b_{mm'}$ will contain, in general, contributions from more than one term of Ψ_1 on the right-hand side of (21A). The terms of $b_{mm'}$ will be labeled by m_1 and m_2, which are the magnetic quantum numbers of the first-order d wave ψ_{d,m_1} and of ψ_{3p,m_2}, respectively. The contribution of m_1 and m_2 to $b_{mm'}$ will be written $b_{mm'(m_1m_2)}$. By multiplying both sides of (21A) by $\Theta_2{}^{m*}(1)\psi^*{}_{3p,m'}(2)$ and integrating over $\sin\theta_1d\theta_1$ and $d\mathbf{r}_2$, one obtains

$$b_{mm'(m_1m_2)}=-\frac{4c_{m_1m_2}}{5^{3/2}}\int_0^\pi\Theta_1{}^{m_2}\Theta_1{}^{m'*}P_2{}^{m'-m_2}$$

$$\times\sin\theta_2d\theta_2\int_0^\pi\Theta_2{}^{m_1}\Theta_2{}^{m*}P_2{}^{m_2-m'}\sin\theta_1d\theta_1, \quad (22A)$$

where $c_{m_1m_2}$ is the coefficient of $\psi_{d,m_1}(1)\psi_{3p,m_2}(2)$ in the square bracket of (21A). In obtaining (22A) it was assumed that $\chi_{d,m}$ is normalized as follows

$$\chi_{d,m}=[w_2'(d'_{ns})/r]\Theta_2{}^m, \quad (23A)$$

where the radial function $w'_2(d'_{ns})$ is determined by

$$M_2w'_2(d'_{ns})=w'_1(d_{ns})f. \quad (24A)$$

Upon summing (22A) over m_1m_2, and inserting the result in (20A) one obtains

$$\Psi_2 = -(4/5^{5/2})[\chi_{d,0}(1)\psi_{3p,1}(2) - 3^{\frac{1}{2}}\chi_{d,1}(1)\psi_{3p,0}(2) + 6^{\frac{1}{2}}\chi_{d,2}(1)\psi_{3p,-1}(2)]. \tag{25A}$$

Only the overlap of the first term $\chi_{d,0}(1)\psi_{3p,1}(2)$ with Ψ_0 contributes to q'. One finds

$$\Delta q'_2 = -4\int \Psi_0\Psi_2 P_2^0(1) r_1^{-3} dV_1 dV_2 = (16/125)J(ns,d_{ns}), \tag{26A}$$

where $J(ns,b)$ is given by

$$J(ns,b) = \int_0^\infty u'_{0,ns} w_2'(b) r^{-3} dr, \tag{27A}$$

and $u'_{0,ns}$ is the unperturbed ns radial function. In analogy with (18A) $J'(ns,b)$ will be defined as $J(ns,b)/\langle r^{-3}\rangle_v$. Thus the total second-order contribution of an s shell is

$$\Delta q'_{ns}/q'_0 = (8/25)J'(d_{ns},d_{ns}) + (16/25)J'(ns,d'_{ns}). \tag{28A}$$

The excitation of np states can be treated in the same manner as the excitation of ns. As shown in Fig. 3 of III, np is excited in first order to a p wave p_{np} and an f wave f_{np}. In second order, p_{np} is excited to a p wave p'_{np} and an f wave f'_{np}. Similarly, f_{np} is excited to a p wave p''_{np} and an f wave f''_{np}. The second-order quadrupole effect arises from terms containing the square of p_{np} and f_{np}, and from the overlap of u'_0 with the second-order perturbations. We will give only the final result. One obtains for the second-order quadrupole effect of a complete p shell,

$$\frac{\Delta q'_{np}}{q'_0} = \frac{168}{625}J'(p_{np},p_{np}) + \frac{336}{625}J'(np,p'_{np}) + \frac{288}{625}J'(f_{np},f_{np}) + \frac{144}{625}J'(np,p''_{np}) + \frac{144}{625}J'(np,f'_{np}) + \frac{576}{625}J'(np,f''_{np}), \tag{29A}$$

where the J' are determined by Eqs. (16A), (18A) and

$$J'(np,b) = \left[\int_0^\infty u'_{0,np} w'_2(b) r^{-3} dr\right] / \langle r^{-3}\rangle_v, \tag{30A}$$

in which $u'_{0,np}$ is the unperturbed radial np function of the core. The radial functions appearing in the J' are determined by the following equations

$$M_1 w'_1(p_{np}) = u'_{0,np}[f - \langle f\rangle_{np}], \tag{31A}$$

$$M_3 w'_1(f_{np}) = u'_{0,np} f, \tag{32A}$$

$$M_1 w'_2(p'_{np}) = w'_1(p_{np})[f - \langle f\rangle_{np}] - \left[\int_0^\infty f w'_1(p_{np}) u'_{0,np} dr'\right] u'_{0,np}(r), \tag{33A}$$

$$M_3 w'_2(f'_{np}) = w'_1(p_{np}) f, \tag{34A}$$

$$M_1 w'_2(p''_{np}) = w'_1(f_{np}) f - \left[\int_0^\infty f w'_1(f_{np}) u'_{0,np} dr'\right] u'_{0,np}(r), \tag{35A}$$

$$M_3 w'_2(f''_{np}) = w'_1(f_{np}) f, \tag{36A}$$

where

$$\langle f\rangle_{np} \equiv \int_0^\infty f u'^2_{0,np} dr. \tag{37A}$$

In Eqs. (33A) and (35A) that function $w'_2(p'_{np})$ or $w'_2(p''_{np})$ must be chosen which is orthogonal to $u'_{0,np}$. It may be noted that the numerical coefficients of Eqs. (28A) and (29A) are proportional to those which appear in the expressions for $\Delta q'_{ns}$ and $\Delta q'_{np}$ for the case of an external point charge, as given by Eqs. (61) and (64) of III; the proportionality factor is 7/10. The contribution of the second-order terms to R_e is $-\sum_n(\Delta q'_{ns} + \Delta q'_{np})/q'_0$ since R_e is defined in terms of minus the interaction energy due to the induced effects.

The radial functions and integrals obtained above were calculated for Cl. Only the 3s and 3p shells had to be considered since the contribution of the inner shells is negligible. It was found that $-(\Delta q'_{3s} + \Delta q'_{3p})/q'_0$ is $\sim +0.005$ and is thus smaller than the uncertainties in the first-order terms of R_e.

It should be noted that the preceding results do not represent the complete second-order correction. There are additional terms[19] which arise from the simultaneous excitation of a core electron and the valence electron by the perturbation e^2/r_{12}. As an example, let us consider the term

$$e^2(r_</r_>^2) \sum_{m=-1}^{1} P_1^m(1) P_1^{-m}(2)$$

of e^2/r_{12}. Let

$$\Psi_0 = s_0(1) p_0(2) \tag{38A}$$

denote the zero-order wave function for a system consisting of a core electron in an s state and a p valence electron. In first order, one obtains the perturbation

$$\Psi_1 = p_1(1)s_1(2) + p_1'(1)d_1(2), \tag{39A}$$

where p_1 and p'_1 are p functions which describe the

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[19] The existence of these terms was pointed out to the author by Professor H. M. Foley.

excitation of electron 1 into higher p states, while s_1 and d_1 are s and d functions, respectively, which describe the excitation of electron 2. The first-order overlap $\Psi_0\Psi_1$ does not contribute to q' because $s_0(1)$ is orthogonal to $p_1(1)$ and $p'_1(1)$, and similarly $p_0(2)$ is orthogonal to $s_1(2)$ and $d_1(2)$. However, Ψ_1^2 contributes three second-order terms to q' which arise from $[p_1(1)]^2$, $[p'_1(1)]^2$, and $[d_1(2)]^2$. Second-order terms of the type Ψ_1^2 are also obtained from the simultaneous $P_1{}^m$ excitation of a core electron in a p state and the valence electron. A similar class of terms is obtained using the $P_2{}^m$ part of e^2/r_{12}. These terms were not evaluated because of the difficulty of determining the functions of type p_1, s_1, p'_1, and d_1. Thus p_1 and s_1 satisfy a set of two simultaneous differential equations. The same applies for p'_1 and d_1. The numerical solution of these sets would be much more complicated than the solution of Eqs. (5A) and (24A) which involve a single unknown function. However, there seems to be no reason to believe that the two-electron terms would be appreciably larger than the one-electron excitation terms which were shown to be very small for the case of Cl.

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Cross Sections for the Reactions $Ti^{48}(d,2n)V^{48}$; $Cr^{52}(d,2n)Mn^{52}$; and $Fe^{56}(d,2n)Co^{56}$†

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Measurements have been made of the $(d,2n)$ cross sections of the nuclear species Ti^{48}, Cr^{52}, and Fe^{56}. Results are given for incident deuterons in the energy region 1–20 Mev.

THE cross sections for the reactions $Ti^{48}(d,2n)V^{48}$, $Cr^{52}(d,2n)Mn^{52}$, and $Fe^{56}(d,2n)Co^{56}$ have been measured as functions of energy of the bombarding deuterons, using the conventional stacked foil method, for energies of 1 to 20 Mev. A beam of deuterons was provided by the 60-inch cyclotron of the Crocker Laboratory of the University of California.

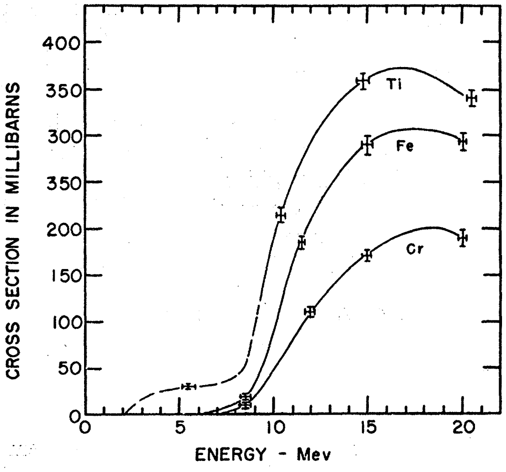

FIG. 1. Cross sections for the reactions $Fe^{56}(d,2n)Co^{56}$, $Cr^{52}(d,2n)Mn^{52}$, and $Ti^{48}(d,2n)V^{48}$.

The range distribution of deuterons in the beam, which was collected in a Faraday cup, was measured before each run by placing absorber foils of known thickness of aluminum in the beam and measuring the charge I_f collected on the foils, and the charge I_c passing through the foils and collected by the Faraday cup. These charges were measured by two electrometers and recorded. The ratio $I_c/(I_c+I_f)$ was determined as a function of thickness of aluminum absorber, giving the range distribution of deuterons. The target foils of Ti metal, Fe metal, and stainless steel were then placed in the beam and bombarded. The beam current was monitored by reading both I_c and I_f. The equivalent Al thickness of the target foils was determined by placing Al foils of varying thickness behind the target foil in the beam and again measuring $I_c/(I_c+I_f)$. Comparison of this measurement with that for the Al absorber foils determined the equivalent aluminum thickness of the stack of target foils and thereby the energies of the deuterons that struck each foil in the target stack.

Absolute cross-section measurements were made by chemical separation of the end products, with subsequent absolute β^+ counting. The absolute counting was done using a thin-window methane-flow proportional counter and correcting for scattering and absorption. The results for V^{48} and Mn^{52} were checked by 4π counting of very thin samples, and good agreement was obtained.

The absolute cross-section values depend on the fact that the end products of the bombardment decay

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