

Shielding and Antishielding Effects for Various Ions and Atomic Systems*

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We report the results of calculations of several shielding and antishielding effects pertaining to the hyperfine structure of various ions and atomic systems. The following shielding (or antishielding) parameters have been considered in the present work: (1) the parameter σ_2 for the rare-earth ions, which measures the reduction of the $A_2P_2(\cos\theta)$ term of the crystal field at the location of the $4f$ electrons due to the shielding effect of the more external $5s$ and $5p$ electrons; (2) the quadrupole antishielding factor γ_∞ which gives the total quadrupole moment induced in the closed shells of an ion by the nuclear quadrupole moment Q ; (3) the corresponding atomic shielding factor R which describes the effect of the induced quadrupole moment on the valence electrons; (4) the hexadecapole antishielding factor η_∞ , which is analogous to γ_∞ , except that it pertains to the induced hexadecapole (16-pole) moment produced by a possible nuclear electric hexadecapole moment. The calculated values of σ_2 for the Pr^{3+} and Tm^{3+} ions are in good agreement with the experimental results. We have obtained improved values of γ_∞ for the following ions: Al^{3+} , Cs^+ , I^- , Pr^{3+} , and Tm^{3+} . The atomic shielding factor R has been calculated for the $4f$ electrons of Pr^{3+} and Tm^{3+} , and was found to be in reasonable agreement with experiment. A discussion is given of the most likely regions of atomic number for which it might be possible to detect a nuclear hexadecapole moment. In addition, an evaluation of the second-order terms in the antishielding factor γ_∞ for the Cl^- ion has been carried out. Expressions for $\gamma_\infty(nl \rightarrow l \pm 2)$ for the case of hydrogenic wave functions have been obtained.

I. INTRODUCTION

THE purpose of the present paper is to give the results of calculations of several shielding and antishielding effects pertaining to the hyperfine structure for various ions and atomic systems. In particular, we have obtained values for the shielding parameter^{1,2} σ_2 for the $4f$ electrons in rare-earth ions and for the quadrupole antishielding factors^{3,4} γ_∞ and

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¹The shielding parameter σ_2 has been experimentally determined by D. T. Edmonds, *Phys. Rev. Letters* **10**, 129 (1963); R. G. Barnes, R. L. Mössbauer, E. Kankleit, and J. M. Poin-dexter, *ibid.* **11**, 253 (1963); *Phys. Rev.* **136**, A175 (1964); J. Blok and D. A. Shirley, *J. Chem. Phys.* **39**, 1128 (1963); *Phys. Rev.* **143**, 278 (1966); H. H. Wickman and I. Nowik, *ibid.* **142**, 115 (1966). The existence of quadrupole antishielding effects for the rare-earth ions was first demonstrated by the work of B. R. Judd, C. A. Lovejoy, and D. A. Shirley, *Phys. Rev.* **128**, 1733 (1962).

²Previous calculations of σ_2 have been reported in the following papers: C. J. Lenander and E. Y. Wong, *J. Chem. Phys.* **38**, 2750 (1963); D. K. Ray, *Proc. Phys. Soc. (London)* **82**, 47 (1963); R. E. Watson and A. J. Freeman, *Phys. Rev.* **133**, A1571 (1964); **139**, A1606 (1965); G. Burns, *ibid.* **128**, 2121 (1962); *J. Chem. Phys.* **42**, 377 (1965).

³R. M. Sternheimer, *Phys. Rev.* **80**, 102 (1950); **84**, 244 (1951); **86**, 316 (1952); **95**, 736 (1954); **105**, 158 (1957); **130**, 1423 (1963); **132**, 1637 (1963); H. M. Foley, R. M. Sternheimer, and D. Tycko, *ibid.* **93**, 734 (1954); R. M. Sternheimer and H. M. Foley, *ibid.* **92**, 1460 (1953); **102**, 731 (1956).

⁴Calculations of γ_∞ by the variational method of T. P. Das and R. Bersohn, *Phys. Rev.* **102**, 733 (1956) have been published in the following papers: E. G. Wikner and T. P. Das, *Phys. Rev.* **109**, 360 (1958); G. Burns, *ibid.* **115**, 357 (1959); **124**, 524 (1961); *J. Chem. Phys.* **31**, 1253 (1959); G. Burns and E. G. Wikner, *Phys. Rev.* **121**, 155 (1961); *Phys. Letters* **2**, 225 (1962); R. G. Khubchandani, R. R. Sharma, and T. P. Das, *Phys. Rev.* **126**, 594 (1962). Extensive calculations of γ_∞ by means of the unrestricted Hartree-Fock method have been carried out by R. E. Watson and A. J. Freeman, *Phys. Rev.* **131**, 250 (1963); **135**, A1209 (1964); A. J. Freeman and R. E. Watson, *ibid.* **131**, 2566 (1963); **132**, 706 (1963). A calculation of R for the ferrous ion (Fe^{2+}) has been performed by R. Ingalls, *Phys. Rev.* **128**, 1155 (1962); **133**, A787 (1964). The subject of antishielding factors and polarizabilities has been recently reviewed by A. Dalgarno, *Advan. Phys.* **11**, 281 (1962). An extensive review of

R for a number of ions. In addition, the paper contains results on the hexadecapole antishielding factor⁵ η_∞ , the second-order antishielding for the Cl^- ion, and on the values of γ_∞ which one would obtain using hydrogenic wave functions.

In Sec. II, we give the results of calculations of the shielding parameter σ_2 for the Pr^{3+} and Tm^{3+} ions. The constant σ_2 gives a measure of the shielding of the $A_2P_2(\cos\theta)$ term of the crystal field, which is produced by the external $5s$ and $5p$ shells at the location of the $4f$ electrons of the rare-earth ions. In order to obtain σ_2 , we have used the same procedure as was previously employed in the calculation of the quadrupole antishielding factor³ γ_∞ and the dipole and quadrupole polarizabilities⁶ α_d and α_q , namely, the direct solution of the inhomogeneous Schrödinger equation for the perturbed wave functions. The resulting calculated values of σ_2 , namely, $\sigma_2(\text{Pr}^{3+})=0.60$ and $\sigma_2(\text{Tm}^{3+})=0.48$ are in good general agreement with the corresponding experimental values.¹ It should be noted that the present results include the contribution from the exchange terms of the electrostatic interaction between the $4f$ and $5s$ (or $5p$) electrons. It was found that the exchange terms are small compared to the dominant direct terms ($<10\%$ of the total σ_2).

In Sec. III, we obtain improved values of the quadrupole antishielding factor γ_∞ for the following ions: Al^{3+} , Cs^+ , I^- , Pr^{3+} , and Tm^{3+} . The results for Cs^+ and

the calculations of γ_∞ and R has been given by A. J. Freeman and R. E. Watson, in *Treatise on Magnetism*, edited by G. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. IIA, p. 167. See also C. H. Townes, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 38/1, p. 377.

⁵R. M. Sternheimer, *Phys. Rev. Letters* **6**, 190 (1961); *Phys. Rev.* **123**, 870 (1961).

⁶R. M. Sternheimer, *Phys. Rev.* **96**, 951 (1954); **107**, 1565 (1957); **115**, 1198 (1959); **127**, 1220 (1962). Calculations of the ionic polarizabilities by the variational method have been carried out by E. G. Wikner and T. P. Das, *Phys. Rev.* **107**, 497 (1957); P. W. Langshoff and R. P. Hurst, *ibid.* **139**, A1415 (1965).

I^- were obtained by means of the Hartree-Fock wave functions for these ions which have been calculated by Freeman and Watson.⁷ The values for Pr^{3+} and Tm^{3+} represent an improvement over those previously reported,⁸ on account of the fact that the terms $\gamma_\infty(2p \rightarrow p)$, $\gamma_\infty(3p \rightarrow p)$, $\gamma_\infty(3d \rightarrow d)$, and $\gamma_\infty(4d \rightarrow d)$ which had not been previously calculated are included in the present results. For Cs^+ , the present result, $\gamma_\infty = -102.5$, is appreciably smaller in magnitude than the previously published value⁹ (-143.5) which was based on Hartree wave functions (excluding exchange). In Sec. III, we have also given a table of all of the values of γ_∞ which have been calculated by the method of direct solution of the inhomogeneous wave equation.³ For a given zero-order wave function, this method gives values which are believed to be accurate to $\sim 3\%$. This table also includes the calculated values of the quadrupole polarizability α_q (obtained by the same method⁶), wherever they are available. In addition, Sec. III includes a calculation of the atomic quadrupole shielding factor³ R for the Pr^{3+} and Tm^{3+} ions. The results indicate that there is a small shielding (~ 10 – 20%) for both cases.

Section IV gives a general discussion and an evaluation of the second-order quadrupole antishielding effects for the Cl^- ion. The second-order antishielding arises as a result of including the induced quadrupole moment in the total quadrupole perturbation which produces the distortion of the closed shells of the ion.

In Sec. V, we prove the equivalence of two alternative methods of calculating the second-order antishielding. In the first method, one considers the perturbation due to the nuclear quadrupole moment Q , and subsequently the perturbation due to the resulting induced quadrupole moment Q_{ind} , and its effect on the closed shells, whereas, in the second method, one starts out with the external charge (at a distance R), and calculates in first order the distortion of the closed shells arising from the quadrupole part of the potential due to the external charge, namely, $(e^2r^2/R^3)P_2(\cos\theta)$. In this second method, the antishielding factor γ_∞ is obtained by dividing the field gradient at the nucleus due to the quadrupole distortion of the closed shells by the field gradient $2e/R^3$ which would be produced by the external charge acting alone. The second-order effect which is considered here arises from the field gradient at the nucleus which is due to the closed-shell distortion produced by the quadrupole potential arising from the first-order perturbation. In first order, it has been proved some time ago that the two methods are equivalent,¹⁰ and it is here shown that the equivalence also holds for the second-order terms of γ_∞ .

In Sec. VI, we give some additional results for the

⁷ A. J. Freeman and R. E. Watson (private communication).

⁸ R. M. Sternheimer, Phys. Rev. **132**, 1637 (1963).

⁹ R. M. Sternheimer and H. M. Foley, Phys. Rev. **102**, 731 (1956).

¹⁰ R. M. Sternheimer and H. M. Foley, Phys. Rev. **92**, 1460 (1953).

hexadecapole antishielding factor η_∞ . This factor pertains to the 16-pole moment induced in the closed shells by a possible electric 16-pole moment of the nucleus. We also give a discussion concerning the question as to the types of nuclei which are likely to have a relatively large and therefore measurable hexadecapole moment.

In Sec. VII, we obtain the values of $\gamma_\infty(nl \rightarrow l')$ for $l' = l \pm 2$ (shielding modes) assuming hydrogenic wave functions for the unperturbed closed-shell functions. The results are, of course, only of academic interest as far as the evaluation of an actual antishielding factor is concerned, since in this case one must always use accurate (preferably Hartree-Fock) wave functions for the ion considered. Nevertheless, the results are interesting from a theoretical point of view, for two reasons: (1) It was found that in all cases considered, namely, $ns \rightarrow d$, $np \rightarrow f$, $nd \rightarrow s$, and $nf \rightarrow p$, $\gamma_\infty(nl \rightarrow l \pm 2)$ is simply a linear function of the principal quantum number: $\gamma_\infty(nl \rightarrow l') = an + b$, where a and b depend only on l and l' (but not on n), and are inversely proportional to the atomic number Z . (2) In the course of the calculation of γ_∞ , an interesting orthogonality property of the hydrogenic wave functions has been discovered.

Finally, Sec. VIII gives a brief summary of the main results obtained in the present work.

II. THE SHIELDING PARAMETER σ_2

In this section, we will obtain the general expression for σ_2 for the case of a valence $4f$ electron, which is being considered in the present work.¹¹ We will also give some details of the actual calculation of σ_2 .

The shielding parameter σ_2 represents the electrostatic effect of the shielding^{1,2} of the internal $4f$ electrons by the more external $5s$ and $5p$ electrons of the rare-earth ions Pr^{3+} and Tm^{3+} . We note that there will also be some shielding by the other shells of the atom, besides $5s$ and $5p$. However, this effect due to the inner shells is expected to be small compared to that of $5s$ and $5p$, and it has been neglected in the present work.

In the shielding parameter σ_2 , there will be terms due to the direct electrostatic interaction between $5s$ (or $5p$) and $4f$, and also the corresponding exchange terms. We will first discuss the direct terms.

We assume a unit external charge $+e$ placed along the positive z axis at a distance R from the nucleus of the ion which we are considering. The quadrupole potential energy due to this charge is given by

$$V_R = -(2r^2/R^3)P_2(\cos\theta), \quad (1)$$

where V_R is in Rydberg units, r and θ are the polar coordinates of a point within the ion, measured with respect to the nucleus and the z axis (defined above); r

¹¹ A preliminary account of this work has been given in Bull. Am. Phys. Soc. **10**, 597 (1965).

and R are in units of the Bohr radius a_H , and P_2 is the Legendre polynomial.

Now we consider the perturbation due to V_R of a closed shell wave function $u_0(nlm)$ of the ion. Obviously, we will be interested in the cases where $nl=5s$ and $5p$. The potential V_R gives rise, in first order, to a perturbation $u_1(nl \rightarrow l_1)$ in the zero-order wave function, which is determined by the equation

$$(H_0 - E_0)u_1(nl \rightarrow l_1) = (E_1 - H_1)u_0(nl), \quad (2)$$

where H_0 and E_0 are the unperturbed Hamiltonian and energy eigenvalue pertaining to nl ; H_1 and E_1 are the corresponding first-order perturbations of H_0 and E_0 , respectively. We have $H_1 = V_R$, and

$$E_1 = \int_0^\infty \int_0^\pi u_0^2 H_1 dr \sin\theta d\theta, \quad (3)$$

where we should note that u_0 and u_1 actually refer to r times the corresponding wave functions, and the normalization for the radial part of u_0 , to be denoted by u_0' is given by

$$\int_0^\infty u_0'^2 dr = 1. \quad (4)$$

As discussed in several earlier papers,^{3,6,12} the perturbation V_R will produce the following types of perturbations: $5s \rightarrow d$, $5p \rightarrow p$, and $5p \rightarrow f$. The following discussion is very similar to that of Ref. 12 (see Sec. II). We write

$$u_1(nl \rightarrow l_1) = (2/R^3)du_1'(nl \rightarrow l_1)\Theta_{l_1}^m, \quad (5)$$

$$u_0(nlm) = u_0'(nl)\Theta_l^m, \quad (6)$$

where the spherical harmonics Θ_l^m are normalized to 1:

$$\int_0^\pi (\Theta_l^m)^2 \sin\theta d\theta = 1. \quad (7)$$

In Eq. (5), d is a constant to be determined below. The radial function $u_1'(nl \rightarrow l_1)$ is defined by the condition that it should satisfy the following inhomogeneous Schrödinger equation:

$$\left(-\frac{d^2}{dr^2} + \frac{l_1(l_1+1)}{r^2} + V_0 - E_0 \right) u_1'(nl \rightarrow l_1) = u_0'(nl) [r^2 - \langle r^2 \rangle_{nl} \delta_{ll_1}] \quad (8)$$

and moreover, for $l_1=l$, the orthogonality condition

$$\int_0^\infty u_0'(nl)u_1'(nl \rightarrow l)dr = 0. \quad (9)$$

In Eq. (8), the effective potential V_0 is obtained directly from the unperturbed wave function $u_0'(nl)$ by a pro-

cedure previously described by Sternheimer^{3,6}:

$$V_0 - E_0 = \frac{1}{u_0'} \frac{d^2 u_0'}{dr^2} - \frac{l(l+1)}{r^2}. \quad (10)$$

From Eqs. (2), (5), (6), and (8), we obtain for d

$$d = \int_0^\pi P_2 \Theta_l^m \Theta_{l_1}^m \sin\theta d\theta. \quad (11)$$

Thus, d is defined by the condition that Eq. (5), with $u_1'(nl \rightarrow l_1)$ obtained from Eq. (8), should represent the solution to Eq. (2).

The integral of Eq. (11) was previously denoted by $I_{ll_1}^{(2)m}$ in Ref. 12. The overlap density $2u_0u_1$ for the state nlm can be written as follows:

$$2u_0(nlm)u_1(nl \rightarrow l_1) = (4/R^3)I_{ll_1}^{(2)m}u_0'u_1'(nl \rightarrow l_1)\Theta_l^m\Theta_{l_1}^m. \quad (12)$$

The quadrupole part of the potential due to the density (12) is

$$V_q(nlm) = \frac{8}{R^3} [I_{ll_1}^{(2)m}]^2 P_2(\cos\theta) \left[\frac{1}{r^3} \int_0^r u_0'u_1'r'^2 dr' + r^2 \int_r^\infty u_0'u_1'r'^{-3} dr' \right], \quad (13)$$

where u_0' and u_1' are to be evaluated at the radius r' (the variable of integration). In Eq. (13), as compared to Eq. (12), a factor of 2 arises from the fact that the quadrupole part of the electrostatic interaction energy is: $2(r <^2 / r >^3)P_2(\cos\theta)$, when expressed in Rydberg units $e^2/2a_H$, as is done here.

In order to obtain the total V_q due to a closed shell, we must sum over all m values in Eq. (13), and multiply by 2 to take into account the two spin states for each m .

If we denote the function in square brackets in (13) by $f(r)$, we can therefore write

$$V_q(nl) = \frac{16}{R^3} f(r) P_2(\cos\theta) \sum_{m=-l}^l [I_{ll_1}^{(2)m}]^2, \quad (14)$$

for the potential due to the filled nl shell. We note that

$$16 \sum_{m=-l}^{+l} [I_{ll_1}^{(2)m}]^2 = 2C_{ll_1}^{(2)}, \quad (15)$$

where $C_{ll_1}^{(2)}$ is the angular factor for the quadrupole antishielding factor, as previously defined in Ref. 12 [see Eq. (28)]. For the excitations which are relevant to the present work, we have $C_{02}^{(2)} = 8/5$ for $5s \rightarrow d$, $C_{11}^{(2)} = 48/25$ for $5p \rightarrow p$, and $C_{13}^{(2)} = 72/25$ for $5p \rightarrow f$.

We now consider a valence $4f$ electron with magnetic quantum number m_e . The wave function of this electron times r will be denoted by v . Thus,

$$v(4f, m_e) = v'(r) \Theta_3^{m_e}, \quad (16)$$

¹² R. M. Sternheimer, Phys. Rev. **127**, 812 (1962).

where v' is the radial part of v , with the normalization [cf. Eq. (4)]:

$$\int_0^\infty v'^2 dr = 1. \quad (17)$$

The energy change E_q due to the potential $V_q(nl)$ acting on the $4f$ electron is given by

$$E_q(nl) = \frac{2C_{ll_1}^{(2)}}{R^3} \int_0^\infty v'^2 f(r) dr \int_0^\pi P_2(\Theta_3^{m_e})^2 \sin\theta d\theta, \quad (18)$$

which can be rewritten as follows [cf. Eq. (11) and the definition of $I_{ll_1}^{(2)m}$]:

$$E_q(nl) = \frac{2C_{ll_1}^{(2)} I_{l_e l_e}^{(2)m_e}}{R^3} \int_0^\infty v'^2 f(r) dr, \quad (19)$$

where $l_e \equiv 3$.

The energy $E_q(nl)$ has to be compared to the direct interaction energy with the external charge, in order to obtain the contribution of the $nl \rightarrow l_1$ perturbation to σ_2 , to be denoted by $\sigma_2(nl \rightarrow l_1)$.

The direct interaction energy E_R is given by

$$E_R = \int_0^\infty \int_0^\pi V_R v^2 dr \sin\theta d\theta = -\frac{2}{R^3} I_{l_e l_e}^{(2)m_e} \int_0^\infty v'^2 r^2 dr. \quad (20)$$

The integral in Eq. (20) will be denoted by $\langle r^2 \rangle_{4f}$. A comparison of the signs of Eqs. (19) and (20) shows that the effect of E_q is a shielding (decrease in magnitude of the original interaction), provided that the integral $\int_0^\infty v'^2 f(r) dr$ is positive. It turns out that the integral over $f(r)$ is positive for $5s \rightarrow d$ and $5p \rightarrow f$, but that it is negative for $5p \rightarrow p$, corresponding to an antishielding in this last case. This result is not too surprising when one considers the fact that the $5p \rightarrow p$ excitation mode provides the dominant (negative) term in the total quadrupole antishielding factor³ γ_∞ .

The contribution $\sigma_2(nl \rightarrow l_1)$ is defined as

$$-E_q(nl \rightarrow l_1)/E_R,$$

so that we obtain

$$\begin{aligned} \sigma_2(nl \rightarrow l_1) &= -\frac{E_q(nl \rightarrow l_1)}{E_R} \\ &= C_{ll_1}^{(2)} \left(\int_0^\infty v'^2 f(r) dr / \langle r^2 \rangle_{4f} \right). \end{aligned} \quad (21)$$

The total direct (i.e., nonexchange) term of σ_2 is then given by

$$\sigma_2(\text{direct}) = \sigma_2(5s \rightarrow d) + \sigma_2(5p \rightarrow p) + \sigma_2(5p \rightarrow f), \quad (22)$$

provided that the perturbation of the inner core electrons ($n \leq 4$) can be neglected. The effect of the positive

terms $\sigma_2(5s \rightarrow d)$ and $\sigma_2(5p \rightarrow f)$ predominates, leading to a net shielding.

Before proceeding to a discussion of the exchange terms of σ_2 , we wish to point out the connection of the integrals of Eq. (13) with the antishielding factor³ γ_∞ and the quadrupole polarizability⁶ α_q .

Thus, the contribution of $nl \rightarrow l_1$ to γ_∞ is given essentially by the second integral of Eq. (13) evaluated for $r=0$. We have

$$\gamma_\infty(nl \rightarrow l_1) = C_{ll_1}^{(2)} \int_0^\infty u_0' u_1' r^{-3} dr. \quad (23)$$

Similarly, the contribution to the polarizability α_q is obtained from the first integral evaluated for $r = \infty$:

$$\alpha_q(nl \rightarrow l_1) = C_{ll_1}^{(2)} \int_0^\infty u_0' u_1' r^2 dr. \quad (24)$$

The values of $\gamma_\infty(5p \rightarrow p)$ for Pr^{3+} and Tm^{3+} have been previously obtained by considering the perturbation of the $5p$ electrons by the nuclear quadrupole moment Q . We can, therefore, obtain a check on the present wave functions $u_1'(5p \rightarrow p)$ by comparing the resulting values of $\gamma_\infty(5p \rightarrow p)$ with those previously calculated using the nuclear perturbation. It turns out that the agreement is very satisfactory (to $\lesssim 5\%$), as will be shown below (see Sec. III.)

We will now obtain the exchange terms of σ_2 . For simplicity of notation, in order to avoid the subscript: "exchange" each time, we will refer to these terms as ζ_2 . We consider first the $5s \rightarrow d$ perturbation. The exchange arises from the interaction of the density $u_0(5s)v_{4f}$ with the density $u_1(5s \rightarrow d)v_{4f}$. The electrostatic interaction energy can be written as follows:

$$V_{e1} = 2 \sum_{L=0}^\infty \frac{r_{<}^L}{r_{>}^{L+1}} P_L(\cos\theta_{12}), \quad (25)$$

where θ_{12} is the angle between the two electrons as measured from the common origin (nucleus); $r_{<}$ and $r_{>}$ are the smaller and the larger, respectively, of the distances r_1 and r_2 of the two electrons from the nucleus. We also have

$$\begin{aligned} P_L(\cos\theta_{12}) &= 2\pi \sum_{M=-L}^L P_L^M(1) P_L^M(2) \Phi_M(1) \Phi_M^*(2), \end{aligned} \quad (26)$$

where $\Phi_M \equiv (2\pi)^{-1/2} e^{iM\varphi}$, φ is the azimuthal angle, and the parentheses (1) and (2) indicate that the variable of the angular function is the coordinate (θ or φ) of electron 1 and 2, respectively. In Eq. (25), the factor 2 arises from the fact that V_{e1} is given in Rydberg units.

In the case of $5s \rightarrow d$ considered above, since the density $u_0(5s)v_{4f}$ behaves as $\Theta_3^{m_e}$, it is obvious that only the term $L=3$ of Eq. (25) will contribute. Similarly, for $5p \rightarrow p$, we have $u_0(5p)v_{4f}$ interacting with

$u_1(5p \rightarrow p)v_{4f}$. Each density is the sum of two terms which behave as Θ_2^m and Θ_4^m . Hence, both $L=2$ and $L=4$ will contribute exchange terms to ζ_2 . Finally, for $5p \rightarrow f$, $u_0(5p)v_{4f}$ ($\propto \Theta_2^m$ and Θ_4^m) interacts with $u_1(5p \rightarrow f)v_{4f}$ ($\propto \Theta_0^0, \Theta_2^m, \Theta_4^m$, and Θ_6^m), so that we will again have two terms in ζ_2 arising from $L=2$ and $L=4$.

We will now discuss the general exchange integral for the $nl \rightarrow l_1$ perturbation of $u_0(nl)$ in order to obtain the relevant radial integral and the coefficient C which replaces $C_{l_1}^{(2)}$ for the direct term of σ_2 [see Eq. (21)].

From Eqs. (5) and (16), the overlap density

$$2u_1(nl \rightarrow l_1, m)v_{4f}(m_e)$$

can be written as follows:

$$\rho_{\text{exch}} = 2u_1v_{4f} = (4/R^3)du_1'(nl \rightarrow l_1)v_{4f}'\Theta_{l_1}^m\Theta_{l_e}^{m_e}, \quad (27)$$

with $l_e=3$.

As has been pointed out after Eq. (11), $d=I_{l_1}^{(2)m}$, and this integral is in turn a special case of the coefficient $C^{(L)}(lm; l_1m_1)$ of Condon and Shortley¹³ which can be written as follows:

$$C^{(L)}(lm; l_1m_1) = \int_0^\pi P_L^{m-m_1}\Theta_l^m\Theta_{l_1}^{m_1} \sin\theta d\theta, \quad (28)$$

where the arguments (lm) and (l_1m_1) must be so labeled that $m-m_1 \geq 0$. Thus, from Eq. (11), we have

$$d = I_{l_1}^{(2)m} = C^{(2)}(lm; l_1m), \quad (29)$$

i.e., the special case of (28) with $L=2$ and $m_1=m$.

The density $u_0(nl)v_{4f}(m_e)$ which interacts with ρ_{exch} [Eq. (27)] is obtained by means of Eqs. (6) and (16):

$$u_0(nl)v_{4f}(m_e) = u_0'(nl)v_{4f}'\Theta_l^m\Theta_{l_e}^{m_e}. \quad (30)$$

The P_L term of the electrostatic potential energy due to (27) is given by

$$V_{\text{exch}}(nl \rightarrow l_1, L) = \frac{8}{R^3}C^{(2)}(lm; l_1m) \times C^{(L)}(l_1m; l_e m_e)P_L^{m-m_e}(\theta)G(r), \quad (31)$$

where $G(r)$ is the following radial integral:

$$G(r) \equiv \frac{1}{r^{L+1}} \int_0^r u_1'(nl \rightarrow l_1)v_{4f}'r'^L dr' + r^L \int_r^\infty u_1'(nl \rightarrow l_1)v_{4f}'r'^{-L-1} dr', \quad (32)$$

where r' is the variable of integration at which u_1' and v_{4f}' are to be evaluated.

In Eqs. (27), (30), and (31), we have omitted the dependence on the angle φ , since the φ dependence is integrated out by the factor Φ_{m-m_e} which multiplies $P_L^{m-m_e}$ in Eq. (26). In Eq. (31), the factor $C^{(L)}(l_1m; l_e m_e)$ arises from the integration over $\Theta_{l_1}^m\Theta_{l_e}^{m_e}$ in Eq. (27).

Upon using Eq. (30), the exchange energy $E_{\text{exch}}(nl \rightarrow l_1, L)$ becomes

$$E_{\text{exch}}(nl \rightarrow l_1) = -(8/R^3)C^{(2)}(lm; l_1m) \times C^{(L)}(l_1m; l_e m_e)C^{(L)}(lm; l_e m_e)K, \quad (33)$$

where K is defined as the integral

$$K \equiv \int_0^\infty u_0'(nl)v_{4f}'G(r)dr. \quad (34)$$

In Eq. (33), the last angular factor, $C^{(L)}(lm; l_e m_e)$ arises from the integration over $\Theta_l^m\Theta_{l_e}^{m_e}$ in (30). We have included a minus sign in Eq. (33), because the exchange energy as calculated from the determinant

$$\Psi(1,2) \equiv \begin{vmatrix} (u_0+u_1)(1) & (u_0+u_1)(2) \\ v(1) & v(2) \end{vmatrix}, \quad (35)$$

corresponds to terms in the density $\Psi^*\Psi$ of the form $-u_1(1)v(2)u_0^*(2)v^*(1) = -u_1(1)v^*(1)u_0^*(2)v(2)$ which carry a minus sign, as is well known.

The total exchange energy for a closed shell, for the perturbation $(nl \rightarrow l_1, L)$ is obtained by summing Eq. (33) over all m values (from $-l$ to $+l$).

In order to obtain the contribution to ζ_2 (exchange part of σ_2), we must divide $-E_{\text{exch}}(nl \rightarrow l_1, L)$ by the direct interaction energy with the external charge E_R , as given by Eq. (20). Note that $I_{l_e}^{(2)m_e} = C^{(2)}(l_e m_e; l_e m_e)$. We thus obtain

$$\zeta_2(nl \rightarrow l_1, L) = \frac{-4K(nl \rightarrow l_1, L)}{\langle r^2 \rangle_{4f} C^{(2)}(l_e m_e; l_e m_e)} \sum_{m=-l}^l C^{(2)}(lm; l_1m) \times C^{(L)}(l_1m; l_e m_e)C^{(L)}(lm; l_e m_e). \quad (36)$$

The result, Eq. (36), is independent of the value of m_e (magnetic quantum number of the valence electron). This fact can be used as a check on the calculation of the sum over m (by repeating the calculation for two values of m_e). We can write (36) as follows:

$$\zeta_2(nl \rightarrow l_1; L) = - \frac{K(nl \rightarrow l_1, L)C(nl \rightarrow l_1, L)}{\langle r^2 \rangle_{4f}}, \quad (36a)$$

where $C(nl \rightarrow l_1, L)$ is defined as follows:

$$C(nl \rightarrow l_1, L) \equiv \frac{4 \sum_{m=-l}^l C^{(2)}(lm; l_1m)C^{(L)}(lm; l_e m_e)C^{(L)}(l_1m; l_e m_e)}{C^{(2)}(l_e m_e; l_e m_e)}. \quad (37)$$

¹³ E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, London, 1935), p. 175.

It may be noted that the coefficient $C_{il_1}^{(2)}$ for the direct interaction [Eq. (15)] can be obtained from (38) by multiplying by 2 (summation over spin states), setting $L=2$, and changing $C^{(2)}(lm; l_e m_e)C^{(2)}(l_1 m; l_e m_e)$ to $C^{(2)}(lm; l_1 m)C^{(2)}(l_e m_e; l_e m_e)$. This gives

$$C_{il_1}^{(2)} = 8 \sum_{m=-l}^{+l} [C^{(2)}(lm; l_1 m)]^2, \quad (37a)$$

which is identical with Eq. (15) [see also Ref. 12, Eq. (28)].

The relevant values of $C(nl \rightarrow l_1, L)$ for the present case ($l_e=3$) were obtained using the tables of $C^{(L)}(l_1 m_1; l_2 m_2)$ of Condon and Shortley.¹³ The results for the $5s$ and $5p$ shells are as follows:

$$\begin{aligned} C(ns \rightarrow d; L=3) &= 4/7; & C(np \rightarrow p; L=2) &= 108/175; \\ C(np \rightarrow p; L=4) &= 4/21; & C(np \rightarrow f; L=2) &= 72/175; \\ C(np \rightarrow f; L=4) &= 4/7. \end{aligned} \quad (38)$$

In connection with Eq. (37), we note that this equation could be used to obtain the values of $C(nl \rightarrow l_1, L)$ for the case of an external p electron ($l_e=1$). These values have been previously calculated.¹⁴ Thus, we find for $l_e=1$, and for the s and p electrons of the core

$$\begin{aligned} C(ns \rightarrow d; L=1) &= 4/3; & C(np \rightarrow p; L=0) &= 4, \\ C(np \rightarrow p; L=2) &= 4/25, & C(np \rightarrow f; L=2) &= 36/25. \end{aligned} \quad (38a)$$

By means of Eq. (36a), we obtain for the total exchange term of σ_2 for the rare-earth ion

$$\begin{aligned} \zeta_2 &= \zeta_2(5s \rightarrow d; L=3) + \zeta_2(5p \rightarrow p; L=2) \\ &+ \zeta_2(5p \rightarrow p; L=4) + \zeta_2(5p \rightarrow f; L=2) \\ &+ \zeta_2(5p \rightarrow f; L=4). \end{aligned} \quad (38b)$$

In all of the terms of (38b) the coefficient $C(nl \rightarrow l_1; L)$ is positive [Eq. (38)]. The integrals $K(nl \rightarrow l_1; L)$ are positive for $5s \rightarrow d$ and $5p \rightarrow f$, while they are negative for $5p \rightarrow p$. The sum of the $5s \rightarrow d$ and $5p \rightarrow f$ terms predominates, and hence the net effect of ζ_2 is equivalent to a small antishielding, on account of the minus sign in Eq. (36a). However, the magnitude of ζ_2 is considerably smaller than that of the direct term σ_2 , [Eq. (22)], so that both for Pr^{3+} and for Tm^{3+} ,

TABLE I. Contributions of the direct electrostatic terms to the shielding factor σ_2 for the Pr^{3+} ion. The values of $\gamma_\infty(nl \rightarrow l_1)$ and $\alpha_q(nl \rightarrow l_1)$ are also given.

Perturbation	$\sigma_{2,\text{int}}$	$\sigma_{2,\text{ext}}$	σ_2	γ_∞	$\alpha_q (\text{\AA}^5)$
$5s \rightarrow d$	0.0814	0.2081	0.2895	0.577	0.300
$5p \rightarrow p$	-0.0572	-0.1301	-0.1873	-73.7	0.273
$5p \rightarrow f$	0.0609	0.5150	0.5759	0.515	1.140
Total	0.0851	0.5930	0.6781	...	1.713

¹⁴ R. M. Sternheimer, Phys. Rev. **95**, 736 (1954).

TABLE II. Contributions of the direct electrostatic terms to the shielding factor σ_2 for the Tm^{3+} ion. The values of $\gamma_\infty(nl \rightarrow l_1)$ and $\alpha_q(nl \rightarrow l_1)$ are also given.

Perturbation	$\sigma_{2,\text{int}}$	$\sigma_{2,\text{ext}}$	σ_2	γ_∞	$\alpha_q (\text{\AA}^5)$
$5s \rightarrow d$	0.0765	0.1972	0.2737	0.468	0.1200
$5p \rightarrow p$	-0.0838	-0.1563	-0.2401	-65.5	0.1284
$5p \rightarrow f$	0.0216	0.4785	0.5001	0.491	0.4755
Total	0.0143	0.5194	0.5337	...	0.7239

the complete result is a (positive) shielding of the order of 50%, in good agreement with the experimental data.

We will now briefly describe the calculation of the terms $\sigma_2(nl \rightarrow l_1)$ and $\zeta_2(nl \rightarrow l_1, L)$ using the wave functions $u_1'(nl \rightarrow l_1)$ determined by Eq. (8). The functions $u_1'(nl \rightarrow l_1)$ were obtained by numerical integration in the same manner as in our earlier work.¹⁵ We note that the present $u_1'(nl \rightarrow l_1)$ are the same functions as those occurring in the calculation of the quadrupole polarizability $\alpha_q(nl \rightarrow l_1)$. The term $-u_0'(nl)(r^2)_{nl} \delta_{ll'}$ on the right-hand side of Eq. (8) arises from the energy term E_{1u_0} in Eq. (2). For the unperturbed functions, $u_0'(5s)$ and $u_0'(5p)$, we used the Hartree wave functions of Ridley.¹⁶ The corresponding values of $\langle r^2 \rangle_{5p}$ which enter into Eq. (8) are as follows: $3.74a_H^2$ for Pr^{3+} and $2.73a_H^2$ for Tm^{3+} . For the case of $5p \rightarrow p$, the inward integrations of Eq. (8) were carried out on the Brookhaven IBM-7094 computer by means of a program used previously in the calculations of the antishielding factor $\gamma_\infty(nl \rightarrow l)$. For $5s \rightarrow d$ and $5p \rightarrow f$, the calculations are equivalent to the solution of an eigenvalue problem, and were done on a desk computer. Thus, the inward integrations are started at a large radius $r_1 (\sim 5-6a_H)$, with various starting values $u_1'(r_1)$. Only for the correct value of $u_1'(r_1)$ will the resulting function be well-behaved (i.e., go to zero as r^{L+1}) at the origin $r=0$. In practice, of the order of 10-15 trial integrations must be performed until one

TABLE III. Values of the exchange terms pertaining to the shielding factor σ_2 for the Pr^{3+} ion.

Perturbation	$\zeta_{2,\text{int}}$	$\zeta_{2,\text{ext}}$	ζ_2
$5s \rightarrow d (L=3)$	-0.0071	-0.0290	-0.0361
$5p \rightarrow p (L=2)$	+0.0229	+0.0109	+0.0338
$5p \rightarrow p (L=4)$	+0.0054	+0.0035	+0.0089
$5p \rightarrow f (L=2)$	-0.0295	-0.0134	-0.0429
$5p \rightarrow f (L=4)$	-0.0239	-0.0149	-0.0388
Total	-0.0322	-0.0429	-0.0751

¹⁵ Tables of the perturbed wave functions $u_1'(nl \rightarrow l')$ which represent the effect of the crystal-field perturbation are given in a supplementary paper "Wave Functions for Crystal Field Calculations." This paper has been deposited as Document No. 8800 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 \$1.25 for photoprints, or \$1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

¹⁶ E. C. Ridley, Proc. Cambridge Phil. Soc. **56**, 41 (1960).

TABLE IV. Values of the exchange terms pertaining to the shielding factor σ_2 for the Tm^{3+} ion.

Perturbation	$\zeta_{2,\text{int}}$	$\zeta_{2,\text{ext}}$	ζ_2
$5s \rightarrow d$ ($L=3$)	-0.0068	-0.0267	-0.0335
$5p \rightarrow p$ ($L=2$)	+0.0231	+0.0128	+0.0359
$5p \rightarrow p$ ($L=4$)	+0.0055	+0.0039	+0.0094
$5p \rightarrow f$ ($L=2$)	-0.0271	-0.0065	-0.0336
$5p \rightarrow f$ ($L=4$)	-0.0199	-0.0083	-0.0282
Total	-0.0252	-0.0248	-0.0500

obtains the solution $u_1'(nl \rightarrow l_1, L)$ over the entire region of r . For the valence $4f$ wave functions, we used the Hartree-Fock functions v' of Freeman and Watson.¹⁷ The corresponding values of $\langle r^2 \rangle_{4f}$ are as follows: $1.088a_H^2$ for Pr^{3+} , and $0.646a_H^2$ for Tm^{3+} .

The results of the calculations are given in Tables I–IV. The direct terms $\sigma_2(nl \rightarrow l_1)$ are given in Tables I and II; the exchange terms $\zeta_2(nl \rightarrow l_1, L)$ are presented in Tables III and IV. In connection with the direct terms $\sigma_2(nl \rightarrow l_1)$, we have given for each case the contributions of both parts of $f(r)$ as shown in Eq. (13). Thus we can write for $f(r)$:

$$f(r) \equiv f_{\text{int}}(r) + f_{\text{ext}}(r), \quad (39)$$

where

$$f_{\text{int}}(r) \equiv \frac{1}{r^3} \int_0^r u_0' u_1' r'^2 dr' \quad (39a)$$

$$f_{\text{ext}}(r) \equiv r^2 \int_r^\infty u_0' u_1' r'^{-3} dr'. \quad (39b)$$

Upon substituting Eq. (39) into Eq. (21), we obtain

$$\sigma_2(nl \rightarrow l_1) = \sigma_{2,\text{int}}(nl \rightarrow l_1) + \sigma_{2,\text{ext}}(nl \rightarrow l_1), \quad (40)$$

where $\sigma_{2,\text{int}}$ and $\sigma_{2,\text{ext}}$ are defined by

$$\sigma_{2,\text{int}}(nl \rightarrow l_1) \equiv C u_1^{(2)} [\langle r^2 \rangle_{4f}]^{-1} \int_0^\infty v'^2 f_{\text{int}}(r) dr, \quad (40a)$$

$$\sigma_{2,\text{ext}}(nl \rightarrow l_1) \equiv C u_1^{(2)} [\langle r^2 \rangle_{4f}]^{-1} \int_0^\infty v'^2 f_{\text{ext}}(r) dr. \quad (40b)$$

In Tables I and II, we have listed $\sigma_{2,\text{int}}$, $\sigma_{2,\text{ext}}$, and the total σ_2 for each perturbation $nl \rightarrow l_1$. As indicated by the notation, $\sigma_{2,\text{int}}$ represents the effect of the shielding density $u_0' u_1'$ which is internal to the $4f$ electron, whereas, $\sigma_{2,\text{ext}}$ gives the effect of the part of the density $u_0' u_1'$ which lies outside the $4f$ shell. As would be expected since $u_0'(5s)$ and $u_0'(5p)$ are mostly external to $v'(4f)$, we find that in all cases $|\sigma_{2,\text{ext}}|$ is appreciably larger than $|\sigma_{2,\text{int}}|$. Tables I and II also give the values of the quadrupole polarizability $\alpha_q(nl \rightarrow l_1)$ and the antishielding factor $\gamma_\infty(nl \rightarrow l_1)$ connected with the mode $nl \rightarrow l_1$. These values were obtained from Eqs. (23) and (24).

¹⁷ A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962), and private communication.

It is seen that the total direct term σ_2 is 0.678 for Pr^{3+} and 0.534 for Tm^{3+} . As will be discussed below, these values and also the decrease with increasing Z are in general agreement with the experimental observations. For the quadrupole polarizability, only the outermost ($n=5$) shell contributes appreciably, so that the sum, namely, 1.71\AA^5 for Pr^{3+} and 0.724\AA^5 for Tm^{3+} is a good estimate of the total α_q . As concerns the antishielding factor γ_∞ , there are small contributions, mostly from $\gamma_\infty(4p \rightarrow p)$, which are not included in the terms given in Tables I and II. Our best present values for $\gamma_\infty(\text{total})$ are as follows: -81 for Pr^{3+} and -75 for Tm^{3+} . The values for $\gamma_\infty(5p \rightarrow p)$ as listed in Tables I and II (-73.7 for Pr^{3+} and -65.5 for Tm^{3+}) are in good agreement with the results previously obtained from the perturbation $v_1'(5p \rightarrow p)$ due to the nuclear quadrupole moment Q (these values are -69.7 and -67.2 for Pr^{3+} and Tm^{3+} , respectively).⁸

For the exchange terms $\zeta_2(nl \rightarrow l_1, L)$ listed in Tables III and IV, we have made a similar separation into internal and external contributions denoted by $\zeta_{2,\text{int}}$ and $\zeta_{2,\text{ext}}$, respectively. Thus, in connection with Eq. (32), we write

$$G(r) \equiv G_{\text{int}}(r) + G_{\text{ext}}(r),$$

where $G_{\text{int}}(r)$ and $G_{\text{ext}}(r)$ are defined by

$$G_{\text{int}}(r) \equiv \frac{1}{r^{L+1}} \int_0^r u_1'(nl \rightarrow l_1) v_{4f}' r'^L dr', \quad (41)$$

$$G_{\text{ext}}(r) \equiv r^L \int_r^\infty u_1'(nl \rightarrow l_1) v_{4f}' r'^{-L-1} dr'. \quad (42)$$

Then we obtain from Eq. (36a)

$$\zeta_2(nl \rightarrow l_1, L) = \zeta_{2,\text{int}}(nl \rightarrow l_1, L) + \zeta_{2,\text{ext}}(nl \rightarrow l_1, L), \quad (43)$$

where $\zeta_{2,\text{int}}$ and $\zeta_{2,\text{ext}}$ are defined as follows:

$$\zeta_{2,\text{int}}(nl \rightarrow l_1; L) \equiv -\frac{K_{\text{int}}(nl \rightarrow l_1, L) C(nl \rightarrow l_1, L)}{\langle r^2 \rangle_{4f}}, \quad (44)$$

$$\zeta_{2,\text{ext}}(nl \rightarrow l_1; L) \equiv -\frac{K_{\text{ext}}(nl \rightarrow l_1, L) C(nl \rightarrow l_1, L)}{\langle r^2 \rangle_{4f}}. \quad (45)$$

In Eqs. (44) and (45), we have

$$K_{\text{int}} \equiv \int_0^\infty u_0'(nl) v_{4f}' G_{\text{int}}(r) dr, \quad (46)$$

$$K_{\text{ext}} \equiv \int_0^\infty u_0'(nl) v_{4f}' G_{\text{ext}}(r) dr, \quad (47)$$

so that [cf. Eq. (34)]

$$K = K_{\text{int}} + K_{\text{ext}}. \quad (48)$$

The values of $\zeta_{2,\text{int}}$, $\zeta_{2,\text{ext}}$, and the total ζ_2 are listed in Tables III and IV. It is seen that the net $\zeta_2(\text{total})$

corresponds to a small antishielding ($\zeta_2 < 0$) for both Pr^{3+} and Tm^{3+} . Thus, in view of the previous results for $\sigma_2(\text{direct})$, the total value of σ_2 including exchange is positive, corresponding to shielding. The calculated values are as follows:

$$\sigma_2(\text{Pr}^{3+}) = 0.678 - 0.075 = 0.603, \quad (49)$$

$$\sigma_2(\text{Tm}^{3+}) = 0.534 - 0.050 = 0.484. \quad (50)$$

The preceding results are in good general agreement with the experimental values. Thus, Barnes *et al.*¹ have obtained the following results: $\sigma_2 = 0.71$ for Tm^{3+} in thulium ethyl sulfate, and $\sigma_2 = 0.41$ for Tm^{3+} in thulium oxide. Our result $\sigma_2 = 0.48$ is in good agreement with an average of these two values. Moreover, Wickman and Nowik¹ have obtained $\sigma_2 = 0.69$ for the Dy^{3+} ion in the ethyl-sulfate lattice. In addition, these authors have presented good evidence (partly from data of Blok and Shirley) that σ_2 decreases with increasing number of $4f$ electrons. We have obtained a similar result from the present calculations, namely, an appreciable decrease of σ_2 in going from Pr^{3+} to Tm^{3+} .

III. CALCULATIONS OF γ_∞ AND R

In this section, we will present the results of the calculation of the quadrupole antishielding factors¹⁸ γ_∞ and R for several ions.³ We have obtained improved values of the ionic factor γ_∞ for the following ions: Al^{3+} , Cs^+ , I^- , Pr^{3+} , and Tm^{3+} . As concerns the atomic correction term R , we have obtained values pertaining to the $4f$ electron in the Pr^{3+} and Tm^{3+} ions.

The calculation of γ_∞ proceeds in the same manner as described in several previous publications.³ For Cs^+ and I^- , the Hartree-Fock wave functions obtained by Freeman and Watson were used. For Pr^{3+} and Tm^{3+} , we have employed the Hartree wave functions of Ridley.¹⁶ The effect of the radial modes of excitation $nl \rightarrow l$ was obtained by solving the equation

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_0 - E_0 \right] v_1'(nl \rightarrow l) = u_0'(nl) \left[\frac{1}{r^3} - \left\langle \frac{1}{r^3} \right\rangle_{nl} \right], \quad (51)$$

where the effective values of $V_0 - E_0$ are obtained from the unperturbed wave function $u_0'(nl)$ by means of Eq. (10). The integrations of Eq. (51) were carried out by means of the Brookhaven IBM-7094 computer. The solution $v_1'(nl \rightarrow l)$ represents the effect of the distortion of $u_0'(nl)$ due to the potential produced by the nuclear quadrupole moment Q , namely,

$$V_Q = -QP_2^0(\cos\theta)/r^3 \quad (52)$$

in Rydberg units; here Q and r are expressed in units a_H^2 and a_H , respectively.

¹⁸ A preliminary account of this work has been given in Bull. Am. Phys. Soc. **9**, 14 (1964).

TABLE V. Values of $\gamma_\infty(nl \rightarrow l)$ for several ions. For Al^{3+} , the various terms of $\gamma_\infty(\text{ang})$ are given in the text [see discussion preceding Eq. (54)].

Ion	Al^{3+}	Cs^+	I^-	Pr^{3+}	Tm^{3+}
$\gamma_\infty(2p \rightarrow p)$	-2.82	-0.266	-0.280	-0.243	-0.196
$\gamma_\infty(3p \rightarrow p)$		-1.662	-1.775	-1.545	-1.175
$\gamma_\infty(3d \rightarrow d)$		-0.360	-0.391	-0.322	-0.237
$\gamma_\infty(4p \rightarrow p)$		-9.99	-10.78	-8.81	-6.79
$\gamma_\infty(4d \rightarrow d)$		-2.89	-3.54	-2.83	-2.18
$\gamma_\infty(5p \rightarrow p)$		-90.25	-124.85	-69.7	-67.2
$\gamma_\infty(\text{ang})$	+0.46	+2.9	+3.2	+2.5	+2.5
$\gamma_\infty(\text{total})$	-2.36	-102.5	-138.4	-80.9	-75.3

The resulting contribution to γ_∞ is given by

$$\gamma_\infty(nl \rightarrow l) = C_U^{(2)} \int_0^\infty u_0' v_1'(nl \rightarrow l) r^2 dr, \quad (53)$$

where $C_U^{(2)} = 48/25$ for $np \rightarrow p$, and $16/7$ for $nd \rightarrow d$. The term $\gamma_\infty(\text{ang})$ due to the angular modes of excitation, $nl \rightarrow l \pm 2$, is obtained by using the Thomas-Fermi model, as discussed previously.

The resulting values of γ_∞ are given in Table V. The value -102.5 for Cs^+ is appreciably smaller in magnitude than that previously obtained (-143.5) using Hartree wave functions.⁹ The difference is due to the inclusion of exchange in the Hartree-Fock wave functions, which contracts the outermost parts of the electron density, in particular for the $5p$ electrons. A similar difference has been previously noted for Rb^+ ($\gamma_\infty = -47.2$ as compared to -70.7 without exchange).^{8,9} For Pr^{3+} and Tm^{3+} , the present values of γ_∞ are essentially the same as those previously published in Ref. 8. We have now obtained $\gamma_\infty \cong -81$ for Pr^{3+} and $\gamma_\infty \cong -75$ for Tm^{3+} , showing that $|\gamma_\infty|$ remains essentially constant in going through the rare-earth region, although there may actually be a small decrease with increasing Z from Pr to Tm.

For Al^{3+} , we used the Hartree-Fock wave functions of Froese.¹⁹ The results are as follows: $\gamma_\infty(1s \rightarrow d) = 0.0530$, $\gamma_\infty(2s \rightarrow d) = 0.1744$, $\gamma_\infty(2p \rightarrow f) = 0.2352$, giving a total $\gamma_\infty(\text{ang}) = +0.463$. The radial term $\gamma_\infty(2p \rightarrow p)$ has the value -2.821 , so that the total γ_∞ is

$$\gamma_\infty(\text{Al}^{3+}) = \gamma_\infty(\text{ang}) + \gamma_\infty(2p \rightarrow p) = 0.463 - 2.821 = -2.358. \quad (54)$$

The term $\gamma_\infty(1s \rightarrow d)$ was obtained from the expression for hydrogenic wave functions,³ namely, $\gamma_\infty = (\frac{2}{3})Z_e^{-1}$, where Z_e is a suitable effective nuclear charge ($Z_e \cong 12.6$). The angular terms $\gamma_\infty(2s \rightarrow d)$ and $\gamma_\infty(2p \rightarrow f)$ were calculated by integrating the corresponding inhomogeneous equation:

$$\left[-\frac{d^2}{dr^2} + \frac{l_1(l_1+1)}{r^2} + V_0 - E_0 \right] v_1'(nl \rightarrow l_1) = u_0'(nl)/r^3, \quad (55)$$

¹⁹ C. Froese, Proc. Cambridge Phil. Soc. **53**, 206 (1957).

TABLE VI. List of the values of γ_∞ and α_q obtained by direct solution of Eq. (51) for γ_∞ and Eq. (8) for α_q . The notation (*H*) indicates that the unperturbed wave functions $u_0'(nl)$ were Hartree functions. In all other cases, Hartree-Fock wave functions were used for the $u_0'(nl)$. The superscripts (a-f) give the reference to the paper in which the calculation of γ_∞ or α_q was carried out.

Ion	γ_∞	α_q (\AA^6)
H ⁻	+1.131 ^e	66.5 ^b
He	+0.424 ^e	0.0993 ^b
Li ⁺	+0.263 ^e	4.73×10^{-3b}
Be ²⁺	+0.189 ^e	6.37×10^{-4b}
B ⁺	+0.768(<i>H</i>) ^e	
F ⁻	-22.53 ^e	
Na ⁺	-4.56 ^{e,d}	0.0634 ^e
Al ³⁺	-2.36 ^f	
Cl ⁻	-56.6 ^a	13.77 ^b
K ⁺	-17.32 ^{e,d}	0.733 ^b
Mn ²⁺	-11.37 ^d	
Fe ³⁺	-9.14 ^d	
Cu ⁺	-15.0 ^a	1.280 ^b
Ga ³⁺	-9.50 ^d	
Br ⁻	-123.0 ^e	
Rb ⁺	-47.2 ^e	2.99(<i>H</i>) ^b
Ag ⁺	-34.9 ^d	
I ⁻	-138.4 ^f	
Cs ⁺	-102.5 ^f	7.80(<i>H</i>) ^b
Pr ³⁺	-80.9(<i>H</i>) ^f	1.71(<i>H</i>) ^f
Tm ³⁺	-75.3(<i>H</i>) ^f	0.724(<i>H</i>) ^f

^a Reference 9.

^b R. M. Sternheimer, Phys. Rev. **107**, 1565 (1957).

^c R. M. Sternheimer, Phys. Rev. **115**, 1198 (1959).

^d Reference 20.

^e Reference 8.

^f This paper.

where $nl \rightarrow l_1 = 2s \rightarrow d$ or $2p \rightarrow f$, and $u_0'(nl)$ is the corresponding unperturbed wave function ($2s$ or $2p$). The resulting terms of $\gamma_\infty(\text{ang})$ are given by

$$\gamma_\infty(nl \rightarrow l_1) = C_{l_1}^{(2)} \int_0^\infty u_0' v_1'(nl \rightarrow l_1) r^2 dr, \quad (56)$$

where $C_{l_1}^{(2)} = 8/5$ for $2s \rightarrow d$, and $72/25$ for $2p \rightarrow f$.

In connection with the preceding results for Al³⁺ and the values of γ_∞ for Cs⁺, I⁻, Pr³⁺, and Tm³⁺, as given in Table V, it seems useful to collect all of the values of γ_∞ (calculated by the present numerical method) into a single table. Such a table has been previously published²⁰ in Ref. 20. The present table includes these earlier results, as well as those obtained in Ref. 8 and in the present work.

In Table VI, we have listed all of the values of γ_∞ obtained up to date (altogether 21 ions). Except for B⁺, Pr³⁺, and Tm³⁺, the wave functions used in the calculations were Hartree-Fock functions. Since the quadrupole polarizabilities α_q are closely related to γ_∞ , and since values of α_q cannot, in general, be obtained experimentally, so that one has to rely on calculations, we have also listed the values of α_q when they are available (for 12 ions). In the calculations of α_q , the zero-order wave functions u_0' were Hartree-Fock functions in all cases, except for Rb⁺, Cs⁺, Pr³⁺, and Tm³⁺. Thus because of the loose binding of the outermost p

²⁰ R. M. Sternheimer, Phys. Rev. **130**, 1423 (1963).

TABLE VII. Values of quantities involved in the calculation of the atomic shielding factor R for the Pr³⁺ and Tm³⁺ ions. The values of Γ and $\langle r^{-3} \rangle$ are in units a_H^{-3} .

Ion	Pr ³⁺	Tm ³⁺
Γ_{ang}	1.585	2.890
Γ_{rad}	-0.883	-1.223
Γ_{total}	0.702	1.667
$\langle r^{-3} \rangle_{4f}$	5.369	12.86
R_{ang}	0.2952	0.2247
R_{rad}	-0.1644	-0.0951
$R(\text{total})$	+0.1308	+0.1296

electrons for Rb⁺($4p$) and Cs⁺($5p$), the corresponding values of α_q may be appreciably too large. The same comment probably does not apply to Pr³⁺ and Tm³⁺, where the binding of the outermost ($5p$) electrons is tighter, so that the inclusion of exchange would not contract the $5p$ wave function by a large amount. In Table VI, the notation (*H*) indicates that Hartree wave functions were used for $u_0'(nl)$, and the superscript (a-f) denotes the reference in which the value of γ_∞ or α_q was calculated.

In connection with the perturbed wave functions $v_1'(nl \rightarrow l)$ for the rare-earth ions Pr³⁺ and Tm³⁺, we have also obtained the values of the atomic shielding factor R for the case of a valence $4f$ electron. The Hartree-Fock wave functions of Freeman and Watson were used for v_4f' . The results indicate a net shielding of $\sim 13\%$, i.e., $R \cong +0.13$ for both Pr³⁺ $4f$ and Tm³⁺ $4f$. The various terms which enter into the calculation of R are listed in Table VII. The notation is essentially the same²¹ as in Ref. 21 (see, in particular, Table III). Thus we define

$$\Gamma_{\text{ang}} \equiv \langle \gamma_{\text{ang}}/r^3 \rangle_{4f} = \int_0^\infty \gamma_{\text{ang}} v_{4f}'^2 r^{-3} dr, \quad (57)$$

$$\Gamma_{\text{rad}} \equiv \langle \gamma_{\text{rad}}/r^3 \rangle_{4f} = \int_0^\infty \gamma_{\text{rad}} v_{4f}'^2 r^{-3} dr, \quad (58)$$

where $\gamma_{\text{ang}}(r)$ and $\gamma_{\text{rad}}(r)$ are the effective potentials (times r^3) due to the induced moment (divided by the nuclear Q) for the angular and the radial modes of excitation of the core, respectively. Thus,

$$\gamma_{\text{ang}}(r) = \frac{1}{Q} \left[\int_0^r Q_{i,\text{ang}} dr' + r^5 \int_r^\infty Q_{i,\text{ang}} r'^{-5} dr' \right], \quad (59)$$

$$\gamma_{\text{rad}}(r) = \frac{1}{Q} \left[\int_0^r Q_{i,\text{rad}} dr' + r^5 \int_r^\infty Q_{i,\text{rad}} r'^{-5} dr' \right]. \quad (60)$$

In Eqs. (59) and (60), the induced density $Q_{i,\text{ang}}$ is obtained from the Thomas-Fermi model^{3,14,21}:

$$Q_{i,\text{ang}} = (3/10)Q(\chi x)^{1/2}(x/r), \quad (61)$$

where χ and x are the Thomas-Fermi function and variable, respectively; $x = (Z^{1/3}/0.8853)r$, with r in units a_H .

²¹ R. M. Sternheimer, Phys. Rev. **105**, 158 (1957).

It has been shown in Refs. 3 and 14 that the Thomas-Fermi calculation tends to overestimate the actual value of R_{ang} by about 50%. Thus, it was found for both Cl^- and Cs^+ that when the perturbed wave functions $v_1'(nl \rightarrow l \pm 2)$ are calculated, the resulting values of R_{ang} are smaller by a factor of ~ 1.5 than those obtained with the Thomas-Fermi induced moment density of Eq. (61). For this reason, in obtaining the values of R_{ang} in Table VII, the Thomas-Fermi result was divided by 1.5, i.e., effectively we used a coefficient (1/5) in Eq. (61), instead of (3/10).

The radial density $Q_{i,\text{rad}}$ is obtained from the expression

$$Q_{i,\text{rad}}(r) = Qr^2 \left[\frac{48}{25} \sum_{n=2}^5 u_0'(np)v_1'(np \rightarrow p) + \frac{16}{7} \sum_{n=3}^4 u_0'(nd)v_1'(nd \rightarrow d) \right], \quad (62)$$

where the sums extend over the occupied p and d shells of the ion core. The perturbed wave functions $v_1'(nl \rightarrow l)$ are obtained by means of Eq. (51).^{22,23}

Finally, in terms of the integrals Γ_{ang} and Γ_{rad} of Eqs. (57) and (58), the shielding factor R is given by

$$R = R_{\text{ang}} + R_{\text{rad}}, \quad (63)$$

where

$$R_{\text{ang}} \equiv \Gamma_{\text{ang}} / \langle r^{-3} \rangle_{4f}, \quad (64)$$

$$R_{\text{rad}} \equiv \Gamma_{\text{rad}} / \langle r^{-3} \rangle_{4f}. \quad (65)$$

The value of $\langle r^{-3} \rangle_{4f} [\equiv \int_0^\infty v_{4f}'^2 r^{-3} dr]$ is $5.37a_H^{-3}$ for Pr^{3+} and $12.86a_H^{-3}$ for Tm^{3+} .

It is seen from Table VII that in each case Γ_{ang} predominates over Γ_{rad} , so that the net effect is a shielding of the nuclear moment Q . As is usually the case [cf. Table I of Ref. 21], the radial modes produce some antishielding, but since the $4f$ electron density is

²² Tables of the perturbed wave functions $v_1'(nl \rightarrow l')$ obtained in connection with the present calculations (Sec. III) are given in a supplementary paper "Wave Functions for Quadrupole Antishielding Factors." This paper also contains the wave functions pertaining to Sec. IV (second-order antishielding for the Cl^- ion) and Sec. VI (hexadecapole antishielding factor η_∞ for the Cs^+ ion). The supplementary paper has been deposited as Document No. 8801 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 \$3.75 for photoprints, or \$2.00 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

²³ A complete list of the perturbed wave functions which have been obtained in previous calculations of antishielding factors and polarizabilities (Refs. 3, 5, 6, 8, 9, 12, 20, and 21) is given in a supplementary paper "List of Perturbed Wave Functions Pertaining to the Calculation of Quadrupole Antishielding Factors and Electronic Polarizabilities of Ions." This supplementary paper has been deposited as Document No. 8799 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 \$1.25 for photoprints or \$1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

relatively internal (and mostly inside $5p$), the magnitude of Γ_{rad} is smaller than the angular term Γ_{ang} which always leads to shielding.

It should be emphasized that the calculations of Table VII do not include the exchange terms between v_{4f} and the core excitations. Nevertheless, we may note that a value of R of the order of 0 to +0.1 (shielding) is indicated by the experiment of Barnes *et al.*,¹ who have obtained $R = +0.11$ for Tm^{3+} in thulium ethyl sulfate and $R = -0.01$ for Tm^{3+} in Tm_2O_3 . Moreover, from the data of Cohen²⁴ for Fe_2Tm , Barnes *et al.*¹ have deduced a value of $R = +0.20$. Thus, it can be concluded that our results for R are in reasonable agreement with experiment, provided that the exchange terms can be neglected.²⁵

It should be noted that some of the experimental papers give a somewhat larger value of R than the results quoted above. Thus, Hüfner *et al.*²⁶ obtain $R \cong +0.3$ for erbium metal, and they also give references to earlier work in which a value $R \sim 0.3$ rather than ~ 0.1 was deduced. If the value $R \sim 0.3$ would be the more nearly correct one, the difference between our calculated result and the experimental value could be due to small inaccuracies of the zero-order (Hartree) wave functions or perhaps the neglect of exchange effects. Another possibility is that the reduction factor 1.5 which has been applied to the Thomas-Fermi result for $Q_{i,\text{ang}}$ [Eq. (61)] is too large. In this connection, we may remark that if we would apply no correction to the Thomas-Fermi result, we would obtain: (1) for Pr^{3+} : $\Gamma_{\text{ang}} = 2.377a_H^{-3}$, $R_{\text{ang}} = 0.4427$, and $R(\text{total}) = +0.2782$; (2) for Tm^{3+} : $\Gamma_{\text{ang}} = 4.335a_H^{-3}$, $R_{\text{ang}} = 0.3370$, and $R(\text{total}) = 0.2419$ (see Table VII). The present modified results for $R(\text{total}) \cong +0.25$ would be more nearly in agreement with the value of Hüfner *et al.*²⁶ It appears that at present, both the experimental and theoretical situations are somewhat unresolved as to the exact value of R for the $4f$ electron (in the range of +0.1 to +0.3). However, the important point is that almost all of the relevant experiments definitely indicate the presence of a shielding factor $(1-R)$, and therefore provide evidence for the existence of the shielding effect $(1-R)$ in the rare-earth ions, in good general agreement with the author's calculations.

It may be noted that the values of R_{ang} for Pr^{3+}

²⁴ R. L. Cohen, Phys. Rev. 134, A94 (1964). See also S. Hüfner, M. Kalvius, P. Kienle, W. Wiedemann, and H. Eicher, Z. Physik 175, 416 (1963).

²⁵ In two recent papers by M. N. Ghatikar, A. K. Raychaudhuri, and D. K. Ray, (to be published), calculations of γ_∞ , R , and σ_2 for Pr^{3+} and Tm^{3+} have been carried out, which are very similar to those of Secs. II and III of the present paper, and use essentially the same method as that of Ref. 3 (direct solution of the inhomogeneous wave equation). The results for γ_∞ and R are in close agreement with those obtained here. For σ_2 , the calculation of Ghatikar *et al.* differs slightly from ours, in that it contains the (small) effect of the shielding by the inner shells ($n < 5$), but does not include the exchange term ζ_2 which has been calculated in the present work. I wish to thank Dr. D. K. Ray for sending me an advance copy of his papers.

²⁶ S. Hüfner, P. Kienle, W. Wiedemann, and H. Eicher, Z. Physik 182, 499 (1965).

and Tm^{3+} given above are compatible with the result for Eu^{3+} published by the author in 1950 (see the first paper of Ref. 3). Thus, for Eu^{3+} , we have previously obtained $\Gamma_{\text{ang}} = 0.3 \times 9.29 = 2.787 a_H^{-3}$ using the Thomas-Fermi method [cf. Eq. (61)]. The value for Γ_{ang} was deduced using a $4f$ wave function calculated by means of the Thomas-Fermi potential, giving $\langle r^{-3} \rangle_{4f} = 6.88 a_H^{-3}$. The result is $R_1 = 2.787/6.88 = 0.405$. This may be compared with the value obtained by linear interpolation of the above results for Pr^{3+} ($Z=59$) and Tm^{3+} ($Z=69$). For Eu^{3+} , $Z=63$, one obtains $R_{\text{ang}} = 0.402$, in very good agreement. Since the same method was used in both cases to obtain the induced moment density $Q_{i,\text{ang}}$, the only possibility of a difference between the two results would arise from the use of slightly different radial wave functions for the $4f$ electrons. Indeed, the Thomas-Fermi wave function used in Ref. 3 gives $\langle r^{-3} \rangle_{4f} = 6.88 a_H^{-3}$, as compared to $8.37 a_H^{-3}$ deduced by linear interpolation of the wave functions used in the present calculations (see Table VII). Thus, although the present wave function is appreciably more internal, the results for R_{ang} are very insensitive to such a change of the $4f$ wave function.

Finally, we wish to point out that when second and higher order effects on the values of Γ_{ang} are included,²⁷ the effective value of R is reduced somewhat (by about 30%). Thus, as shown in Ref. 27 (see Table II), the influence of the higher order shielding effects reduces R_{ang} for Eu from 0.405 to 0.292. This effect acts in the same direction as the apparent inadequacy of the Thomas-Fermi method in obtaining the first-order induced moment density, discussed above, which also leads one to decrease the Thomas-Fermi values of R_{ang} by an appreciable factor (~ 1.5).

In connection with the present calculations of the atomic shielding (or antishielding) factor R , we wish to point out that the existence of this correction term has also been strongly supported by two types of recent experiments: (1) In a series of papers, Murakawa²⁸ has shown that the factor $(1-R)$ is required in order to make the values of Q obtained from different spectroscopic levels consistent with one another, and also with values of Q obtained by Coulomb-excitation measurements. Murakawa defines a parameter Δ by the equation: $1+\Delta=1/(1-R)$, so that $\Delta=R/(1-R)$ and $R=\Delta/(1+\Delta)$. The spectroscopic hfs measurements were done for the following nuclei: As^{75} , La^{139} , Lu^{175} , Ta^{181} , Os^{189} , and Hg^{201} . In particular, for the elements in the neighborhood of Lu ($Z=71$), Murakawa finds that for the $6p$ electron, there is a weak antishielding $\Delta = -0.1$ ($R = -0.11$), in good general agreement with the results of Refs. 14 and 21. For the configurations $5d$, $5d^2$, $5d^3$, and $5d6s$, the experimental hfs values lead to $\Delta \cong -0.3$ ($R \cong -0.43$) for the $5d$ electron,

whereas, for the configurations $5d^46s$ of TaI and $5d^66s$ of OsI, the results indicate a strong shielding of the $5d$ electrons. At present, our knowledge of the Hartree-Fock wave functions in this region of the periodic table seems to be insufficient to enable one to make a reliable calculation, which could be compared with the results for $\Delta(5d^n)$ and $\Delta(5d^n6s)$.

(2) In the papers of Refs. 14 and 21, the author has predicted the existence of a weak antishielding (of the order of 20%) for the excited (p) states of the alkali atoms. Measurements of the hyperfine structure of the excited states of rubidium $5^2P_{3/2}$, $6^2P_{3/2}$, and $7^2P_{3/2}$ by zu Putnitz, Schenck, and Schüssler,²⁹ using the method of optical double resonance, have confirmed the existence of the antishielding correction $1/(1-R)$. Upon using the values of R given in Ref. 21, namely, $R(5p) = -0.271$, $R(6p) = -0.209$, and $R(7p) = -0.183$ (by extrapolation), the values of $Q(\text{Rb}^{85})$ and $Q(\text{Rb}^{87})$ as obtained from the $5p$, $6p$, and $7p$ states are brought into better agreement with one another than if the correction $1/(1-R)$ were not applied. This result constitutes indirect evidence for the existence of R and for its calculated variation with the principal quantum number n . Moreover, the experimental value of Q is reduced from $0.14 \times 10^{-24} \text{ cm}^2$ to $0.11 \times 10^{-24} \text{ cm}^2$ for Rb^{87} , and from $0.29 \times 10^{-24} \text{ cm}^2$ to $0.24 \times 10^{-24} \text{ cm}^2$ for Rb^{85} by making the correction for the antishielding effect.

It should be noted that besides the quadrupole shielding and antishielding factors γ_∞ and R , there exist also shielding terms associated with the magnetic hyperfine structure. These terms arise from the exchange interaction of the core with the valence electron, which leads to differences between the core wave functions pertaining to a given shell (nl), but having different magnetic quantum numbers³⁰ m_l or different spin orientations³⁰⁻³² m_s . A comprehensive review of these magnetic exchange polarization effects has been given by Freeman and Watson.³³

IV. SECOND-ORDER ANTISHIELDING FOR THE Cl^- ION

We have obtained an estimate of the second-order effect for the antishielding factor γ_∞ of the Cl^- ion. It has been found that the effect of taking into account the direct (nonexchange) terms of the electrostatic inter-

²⁹ G. zu Putnitz and A. Schenck, *Z. Physik* **183**, 428 (1965); H. A. Schüssler, *ibid.* **182**, 289 (1965); H. Bucka, H. Kopfermann, M. Rasiwala, and H. Schüssler, *ibid.* **176**, 45 (1963). See also the review article of G. zu Putnitz, *Ergeb. Exakt. Naturw.* **37**, 105 (1965).

³⁰ R. M. Sternheimer, *Phys. Rev.* **86**, 316 (1952).

³¹ E. Fermi and E. Segrè, *Rend. reale accad. naz. Lincei* **4**, 18 (1933); *Z. Physik* **82**, 729 (1933).

³² G. F. Koster, *Phys. Rev.* **86**, 148 (1952); A. Abragam, J. Horowitz, and M. H. L. Pryce, *Proc. Roy. Soc. (London)* **A230**, 169 (1955).

³³ A. J. Freeman and R. E. Watson, in *Treatise on Magnetism*, edited by G. Rado and H. Suhl (Academic Press Inc., New York, 1963), Vol. IIA, p. 167.

²⁷ R. M. Sternheimer, *Phys. Rev.* **84**, 244 (1951).

²⁸ K. Murakawa and T. Kamei, *Phys. Rev.* **105**, 671 (1957); K. Murakawa, *ibid.* **110**, 393 (1958); *J. Phys. Soc. Japan* **16**, 2533 (1961); **17**, 891 (1962).

action in second order is to reduce the value of $|\gamma_\infty|$ from 57.1 to 45.9. The reduction arises from the shielding effect of the angular modes of excitation of the Cl^- core and the shielding due to the (radial) $2p \rightarrow p$ and $3p \rightarrow p$ modes in the region near the nucleus.¹⁸

We will first consider only the contributions of the $2p \rightarrow p$ and $3p \rightarrow p$ perturbed wave functions. In first order,⁹ one obtains from the wave functions $v_1'(2p \rightarrow p)$ and $v_1'(3p \rightarrow p)$ the values $\gamma_\infty(2p \rightarrow p) = -1.51$ and $\gamma_\infty(3p \rightarrow p) = -57.0$, respectively. Here the functions $v_1'(nl \rightarrow l)$ represent the perturbation due to the nuclear quadrupole moment. The $v_1'(nl \rightarrow l)$ are determined by the equation:

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_0 - E_0 \right] v_1'(nl \rightarrow l) = u_0'(nl) \left[\frac{1}{r^3} - \left\langle \frac{1}{r^3} \right\rangle_{nl} \right], \quad (66)$$

where the effective $(V_0 - E_0)$ is obtained from Eq. (10). Moreover, we have the orthogonality condition

$$\int_0^\infty u_0'(nl) v_1'(nl \rightarrow l) dr = 0. \quad (67)$$

The second-order calculation is carried out by taking $Q + Q_{\text{ind}}$ for the perturbation instead of Q , where Q is the nuclear quadrupole moment and Q_{ind} is the (first-order) induced moment. This means that instead of Eq. (66) we are led to solve the following equation:

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_0 - E_0 \right] \tilde{v}_1'(nl \rightarrow l) = u_0'(nl) \left[\frac{1 - \gamma_{\text{rad}}}{r^3} - \left\langle \frac{1 - \gamma_{\text{rad}}}{r^3} \right\rangle \right], \quad (68)$$

where γ_{rad} is defined by Eqs. (60) and (62); thus $\gamma_{\text{rad}} Q / r^3$ gives the potential due to the induced moment $Q_{\text{ind,rad}}$ arising from the radial modes ($2p \rightarrow p$ and $3p \rightarrow p$). The modified values of the antishielding factor $\tilde{\gamma}_\infty(nl \rightarrow l)$ are obtained in the same manner as the first-order $\gamma_\infty(nl \rightarrow l)$, namely,

$$\tilde{\gamma}_\infty(nl \rightarrow l) = C_{II}^{(2)} \int_0^\infty u_0' \tilde{v}_1'(nl \rightarrow l) r^2 dr. \quad (69)$$

In the present case, $C_{II}^{(2)} = 48/25$.

The inward integration of (68) can be carried out by means of the IBM-7094 program, in the same manner as for Eq. (66). We thus obtain

$$\tilde{\gamma}_\infty(2p \rightarrow p) = -1.48; \quad \tilde{\gamma}_\infty(3p \rightarrow p) = -50.57, \quad (70)$$

giving a total $\tilde{\gamma}_\infty(\text{rad}) = -52.05$, as compared to $-57.0 - 1.51 = -58.51$ for the first-order calculation. The decrease of $|\gamma_\infty(\text{rad})|$ is due to the shielding

TABLE VIII. Values of $\gamma_\infty(2p \rightarrow p)$ and $\gamma_\infty(3p \rightarrow p)$ which enter into the calculation of the second-order effects for Cl^- . For comparison, the values of γ_∞ in the first row of the table are obtained from the usual first-order calculation. The column $\gamma_\infty(\text{rad})$ gives the sum of the $2p \rightarrow p$ and $3p \rightarrow p$ terms. In the last column, $\gamma_\infty(\text{total}) = \gamma_\infty(\text{rad}) + \gamma_\infty(\text{ang})$, with the angular term $\gamma_\infty(\text{ang}) = +1.4$. The quantities $\tilde{\gamma}_\infty$, $\tilde{\gamma}_\infty(\xi)$, and $\tilde{\gamma}_\infty(\xi)$ are defined in the text.

Term	$2p \rightarrow p$	$3p \rightarrow p$	$\gamma_\infty(\text{rad})$	$\gamma_\infty(\text{total})$
γ_∞	-1.51	-57.00	-58.51	-57.11
$\tilde{\gamma}_\infty$	-1.48	-50.57	-52.05	-50.65
$\tilde{\gamma}_\infty(\xi)$	-1.404	-45.89	-47.29	-45.89
$\tilde{\gamma}_\infty(\xi)$	-3.58	-48.27	-51.85	-50.45

effect of the $2p \rightarrow p$ and $3p \rightarrow p$ modes near $r=0$, which results in values of $\gamma_{\text{rad}} > 0$ in this region.

We note that the present calculations of both the first- and second-order effects were carried out by means of the same Hartree-Fock wave functions (to give a reliable comparison), namely, the functions originally calculated by Hartree.³⁴ The various terms $\tilde{\gamma}_\infty(np \rightarrow p)$, $\tilde{\gamma}_\infty(\xi, np \rightarrow p)$, and $\tilde{\gamma}_\infty(\xi, np \rightarrow p)$ obtained in the present calculation (see below) are listed in Table VIII.

As the next step in the calculation, we can include the shielding effect of the angular modes ($l_1 = l \pm 2$), as obtained from the function $\gamma_{\text{ang}}(r)$ [Eqs. (59) and (61)]. We are thus led to obtain the solutions of the following equation:

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_0 - E_0 \right] \tilde{v}_1'(nl \rightarrow l) = u_0'(nl) \left[\frac{1 - \gamma_{\text{rad}} - \gamma_{\text{ang}}}{r^3} - \left\langle \frac{1 - \gamma_{\text{rad}} - \gamma_{\text{ang}}}{r^3} \right\rangle \right]. \quad (71)$$

The resulting values of $|\tilde{\gamma}_\infty(nl \rightarrow l)|$ are again decreased, as compared to $|\tilde{\gamma}_\infty(nl \rightarrow l)|$. We have obtained

$$\tilde{\gamma}_\infty(2p \rightarrow p) = -1.404; \quad \tilde{\gamma}_\infty(3p \rightarrow p) = -45.89, \quad (71a)$$

giving a total $\tilde{\gamma}_\infty(\text{rad}) = -47.29$. Upon including an angular term^{3,9} $\gamma_\infty(\text{ang}) = +1.4$, we obtain $\tilde{\gamma}_\infty(\text{total}) = -45.9$. For comparison, the first-order calculation⁹ gives

$$\gamma_\infty(\text{total}) = -57.0 - 1.51 + 1.4 = -57.1. \quad (72)$$

Thus, the reduction in second order due to shielding effects is

$$|\tilde{\gamma}_\infty(\text{total}) / \gamma_\infty(\text{total})| = 45.9 / 57.1 = 0.80. \quad (73)$$

As a check on the calculation of $\tilde{\gamma}_\infty(\text{rad})$, we have obtained this quantity by an alternative method, namely, by considering the perturbation due to an external charge. The corresponding equation for the perturbation $u_1'(np \rightarrow p)$ is given by Eq. (8) in first order. The appropriate equation pertaining to the second-order

³⁴ D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London), **A156**, 45 (1936).

perturbation is as follows:

$$-\frac{d^2\bar{u}_1'}{dr^2} + \left[\frac{l(l+1)}{r^2} + V_0 - E_0 \right] \bar{u}_1' = u_0' [r^2(1 - \xi_{\text{rad}}) - \langle r^2(1 - \xi_{\text{rad}}) \rangle_{nl}], \quad (74)$$

where ξ_{rad} is given by

$$\xi_{\text{rad}} = \frac{48}{25} \sum_{n=2}^3 \left[\int_r^\infty u_0'(n\hat{p}) u_1'(n\hat{p} \rightarrow \hat{p}) r'^{-3} dr' + r^{-5} \int_0^r u_0'(n\hat{p}) u_1'(n\hat{p} \rightarrow \hat{p}) r'^2 dr' \right]. \quad (75)$$

The function ξ_{rad} is analogous to γ_{rad} used above. Thus, ξ_{rad} represents the effect of the quadrupole distortion induced in the $2p$ and $3p$ shells (by the external charge) on the total field gradient acting on either $2p$ or $3p$.

The resulting contribution to γ_∞ is given by

$$\bar{\gamma}_\infty(\xi, n\hat{p} \rightarrow \hat{p}) = \frac{48}{25} \int_0^\infty u_0'(n\hat{p}) \bar{u}_1'(n\hat{p} \rightarrow \hat{p}) r^{-3} dr. \quad (76)$$

We thus obtain

$$\bar{\gamma}_\infty(\xi, 2\hat{p} \rightarrow \hat{p}) = -3.58. \quad \bar{\gamma}_\infty(\xi, 3\hat{p} \rightarrow \hat{p}) = -48.27. \quad (77)$$

The total $\bar{\gamma}_\infty(\xi, \text{rad}) = -51.85$ is in very good agreement with the value -52.05 [see Eq. (70)] previously obtained from the functions $\bar{v}_1'(n\hat{p} \rightarrow \hat{p})$. This comparison provides a reliable check on the accuracy of the calculations.

The present calculations of second-order effects for Cl^- were carried out partly in order to provide a comparison with a paper of Watson and Freeman,³⁵ in which they have obtained a total $\gamma_\infty \cong -85$ for Cl^- using the unrestricted Hartree-Fock method. In order to obtain a more accurate comparison with this result, we have recalculated the first-order $\gamma_\infty(3\hat{p} \rightarrow \hat{p})$ using the same (analytic Hartree-Fock) wave function as was employed by Watson and Freeman³⁶ (WF), instead of the (numerical) function calculated by Hartree,³⁴ as was done above. This gives $\gamma_\infty(3\hat{p} \rightarrow \hat{p}) = -68.4$ for the WF function, as compared to -57.0 obtained above. The difference between these two values is due to the fact that the WF $3p$ function is slightly more external than that of Hartree. If we make the reasonable assumption that the second-order shielding effects due to the angular and radial modes decrease $|\gamma_\infty(\text{WF}, 3\hat{p} \rightarrow \hat{p})|$ by approximately the same factor as for the wave function of Hartree, namely, 0.80 [Eq. (73)], we obtain: $\bar{\gamma}_\infty(\text{total}, \text{WF function}) \cong -68.4 \times 0.80 = -54.7$, which is still considerably smaller in magnitude than the result of Ref. 35. The disagreement is by a factor of $85/55 = 1.55$. At present, we have no definite explanation of the discrepancy, especially since for Cu^+ , the value of γ_∞ obtained by Watson and Freeman³⁵ (-17)

³⁵ R. E. Watson and A. J. Freeman, Phys. Rev. **131**, 250 (1963).

³⁶ R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 521 (1961).

is in close agreement with that of Sternheimer and Foley⁹ (-15) using the conventional first-order perturbation theory. There is, of course, the possibility that the discrepancy for Cl^- is due to the presence of exchange³⁷ and orthogonalization effects which are included in the unrestricted Hartree-Fock method of Ref. 35. In this connection, we wish to call attention to our previous calculations of Ref. 27 [see Eqs. (68)–(72)], in which the effect of including the second-order terms was evaluated in connection with the atomic shielding factor R for Cl . In this work, it was shown that besides the direct Coulomb terms (there denoted by β), which lead to a decrease of $|R|$ (see the calculation for $\text{Cl } 2s \rightarrow d$), there may exist a noticeable effect due to the exchange terms acting on the radial excitations $2p \rightarrow \hat{p}$ and $3p \rightarrow \hat{p}$. This effect goes in the direction of increasing the values of $|v_1'(2\hat{p} \rightarrow \hat{p})|$ and $|v_1'(3\hat{p} \rightarrow \hat{p})|$ and, in the present context, it would probably enhance the values of $|\gamma_\infty(\text{Cl}^-)|$, although no specific calculations have been carried out.

In connection with the preceding discussion, it should be stressed that the difference between the two calculated values of $\gamma_\infty(\text{Cl}^-)$ is mainly of academic interest, since the actual $3p$ wave function of the Cl^- ion in a solid lattice will be appreciably different from that in the free ion. Thus, in view of the large radial extent of the Hartree-Fock free-ion $3p$ wave function, we can expect that the wave function in the solid will be appreciably more internal, leading to a decrease of $|\gamma_\infty(\text{Cl}^-)|$. Hence, the preceding calculations for Cl^- (and for negative ions in general) give values which are only of limited accuracy, perhaps leading to an overestimate by $\sim 50\%$. It should be noted that such a situation does not arise, in general, for the positive ions, which are smaller in extent, and more tightly bound. This point has been previously emphasized by Burns and Wikner.³⁸

V. EQUIVALENCE OF THE SECOND-ORDER TERMS OF γ_∞ AND $\gamma_\infty(\xi)$

In connection with the calculations of Sec. IV concerning the second-order terms of γ_∞ , we wish to give the formal proof that the two ways of calculating γ_∞ (by considering the internal or the external perturbation) are completely equivalent for the second-order terms of γ_∞ . The fact that the calculations are equivalent for the first-order terms has been previously shown by Sternheimer and Foley.¹⁰ It should be noted that on physical grounds, one expects that the equivalence is complete, i.e., that it is correct to all orders of the nuclear quadrupole and the interelectronic perturbation.

³⁷ The formal treatment of exchange for the Hartree-Fock equations with a perturbing field has been given by L. C. Allen, Phys. Rev. **118**, 167 (1960); A. Dalgarno, Proc. Roy. Soc. (London) **A251**, 282 (1959); and S. Kaneko, J. Phys. Soc. Japan **14**, 1600 (1959).

³⁸ G. Burns and E. G. Wikner, Phys. Rev. **121**, 155 (1961); G. Burns, *ibid.* **115**, 357 (1959). See also R. Bersohn, J. Chem. Phys. **29**, 326 (1958).

We will consider two electron shells, labeled a and b . The notation for the perturbed wave functions will be the same as previously; i.e., v_1 denotes a perturbed function due to the influence of the nuclear quadrupole moment Q , while u_1 denotes a perturbation due to the Coulomb interaction, either with an external charge or with a different electron in the same atom. The proof to be given below applies to any type of excitation, i.e., both to the radial ($l'=l$) and angular modes ($l'=l\pm 2$).

We will first calculate the term $\Delta\gamma_{\infty,ba}$ defined as the change of γ_{∞} for electron shell b due to the quadrupole moment induced in shell a by the nuclear moment Q . Then we will show that $\Delta\gamma_{\infty,ba}$ is equal to $\Delta\gamma_{\infty,ab}(\xi)$ defined as the change of γ_{∞} for shell a due to the field gradient produced in shell b by an external charge. Obviously, as a special case, for $b=a$, we will then have $\Delta\gamma_{\infty,aa}=\Delta\gamma_{\infty,aa}(\xi)$.

The perturbation $v_{1,a}$ of the wave function for a , due to the effect of the nuclear moment Q , is determined by the equation

$$M_{l_a'l_a}v_{1,a}=u_{0,a}\left[\frac{1}{r^3}-\left\langle\frac{1}{r^3}\right\rangle_a\delta_{l_a'l_a'}\right] \quad (78)$$

and the orthogonality condition

$$\int_0^{\infty} u_{0,a}v_{1,a}dr=0 \quad (\text{for } l_a'=l_a). \quad (79)$$

In Eq. (78), l_a and l_a' are the values of l for the unperturbed and the perturbed state, respectively, with wave functions $u_{0,a}$ and $v_{1,a}$, respectively. Thus, the perturbation considered is $n_a l_a \rightarrow l_a'$. Furthermore, M_l represents the following differential operator:

$$M_l \equiv -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_{0,nl} - E_{0,nl}, \quad (80)$$

where the effective values of $V_{0,nl}-E_{0,nl}$ are obtained from^{3,6}

$$(V_{0,nl}-E_{0,nl})_a = \frac{1}{u_{0,a}} \frac{d^2 u_{0,a}}{dr^2} - \frac{l_a(l_a+1)}{r^2}. \quad (81)$$

The quadrupole potential due to the overlap density $2u_{0,a}v_{1,a}$ involves the function $\Gamma_a(r)$ defined as follows:

$$\Gamma_a(r) \equiv c_a \left[\int_0^r u_{0,a}v_{1,a}r'^2 dr' + r^5 \int_r^{\infty} u_{0,a}v_{1,a}r'^{-3} dr' \right], \quad (82)$$

where $c_a \equiv c(l_a \rightarrow l_a')$ is the angular coefficient pertaining to the excitation $n_a l_a \rightarrow l_a'$; e.g., $c_a=8/5$ for $s \rightarrow d$; $48/25$ for $p \rightarrow p$; $72/25$ for $p \rightarrow f$.

The perturbation $n_b l_b \rightarrow l_b'$ induced in shell b by the quadrupole potential due to $2u_{0,a}v_{1,a}$ will be denoted by $v_{1,ba}$ (radial function). If the unperturbed function is

written as $u_{0,b}$, we have

$$M_{l_b'l_b}v_{1,ba}=u_{0,b}\left[\frac{\Gamma_a}{r^3}-\left\langle\frac{\Gamma_a}{r^3}\right\rangle_b\delta_{l_b'l_b'}\right], \quad (83)$$

$$\int_0^{\infty} u_{0,b}v_{1,ba}dr=0 \quad (\text{for } l_b'=l_b). \quad (84)$$

In Eq. (83), $\langle\Gamma_a/r^3\rangle_b$ denotes the average

$$\langle\Gamma_a/r^3\rangle_b \equiv \int_0^{\infty} (\Gamma_a/r^3)u_{0,b}^2 dr. \quad (85)$$

Finally, the resulting term $\Delta\gamma_{\infty,ba}$ is given by

$$\Delta\gamma_{\infty,ba}=c_b \int_0^{\infty} u_{0,b}v_{1,ba}r^2 dr, \quad (86)$$

where the coefficient $c_b \equiv c(l_b \rightarrow l_b')$.

We will now obtain the expression for $\Delta\gamma_{\infty,ab}(\xi)$. The radial part of the perturbation $u_{1,b}$ of the wave function $u_{0,b}$ for shell b , arising from an external quadrupole field is determined by

$$M_{l_b'l_b}u_{1,b}=u_{0,b}(r^2-\langle r^2\rangle_b\delta_{l_b'l_b'}), \quad (87)$$

$$\int_0^{\infty} u_{0,b}u_{1,b}dr=0 \quad (\text{for } l_b'=l_b). \quad (88)$$

The field gradient due to the overlap density $2u_{0,b}u_{1,b}$ is proportional to the function $\xi_b(r)$ defined as follows:

$$\xi_b(r) \equiv c_b \left[\int_r^{\infty} u_{0,b}u_{1,b}r'^{-3} dr' + r^{-5} \int_0^r u_{0,b}u_{1,b}r'^2 dr' \right], \quad (89)$$

where again $c_b \equiv c(l_b \rightarrow l_b')$.

The perturbation $u_{1,ab}$ of $u_{0,a}$ due to the field gradient $\propto \xi_b(r)$ is the solution of the following equation:

$$M_{l_a'l_a}u_{1,ab}=u_{0,a}(\xi_b r^2 - \langle \xi_b r^2 \rangle_a \delta_{l_a'l_a'}), \quad (90)$$

with

$$\int_0^{\infty} u_{0,a}u_{1,ab}dr=0 \quad (\text{for } l_a'=l_a), \quad (91)$$

$$\langle \xi_b r^2 \rangle_a \equiv \int_0^{\infty} \xi_b r^2 u_{0,a}^2 dr. \quad (92)$$

We note that the values of l_a' and l_b' considered in the present calculation of $\Delta\gamma_{\infty,ab}(\xi)$ are the same as the previous azimuthal quantum numbers l_a' and l_b' pertaining to the calculation of $\Delta\gamma_{\infty,ba}$.

By means of $u_{1,ab}$, we obtain the expression for

$\Delta\gamma_{\infty,ab}(\xi)$:

$$\Delta\gamma_{\infty,ab}(\xi) = c_a \int_0^{\infty} u_{0,a} u_{1,a} b r^{-3} dr, \quad (93)$$

where $c_a \equiv c(l_a \rightarrow l_a')$, as before.

In order to prove that $\Delta\gamma_{\infty,ab}(\xi) = \Delta\gamma_{\infty,ba}$ [Eqs. (86) and (93)], we rewrite $\Delta\gamma_{\infty,ab}(\xi)$ as follows:

$$\begin{aligned} \Delta\gamma_{\infty,ab}(\xi) &= c_a \int_0^{\infty} (M_{l_a'} v_{1,a}) u_{1,ab} dr \\ &= c_a \int_0^{\infty} (M_{l_a'} u_{1,ab}) v_{1,a} dr = c_a c_b \int_0^{\infty} u_{0,a} v_{1,a} \xi b r^2 dr \\ &= c_a c_b \int_0^{\infty} u_{0,a} v_{1,a} r^2 \left[\int_r^{\infty} u_{0,b} u_{1,b} b r'^{-3} dr' \right. \\ &\quad \left. + r^{-5} \int_0^r u_{0,b} u_{1,b} b r'^2 dr' \right]. \quad (94) \end{aligned}$$

In obtaining the various expressions of Eq. (94), we have used Eqs. (78), (79), (89)–(91), and partial integration in obtaining the second expression for $\Delta\gamma_{\infty,ab}(\xi)$. In order to justify this latter step, we note that

$$\begin{aligned} &\int_0^{\infty} (M_{l_a'} v_{1,a}) u_{1,ab} dr - \int_0^{\infty} (M_{l_a'} u_{1,ab}) v_{1,a} dr \\ &= \left(v_{1,a} \frac{du_{1,ab}}{dr} \right) \Big|_0^{\infty} - \left(u_{1,ab} \frac{dv_{1,a}}{dr} \right) \Big|_0^{\infty}. \quad (95) \end{aligned}$$

At $r = \infty$, all of the four functions involved ($v_{1,a}$, $u_{1,ab}$ and their derivatives) are zero. At $r = 0$, the values of $v_{1,a}$ and $dv_{1,a}/dr$ are finite. In general, $v_{1,a}$ and $dv_{1,a}/dr$ are zero for large l_a and l_a' . However, for $ns \rightarrow d$, both $v_{1,a}$ and $dv_{1,a}/dr$ are different from zero as $r \rightarrow 0$ and for $np \rightarrow p$ and $np \rightarrow f$, $v_{1,a}(0) = 0$, but $(dv_{1,a}/dr)(r=0)$ is finite. On the other hand, $u_{1,ab}$ behaves as $r^{l_a'+1}$, so that $u_{1,ab} = 0$ in all cases, and $du_{1,ab}/dr \neq 0$ only for $l_a' = 0$. The only case for which l_a' is 0 corresponds to the $n_a d \rightarrow s$ excitation, and the corresponding $v_{1,a}(n_a d \rightarrow s)$ is proportional to r near the nucleus, and thus vanishes at $r = 0$. Hence Eq. (95) gives a zero result regardless of the types of excitation $n_a l_a \rightarrow l_a'$ and $n_b l_b \rightarrow l_b'$, so that the procedure of Eq. (94) is justified.

For the double integrals in the last expression of (94), we obtain the following expressions by partial integration:

$$\begin{aligned} &\int_0^{\infty} u_{0,a} v_{1,a} r^2 dr \int_r^{\infty} u_{0,b} u_{1,b} b r'^{-3} dr' \\ &= \int_0^{\infty} u_{0,b} u_{1,b} b r^{-3} dr \int_0^r u_{0,a} v_{1,a} r'^2 dr', \quad (96) \end{aligned}$$

$$\begin{aligned} &\int_0^{\infty} u_{0,a} v_{1,a} r^{-3} dr \int_0^r u_{0,b} u_{1,b} b r'^2 dr' \\ &= \int_0^{\infty} u_{0,b} u_{1,b} b r^2 dr \int_r^{\infty} u_{0,a} v_{1,a} r'^{-3} dr'. \quad (97) \end{aligned}$$

Upon inserting Eqs. (96) and (97) into (94), and using Eqs. (82)–(88), we obtain

$$\begin{aligned} \Delta\gamma_{\infty,ab}(\xi) &= c_b \int_0^{\infty} u_{0,b} u_{1,b} b r^{-3} dr = c_b \int_0^{\infty} (M_{l_b'} v_{1,ba}) u_{1,b} dr \\ &= c_b \int_0^{\infty} (M_{l_b'} u_{1,b}) v_{1,ba} dr \\ &= c_b \int_0^{\infty} u_{0,b} v_{1,ba} r^2 dr = \Delta\gamma_{\infty,ba}, \quad (98) \end{aligned}$$

which completes the proof that $\Delta\gamma_{\infty,ab}(\xi) = \Delta\gamma_{\infty,ba}$.

In connection with the results of Sec. IV for the CI- ion, we can write [see also Table VII and Eqs. (70) and (77)]:

$$\begin{aligned} \bar{\gamma}_{\infty}(2p \rightarrow p) &= \gamma_{\infty}(2p \rightarrow p) + \Delta\gamma_{\infty,2p,3p} \\ &\quad + \Delta\gamma_{\infty,2p,2p} = -1.48, \quad (99) \end{aligned}$$

$$\begin{aligned} \bar{\gamma}_{\infty}(3p \rightarrow p) &= \gamma_{\infty}(3p \rightarrow p) + \Delta\gamma_{\infty,3p,2p} \\ &\quad + \Delta\gamma_{\infty,3p,3p} = -50.57, \quad (100) \end{aligned}$$

$$\begin{aligned} \bar{\gamma}_{\infty}(\xi, 2p \rightarrow p) &= \gamma_{\infty}(2p \rightarrow p) + \Delta\gamma_{\infty,2p,3p}(\xi) \\ &\quad + \Delta\gamma_{\infty,2p,2p}(\xi) = -3.58, \quad (101) \end{aligned}$$

$$\begin{aligned} \bar{\gamma}_{\infty}(\xi, 3p \rightarrow p) &= \gamma_{\infty}(3p \rightarrow p) + \Delta\gamma_{\infty,3p,2p}(\xi) \\ &\quad + \Delta\gamma_{\infty,3p,3p}(\xi) = -48.27. \quad (102) \end{aligned}$$

Here $\gamma_{\infty}(2p \rightarrow p) = -1.51$ and $\gamma_{\infty}(3p \rightarrow p) = -57.00$ represent the first-order terms. In view of the theorem proved above, we have

$$\Delta\gamma_{\infty,2p,2p} = \Delta\gamma_{\infty,2p,2p}(\xi) \equiv a_{2p}, \quad (103)$$

$$\Delta\gamma_{\infty,3p,3p} = \Delta\gamma_{\infty,3p,3p}(\xi) \equiv a_{3p}, \quad (104)$$

$$\Delta\gamma_{\infty,2p,3p} = \Delta\gamma_{\infty,3p,2p}(\xi) \equiv b_1, \quad (105)$$

$$\Delta\gamma_{\infty,3p,2p} = \Delta\gamma_{\infty,2p,3p}(\xi) \equiv b_2, \quad (106)$$

where we have defined the terms a_{2p} , a_{3p} , b_1 , and b_2 in order to simplify the notation. Upon inserting Eqs. (103)–(106) and the values of the first-order terms into Eqs. (99)–(102), we obtain the following equations for the a and b terms:

$$b_1 + a_{2p} = +0.03, \quad (107)$$

$$b_2 + a_{3p} = +6.43, \quad (108)$$

$$-b_2 - a_{2p} = +2.07, \quad (109)$$

$$b_1 + a_{3p} = +8.73. \quad (110)$$

It can be easily seen that these equations are not independent of one another, since the sum of (107),

(108), and (109) gives $b_1 + a_{3p}$ on the left-hand side, and the value 8.53 on the right-hand side [cf. Eq. (110)]. In order to make the set (107)–(110) internally consistent, we change the value of (109) from +2.07 to +2.27. This change by 0.20 is well within the errors of the calculations, and corresponds to the small difference between the calculated values of $\gamma_\infty(\text{rad}) (= -52.05)$ and $\bar{\gamma}_\infty(\xi, \text{rad}) (= -51.85)$.

With $b_2 + a_{2p} = -2.27$, Eqs. (107)–(110) give

$$a_{2p} = 0.03 - b_1, \quad a_{3p} = 8.73 - b_1, \quad b_2 = -2.30 + b_1. \quad (111)$$

It appears from Eq. (107) that a_{2p} and b_1 are probably both small. These terms represent the change in γ_∞ for the $2p$ shell as calculated from the nuclear perturbation, due to the effect of the moment induced in the $2p$ and $3p$ shells, respectively. It would be unreasonable to assume a large shielding due to $2p$, i.e., a large positive a_{2p} , because according to Eq. (107), this would force us to assume a large negative $b_1 = \Delta\gamma_{\infty, 2p, 3p}$, contrary to the fact that in the region of the $2p$ charge distribution, the $3p$ induced moment is shielding, i.e., $b_1 > 0$, rather than antishielding.

The simplest assumption is that both b_1 and a_{2p} are very close to zero. Upon taking $b_1 = 0$, we obtain from Eq. (111) $a_{2p} = 0.03$, $a_{3p} = 8.73$, $b_2 = -2.30$.

The rather large positive value of $a_{3p} = \Delta\gamma_{\infty, 3p, 3p}$ corresponds to a shielding of the $3p$ electrons by the part of the $3p \rightarrow p$ perturbation which is internal (close to the nucleus), and which we know to be shielding^{3,27} ($u_{0, 3p} v_{1, 3p \rightarrow p} > 0$). If this term would act alone, it would change $\gamma_\infty(3p \rightarrow p) = -57.00$ to $-57.00 + 8.73 = -48.27$. On the other hand, the $2p$ shell is sufficiently inside the $3p$ distribution that the effect of the $2p$ induced moment on $3p$ is to produce some antishielding ($u_{0, 2p} v_{1, 2p \rightarrow p} < 0$ in the region outside the $2p$ wave function maximum). This effect, here denoted by $b_2 = \Delta\gamma_{\infty, 3p, 2p}$, is therefore negative (i.e., $b_2 = -2.30$). Thus, one obtains $\bar{\gamma}_\infty(3p \rightarrow p) = -48.27 - 2.30 = -50.57$. Alternatively, b_2 represents the extra antishielding of the $2p$ electrons by $3p$ when the calculation is done by considering an external charge. This effect is numerically more important than $\gamma_\infty(2p \rightarrow p)$ itself (-2.30 as compared to -1.51). If one would assume that it acts alone (which it essentially does, since $|\Delta\gamma_{\infty, 2p, 2p}(\xi)|$ is very small, < 0.1), one would obtain $\bar{\gamma}_\infty(\xi, 2p \rightarrow p) = -1.51 - 2.30 = -3.81$, as compared to the value calculated directly, namely, -3.58 . The effect of $\Delta\gamma_{\infty, 2p, 3p}(\xi)$ has been previously pointed out by Watson and Freeman.³⁵ However, our value of $|\Delta\gamma_{\infty, 2p, 3p}(\xi)|$ is considerably smaller than that of Ref. 35 (2.30 as compared to ~ 10).

VI. THE HEXADECAPOLE ANTISHIELDING FACTOR η_∞

We have previously obtained values of the antishielding factor⁵ η_∞ for a possible nuclear hexadecapole moment, for the Cu^+ , Ag^+ , and Hg^{++} ions. The cal-

culated values are as follows:

$$\eta_\infty(\text{Cu}^+) = -1200; \quad \eta_\infty(\text{Ag}^+) = -8050; \\ \eta_\infty(\text{Hg}^{++}) = -63\,000. \quad (112)$$

Since there has been some interest in doing an experiment³⁹ using Cs, we have calculated η_∞ for the Cs^+ ion. The $4d \rightarrow d$ perturbation makes the pre-dominant contribution. The appropriate equation for $v_{1, H'}(4d \rightarrow d)$ is given by

$$\left[-\frac{d^2}{dr^2} + \frac{6}{r^2} + V_0 - E_0 \right] v_{1, H'}(4d \rightarrow d) \\ = u_0'(4d) \left[\frac{1}{r^5} - \left\langle \frac{1}{r^5} \right\rangle_{4d} \right], \quad (113)$$

with the orthogonality condition

$$\int_0^\infty u_0'(4d) v_{1, H'}(4d \rightarrow d) dr = 0. \quad (114)$$

The resulting $\eta_\infty(4d \rightarrow d)$ is obtained from

$$\eta_\infty(4d \rightarrow d) = (80/63) \int_0^\infty u_0'(4d) v_{1, H'}(4d \rightarrow d) r^4 dr. \quad (115)$$

As in the work on γ_∞ for Cs^+ , we used the Hartree-Fock ($4d$) wave function obtained by Freeman and Watson.⁷ The result is $\eta_\infty(4d \rightarrow d) = -662.3$. If one assumes that $\eta_\infty(3d \rightarrow d)$ is of the order of -10 , one thus obtains for the total η_∞ for the Cs^+ ion: $\eta_\infty(\text{Cs}^+) \cong -670$.

This value is considerably less in magnitude than the result for Ag^+ (-8050), the reason being that the $4d$ wave function is very much contracted as compared to that for Ag^+ . This contraction arises from the fact that the $4d$ electrons in Cs^+ are relatively internal, being located inside the main part of the charge distribution of the $5s$ and $5p$ electrons.

In connection with the question of the possible detection of a nuclear hexadecapole moment (HDM), we wish to point out that it is likely that the nuclear HDM can be considerably enhanced by collective effects, in the same manner as the nuclear quadrupole moments. There are two regions of the periodic table with large (collectively enhanced) quadrupole moments.⁴⁰ The first region extends roughly from Pm^{151} ($Z=61$) to Ir^{191} ($Z=77$), while the second region starts approximately at Ac^{227} ($Z=89$) and extends to the highest Z values which have been investigated, in particular, Am^{241} and Am^{243} ($Z=95$). In addition to large collective effects, one requires, of course, that the spin I of the nucleus be ≥ 2 for the hexadecapole interaction to be measurable. In addition, if the experiment

³⁹ W. G. Proctor (private communication).

⁴⁰ G. H. Fuller and V. W. Cohen, *Nuclear Moments*, Appendix 1 to *Nuclear Data Sheets* (Oak Ridge National Laboratory, 1965), pp. 1–17.

is done with an ionic crystal (rather than by an atomic-beam method), one would like to have as large an antishielding factor $|\eta_\infty|$ as possible. As shown previously in Ref. 5, one obtains a large value of $|\eta_\infty|$ if the outermost shell of the ion is a d shell.

In connection with the first region, $Z=61$ to 77 , we note that the $4d$ shell is already filled at Ag ($Z=47$), so that it will be relatively internal in the region of the rare earths. However, it should be pointed out that for rhenium ($Z=75$), the $5d$ shell is at least half-filled, the lowest configurations being $5d^56s^2$ and $5d^66s$. For both Re¹⁸⁵ and Re¹⁸⁷ the quadrupole moment is $\sim +2.6b$ which is quite large ($1b=10^{-24}$ cm²). Moreover, the spin $I=\frac{5}{2}$ for both cases, which may make it possible to observe a hexadecapole interaction, since the half-filled $5d$ shell is expected to lead to a large $|\eta_\infty|$, perhaps of the same order as that for Hg⁺⁺, which differs from Re in two ways which tend to compensate each other: the number of $5d$ electrons is greater for Hg, by a factor of 2, but on the other hand, the $5d$ electrons are on the average more tightly bound than for Re.

In the second (actinide) region, the $5f$ shell is being filled, and for americium, the ground-state configuration is $5f^76s^26p^67s^2$. The nuclear quadrupole moment is $+4.9b$ for both Am²⁴¹ and Am²⁴³, with $I=\frac{5}{2}$ in both cases. Although the f electrons are not as effective in producing a large $|\eta_\infty|$ as are the d electrons⁵ (for the same amount of binding), nevertheless the half-filled $5f$ shell for Am may produce an appreciable antishielding. We also note that for U²³⁵ with $I=\frac{7}{2}$, the quadrupole moment is large (4.1b), and although the ground-state configuration contains only three $5f$ electrons plus one $6d$ electron, the U²³⁵ nucleus may still be a good candidate for detecting a nuclear HDM, possibly by an atomic-beam method.

Summarizing this discussion, we can state that in addition to the nuclei suggested previously⁴¹ for detecting a nuclear HDM, namely Zn⁶⁷, Ge⁷³, In¹¹³, Sb¹²¹, and Sb¹²³, which were chosen on account of the small number of electrons outside closed d shells, it may also be useful to consider nuclei in the lutetium-rhenium region, as well as the actinide elements. In each of these two classes of nuclei, the hexadecapole moment is expected to be considerably enhanced by collective effects.

VII. HYDROGENIC WAVE FUNCTIONS

In this section, we will obtain the values of $\gamma_\infty(nl \rightarrow l')$ for the case of hydrogenic wave functions. It should be emphasized at the outset that these results will be mainly of academic interest, since the actual wave functions are considerably different from hydrogenic functions (except for $1s$, and possibly $2s$ and $2p$), so that the numerical calculations which have been discussed above are required to obtain reliable values of γ_∞ . Nevertheless, the hydrogenic results for

⁴¹ R. M. Sternheimer, Phys. Rev. Letters **6**, 190 (1961).

γ_∞ , in particular, for the angular modes ($l'=l\pm 2$), may be of some interest, because they have led to the discovery of a rather unexpected property of the radial hydrogenic wave functions.

For the case of hydrogenic wave functions, the equations for $u_1'(nl \rightarrow l_1)$ and $v_1'(nl \rightarrow l_1)$ [Eqs. (8) and (51)] can be solved analytically.^{10,42} In the present work, we will obtain $\gamma_\infty(nl \rightarrow l_1)$ by means of the perturbation $v_1'(nl \rightarrow l_1)$, for which the equation is as follows:

$$\left[-\frac{d^2}{dr^2} + \frac{l_1(l_1+1)}{r^2} - \frac{2Z}{r} + \frac{Z^2}{n^2} \right] v_1'(nl \rightarrow l_1) = u_0'(nl)/r^3. \quad (116)$$

The resulting shielding factor $\gamma_\infty(nl \rightarrow l_1)$ is given by

$$\gamma_\infty(nl \rightarrow l_1) = C_{ll_1}^{(2)} \int_0^\infty u_0' v_1' r^2 dr, \quad (117)$$

where $C_{ll_1}^{(2)}=8/5$ for $ns \rightarrow d$ or $nd \rightarrow s$; and $C_{ll_1}^{(2)}=72/25$ for $np \rightarrow f$ or $nf \rightarrow p$.

We have previously⁴² obtained the following results: $\gamma_\infty(1s \rightarrow d)=2/3Z$, $\gamma_\infty(2s \rightarrow d)=4/3Z$, $\gamma_\infty(2p \rightarrow f)=48/25Z$, and $\gamma_\infty(3p \rightarrow f)=78/25Z$.

For the case of $ns \rightarrow d$ with $n \geq 3$ and $np \rightarrow f$ with $n \geq 4$, one encounters the difficulty that the corresponding unperturbed states ns and nd , or np and nf are degenerate, and therefore the unperturbed functions $u_0'(nl_1)$ already satisfy the homogeneous equation corresponding to (116). As a result, Eq. (116) alone is insufficient to determine the function $v_1'(nl \rightarrow l_1)$, and an additional condition is needed.

In order to resolve this difficulty, we will consider the case of $3s \rightarrow d$ as an example. According to the usual first-order perturbation theory, any possible mixing of $3s$ with $3d$ will depend on the matrix element of the perturbation, namely, $H_Q = -QP_2(\cos\theta)/r^3$ between these two states. Thus, we are led to calculate the value

$$(H_1)_{3s,3d} = -Q \int_0^\pi \int_0^\infty u_0(3s) [P_2(\cos\theta)/r^3] u_0(3d) dr \times \sin\theta d\theta, \quad (118)$$

where $u_0(3s)$ and $u_0(3d)$ denote r times the complete wave functions for $3s$ and $3d$, i.e., including both the radial and the angular part. Thus, we have

$$u_0(3s) = u_0'(3s) \Theta_0^0, \quad (119)$$

$$u_0^m(3d) = u_0'(3d) \Theta_2^m, \quad (120)$$

where the superscript m denotes the magnetic quantum number m of the $3d$ state considered. It is clear that for the $3d$ state with $m=0$, the angular part of the integral (118) will not vanish, since $\int_0^\pi \Theta_0^0 \Theta_2^0 P_2 \times \sin\theta d\theta = 1/(5)^{1/2}$. However, we found the rather

⁴² H. M. Foley, R. M. Sternheimer, and D. Tycko, Phys. Rev. **93**, 734 (1954).

surprising result that the radial integral is zero, i.e.,

$$\int_0^{\infty} u_0'(3s)u_0'(3d)r^{-3}dr=0. \quad (121)$$

This property can be easily verified upon using the expressions for $u_0'(3s)$ and $u_0'(3d)$, namely,

$$u_0'(3s)=\frac{2Z^{1/2}}{3(3)^{1/2}}(Zr-\frac{2}{3}Z^2r^2+(2/27)Z^3r^3)e^{-Zr/3}, \quad (122)$$

$$u_0'(3d)=\frac{4Z^{1/2}}{81(30)^{1/2}}(Zr)^3e^{-Zr/3}. \quad (123)$$

The result (121) implies that the perturbation H_Q does not lead to an excitation of $3s$ to $3d$ states in first order, and therefore we must choose that solution of (116) which is orthogonal to $u_0'(3d)$. Thus, the added condition on $v_1'(nl \rightarrow l_1)$ can be written as follows:

$$\int_0^{\infty} v_1'(nl \rightarrow l_1)u_0'(nl_1)dr=0. \quad (124)$$

We will now show that the condition (124) holds in general for all cases where there exists a state nl_1 which is degenerate with the initial state nl .

To start with, it was found that an analogous property to Eq. (121) holds for all $n \geq 3$, that is, we have

$$\int_0^{\infty} u_0'(ns)u_0'(nd)r^{-3}dr=0 \quad \text{for } n \geq 3. \quad (125)$$

The result (125) can be easily verified for $(4s,4d)$ and $(5s,5d)$ using the expressions for the corresponding radial functions $u_0'(ns)$ and $u_0'(nd)$.

For the $nd \rightarrow s$ excitations, the situation is obviously similar to that for $ns \rightarrow d$. Since according to (115), there will be no mixing of $u_0'(ns)$ with the unperturbed function $u_0'(nd)$, we must again impose the condition (124) on the solution of Eq. (116), in which now $l=2$ and $l_1=0$.

Proceeding to the calculation of $\gamma_{\infty}(np \rightarrow f)$ for $n \geq 4$, we would again have a mixing of nf with np , unless the corresponding matrix element $(H_1)_{np,nf}$ vanishes. In similarity to Eq. (118), the angular part of the integral for $(H_1)_{np,nf}$ will not be zero for the state nf with the same value of the magnetic quantum number m as the initial state (np) . However, it is easily verified that the corresponding radial integral vanishes in all cases (for all n). Thus, we find

$$\int_0^{\infty} u_0'(np)u_0'(nf)r^{-3}dr=0 \quad (n \geq 4). \quad (126)$$

Hence, the supplementary condition of Eq. (124) is again appropriate, in which now $l=1$ and $l_1=3$.

In the same manner, for the perturbations $nf \rightarrow p$, we have the condition (124) with $l=3$ and $l_1=1$.

We have subsequently discovered that a property analogous to Eqs. (125) and (126) holds for a wider class of integrals. The complete statement of the orthogonality property is that the integral

$$K_{nlv,s} \equiv \int_0^{\infty} u_0'(nl)u_0'(nl')r^{-s}dr=0, \quad (127)$$

provided that $s=2, 3, \dots, l-l'+1$, where $l > l'$. A proof of Eq. (127) has been given by Pasternack and Sternheimer.⁴⁸

We will now obtain the value of $\gamma_{\infty}(3s \rightarrow d)$. For simplicity of notation, we will take $Z=1$ in the following derivations. It will be shown below that all expressions for $\gamma_{\infty}(nl \rightarrow l')$ are proportional to $1/Z$, so that it will only be necessary to divide the final result by Z . The dependence of the perturbed function $v_1'(nl \rightarrow l')$ on Z will also be derived below.

In view of Eqs. (116), (121), and (122), the equation satisfied by $v_1'(3s \rightarrow d)$ is given by

$$\left(-\frac{d^2}{dr^3} + \frac{6}{r^2} - \frac{2}{r} + \frac{1}{9}\right)v_1'(3s \rightarrow d) = A_{3s}e^{-r/3}\left(\frac{1}{r^2} - \frac{2}{3r} + \frac{2}{27}\right), \quad (128)$$

where $A_{3s} = \frac{2}{3}(3)^{-1/2}$. It is easily shown that a solution of Eq. (128) is given by

$$v_1^{(0)}(3s \rightarrow d) = A_{3s}e^{-r/3}\left(\frac{1}{6} - \frac{1}{18}r\right). \quad (129)$$

We have used the additional superscript (0) for v_1' in order to denote the fact that this function is not yet the actual solution, since it is not orthogonal to $u_0'(3d)$, as is required by Eq. (124). Thus we find, upon using Eq. (123) for $u_0'(3d)$,

$$\int_0^{\infty} v_1^{(0)}(3s \rightarrow d)u_0'(3d)dr = -\frac{1}{18(10)^{1/2}}. \quad (130)$$

Hence the actual solution $v_1'(3s \rightarrow d)$ is given by

$$v_1'(3s \rightarrow d) = v_1^{(0)}(3s \rightarrow d) + \frac{1}{18(10)^{1/2}}u_0'(3d) = \frac{1}{9(3)^{1/2}}e^{-r/3}\left(1 - \frac{1}{3}r + \frac{1}{405}r^3\right). \quad (131)$$

Finally, we obtain from Eq. (117)

$$\gamma_{\infty}(3s \rightarrow d) = \frac{8}{5} \int_0^{\infty} u_0'(3s)v_1'(3s \rightarrow d)r^2dr = +2, \quad (132)$$

so that for arbitrary Z , $\gamma_{\infty}(3s \rightarrow d) = +2/Z$.

⁴⁸ S. Pasternack and R. M. Sternheimer, J. Math. Phys. 3, 1280 (1962).

For $\gamma_\infty(4s \rightarrow d)$ we can proceed in the same manner. The inhomogeneous equation for $v_1'(4s \rightarrow d)$ is given by

$$\left(-\frac{d^2}{dr^2} + \frac{6}{r^2} - \frac{2}{r} + \frac{1}{16}\right)v_1'(4s \rightarrow d) = A_{4s}e^{-\frac{1}{2}r}\left(\frac{1}{r^2} - \frac{3}{4r} + \frac{1}{8} - \frac{r}{192}\right), \quad (133)$$

where $A_{4s} \equiv \frac{1}{4}$. The function $v_1^{(0)}(4s \rightarrow d)$ obtained by direct solution of (133) is as follows:

$$v_1^{(0)}(4s \rightarrow d) = A_{4s}e^{-\frac{1}{2}r}\left(\frac{1}{6} - \frac{5}{72}r + \frac{1}{192}r^2\right). \quad (134)$$

By requiring orthogonality of the actual solution v_1' on $u_0'(4d)$, one finally obtains

$$v_1'(4s \rightarrow d) = v_1^{(0)}(4s \rightarrow d) + \frac{1}{72(5)^{1/2}}u_0'(4d) = -\frac{e^{-\frac{1}{2}r}}{4}\left(\frac{1}{6} - \frac{5}{72}r + \frac{1}{192}r^2 + \frac{1}{5760}r^3 - \frac{1}{69120}r^4\right). \quad (135)$$

The resulting value of $\gamma_\infty(4s \rightarrow d)$ is

$$\gamma_\infty(4s \rightarrow d) = \frac{8}{5} \int_0^\infty u_0'(4s)v_1'(4s \rightarrow d)r^2 dr = +\frac{8}{3}. \quad (136)$$

In the same manner, we have calculated that $\gamma_\infty(5s \rightarrow d) = +10/3$. Upon using this result together with the values of $\gamma_\infty(ns \rightarrow d)$ for $n=1, 2, 3, 4$, it is seen that $\gamma_\infty(ns \rightarrow d)$ is given by

$$\gamma_\infty(ns \rightarrow d) = +\frac{2}{3}n. \quad (137)$$

The simple proportionality of $\gamma_\infty(ns \rightarrow d)$ to the principal quantum number n was rather unexpected. Actually, it will be presently shown that all of the shielding factors $\gamma_\infty(nl \rightarrow l \pm 2)$ to be considered here can be expressed in the form

$$\gamma_\infty(nl \rightarrow l \pm 2) = an + b, \quad (138)$$

where a and b are constant coefficients. Thus, for $\gamma_\infty(ns \rightarrow d)$ we have $a = +\frac{2}{3}$, $b = 0$.

We will now obtain $\gamma_\infty(3d \rightarrow s)$. The equation satisfied by $v_1'(3d \rightarrow s)$ is given by

$$\left(-\frac{d^2}{dr^2} + \frac{2}{r} - \frac{1}{9}\right)v_1'(3d \rightarrow s) = \frac{u_0'(3d)}{r^3} = A_{3d}e^{-\frac{1}{3}r}, \quad (139)$$

where $A_{3d} = 4/[81(30)^{1/2}]$.

The solution obtained by direct integration of Eq. (139) is found to be

$$v_1^{(0)}(3d \rightarrow s) = -\frac{3}{4}A_{3d}re^{-\frac{1}{3}r}. \quad (140)$$

It can be easily verified that the above function is orthogonal to $u_0'(3s)$:

$$\int_0^\infty v_1^{(0)}(3d \rightarrow s)u_0'(3s)dr = 0, \quad (141)$$

so that $v_1^{(0)}(3d \rightarrow s)$ is identical with the actual solution $v_1'(3d \rightarrow s)$ to our problem. Finally, we obtain

$$\gamma_\infty(3d \rightarrow s) = \frac{8}{5} \int_0^\infty v_1'(3d \rightarrow s)u_0'(3d)r^2 dr = -(6/5). \quad (142)$$

The negative sign of $\gamma_\infty(3d \rightarrow s)$ indicates antishielding of the nuclear quadrupole moment.

For $\gamma_\infty(4d \rightarrow s)$, the function $v_1^{(0)}(4d \rightarrow s)$ obtained by direct solution of the inhomogeneous equation is orthogonal to $u_0'(4s)$, in the same manner as for $3d \rightarrow s$. We thus obtain

$$v_1^{(0)}(4d \rightarrow s) = v_1'(4d \rightarrow s) = -\frac{7}{576(5)^{1/2}}e^{-r/4}\left(r - \frac{3}{28}r^2\right), \quad (143)$$

which gives $\gamma_\infty(4d \rightarrow s) = -28/15$.

In an entirely similar fashion, we find $\gamma_\infty(5d \rightarrow s) = -38/15$. It should be noted that these three values of $\gamma_\infty(nd \rightarrow s)$ are antishielding, and that they vary linearly with n . In fact, we can write these values in the form of Eq. (138), namely,

$$\gamma_\infty(nd \rightarrow s) = -\frac{2}{3}n + \frac{4}{5}. \quad (144)$$

Thus $a = -\frac{2}{3}$, $b = +\frac{4}{5}$ in the notation of Eq. (138). We remark that the value of a for $(nd \rightarrow s)$ is just minus the corresponding value of a for $(ns \rightarrow d)$. We shall again find the same situation for $\gamma_\infty(np \rightarrow f)$ and $\gamma_\infty(nf \rightarrow p)$.

For $\gamma_\infty(2p \rightarrow f)$ and $\gamma_\infty(3p \rightarrow f)$, values have been previously obtained in Ref. 42; these values are 48/25 and 78/25, respectively. For $\gamma_\infty(4p \rightarrow f)$, the inhomogeneous equation satisfied by $v_1'(4p \rightarrow f)$ is given by

$$\left(-\frac{d^2}{dr^2} + \frac{12}{r^2} - \frac{2}{r} + \frac{1}{16}\right)v_1'(4p \rightarrow f) = \frac{1}{r^3}u_0'(4p) = A_{4p}e^{-\frac{1}{4}r}\left(\frac{1}{r} - \frac{1}{4} + \frac{1}{80}r\right), \quad (145)$$

where $A_{4p} = \frac{1}{16}(\frac{5}{3})^{1/2}$. By direct solution of (145), we find

$$v_1^{(0)}(4p \rightarrow f) = A_{4p}e^{-r/4}[(1/12)r - (1/80)r^2]. \quad (146)$$

Furthermore,

$$\int_0^\infty v_1^{(0)}(4p \rightarrow f)u_0'(4f)dr = -\frac{1}{24(21)^{1/2}}. \quad (147)$$

Hence, the complete solution $v_1'(4p \rightarrow f)$ is given by

$$v_1'(4p \rightarrow f) = v_1^{(0)'}(4p \rightarrow f) + \frac{1}{24(21)^{1/2}} u_0'(4f) \\ = \left(\frac{5}{3}\right)^{1/2} \left(\frac{1}{64}\right) e^{-2r} \left(\frac{1}{3} - \frac{1}{20}r^2 + \frac{1}{10080}r^4\right), \quad (148)$$

whence

$$\gamma_\infty(4p \rightarrow f) \\ = \frac{72}{25} \int_0^\infty v_1'(4p \rightarrow f) u_0'(4p) r^2 dr = +\frac{108}{25}. \quad (149)$$

In a similar manner, one finds $\gamma_\infty(5p \rightarrow f) = +138/25$. Thus, the values of $\gamma_\infty(np \rightarrow f)$ can be represented as follows:

$$\gamma_\infty(np \rightarrow f) = (6/5)n - 12/25, \quad (150)$$

i.e., Eq. (138) with $a=6/5$, $b=-12/25$.

Finally, we will calculate $\gamma_\infty(4f \rightarrow p)$. The solution $v_1'(4f \rightarrow p)$ is determined by the equation

$$\left(-\frac{d^2}{dr^2} + \frac{2}{r^2} - \frac{1}{r}\right) v_1'(4f \rightarrow p) \\ = \frac{1}{r^3} u_0'(4f) = A_{4f} r e^{-2r}, \quad (151)$$

where $A_{4f} = 1/(768(35)^{1/2})$. By direct solution of (151), we obtain

$$v_1^{(0)'}(4f \rightarrow p) = -A_{4f} r^2 e^{-2r}, \quad (152)$$

and this function is orthogonal to $u_0'(4p)$, as can be easily verified. The present situation, namely, that $v_1'(nl \rightarrow l-2) = v_1^{(0)'}(nl \rightarrow l-2)$ is similar to that previously encountered for $(nd \rightarrow s)$.

From Eq. (152), we obtain

$$\gamma_\infty(4f \rightarrow p) \\ = \frac{72}{25} \int_0^\infty v_1'(4f \rightarrow p) u_0'(4f) r^2 dr = -\frac{72}{25}. \quad (153)$$

Similarly, we find $\gamma_\infty(5f \rightarrow p) = -102/25$. Thus, the terms $\gamma_\infty(nf \rightarrow p)$ are antishielding in the same manner as $\gamma_\infty(nd \rightarrow s)$. We can write

$$\gamma_\infty(nf \rightarrow p) = -(6/5)n - 48/25. \quad (154)$$

As previously noted, we see that the value of a for $(nf \rightarrow p)$ is just the negative of a for $(np \rightarrow f)$ [see Eq. (150)].

Thus, we have found that the terms due to the angular modes $\gamma_\infty(nl \rightarrow l \pm 2)$ can be expressed in the form $an + b$, as a function of the principal quantum number n , for the case of hydrogenic wave functions. Moreover, the coefficients a_\pm for $(nl \rightarrow l \pm 2)$ are related by the

equation $a_- = -a_+$. It is noteworthy that such a linear relation does not appear to hold for the radial antishielding terms $\gamma_\infty(nl \rightarrow l)$, for which $l' = l$. Thus, in Ref. 42, we have obtained $\gamma_\infty(2p \rightarrow p) = -268/25 = -10.72$ and $\gamma_\infty(3p \rightarrow p) = -1008/25 = -40.32$. We have furthermore calculated $\gamma_\infty(4p \rightarrow p) = -2468/25 = -98.72$, from which it is apparent that $|\gamma_\infty(np \rightarrow p)|$ increases faster than linearly with increasing n .

Finally, we will prove that for hydrogenic wave functions $\gamma_\infty(nl \rightarrow l_1)$ is proportional to $1/Z$ in all cases ($l_1 = l$ or $l \pm 2$). For this purpose, we consider Eq. (116) for $v_1'(nl \rightarrow l_1)$ and define $y \equiv Zr$. We thus obtain

$$Z^2 \left[-\frac{d^2}{dy^2} + \frac{l_1(l_1+1)}{y^2} - \frac{2}{y} + \frac{1}{n^2} \right] v_1'(nl \rightarrow l_1) \\ = \frac{Z^3 u_0'(nl)}{y^3}. \quad (155)$$

The unperturbed function $u_0'(nl)$ can be written as follows:

$$u_0' = Z^{1/2} f(y), \quad (156)$$

where $f(y)$ is a function of y only, as indicated. It follows from Eq. (155) that

$$v_1' = Z^{3/2} g(y), \quad (157)$$

where $g(y)$ is a function of $y = Zr$ only. Hence the shielding factor γ_∞ can be written as follows:

$$\gamma_\infty(nl \rightarrow l_1) = C_{ll_1}^{(2)} \int_0^\infty u_0' v_1' r^2 dr \\ = C_{ll_1}^{(2)} \int_0^\infty Z^2 f g \left(\frac{y^2 dy}{Z^3} \right) \\ = C_{ll_1}^{(2)} Z^{-1} \int_0^\infty f g y^2 dy, \quad (158)$$

which completes the proof that $\gamma_\infty(nl \rightarrow l_1)$ is proportional to $1/Z$.

VIII. SUMMARY

In this paper, we have shown that the first-order perturbation theory which has been previously applied to obtain the quadrupole antishielding factors γ_∞ and R , and the polarizabilities α_d and α_q can also be used successfully to calculate the rare-earth ion shielding parameter σ_2 . The values obtained for $\sigma_2(\text{Pr}^{3+})$ and $\sigma_2(\text{Tm}^{3+})$ are in good agreement with the experimental results.¹ The present calculations are more complete than previous ones,² since they include at once the excitation of $5s$ to all possible d states (including the continuum states), and similarly the excitation of $5p$ to all possible p and f states. Moreover, the author's method³ of direct solution of the Schrödinger equation

has been used, which is inherently more accurate than the variational procedure or the method of configuration interaction, using a limited number of excited states. In addition, it has been shown that the effect of the exchange terms of σ_2 is small compared to that of the direct Coulomb terms.

The present calculations of the quadrupole antishielding factor γ_∞ for Cs^+ , Pr^{3+} , and Tm^{3+} give more accurate values than those which have been previously obtained in Refs. 8 and 9. For Cs^+ , the improvement comes from the use of Hartree-Fock wave functions instead of the Hartree functions (excluding exchange), which were the only ones available at the time of our previous calculation⁹ (in 1955). As a result of the use of the Hartree-Fock wave functions of Freeman and Watson,⁷ the value of $|\gamma_\infty(\text{Cs}^+)|$ is reduced by $\sim 30\%$ as compared to the Hartree function value. A similar decrease²⁰ has been previously found for γ_∞ of Rb^+ . For Pr^{3+} and Tm^{3+} , the present results for γ_∞ (-80.9 and -75.3 , respectively) are slightly more accurate than those obtained previously,⁸ because the present work includes a calculation of the $nl \rightarrow l$ modes of excitation of the inner shells ($n \leq 3$, and $4d \rightarrow d$), which had not been carried out in Ref. 8. The quadrupole antishielding factors γ_∞ for the Al^{3+} and I^- ions obtained in this paper have not been previously calculated by the method of direct integration of the inhomogeneous Schrödinger equation. In addition, we have also calculated the atomic shielding factor R for the $4f$ electrons in Pr^{3+} and Tm^{3+} , and the results (corresponding to a shielding of the order of 10–20%) were found to be in reasonable agreement with experiment.

The problem of the detection of a possible nuclear electric hexadecapole moment (HDM) has been discussed, and it has been pointed out that if collective effects play an important role in enhancing the nuclear HDM, then the most promising regions of the periodic table are those extending from Pm ($Z=61$) to Ir ($Z=77$), and from Ac ($Z=89$) to Am ($Z=95$), since both regions exhibit large quadrupole moments. A case of particular interest is that of rhenium (Re^{185} and Re^{187}), because the presence of the half-filled external $5d$ shell of the atom is expected to lead to a very large value of the hexadecapole antishielding factor⁵ $|\eta_\infty|$ (perhaps of order 50 000).

Finally, we have obtained the values of the shielding factor $\gamma_\infty(nl \rightarrow l \pm 2)$ using hydrogenic wave functions. Although this calculation is only of academic interest as far as the practical evaluation of γ_∞ is concerned, it has led to two interesting results (1) the discovery and proof²³ of a new orthogonality property of the hydrogenic radial wave functions; (2) the fact that in all of the cases considered, $\gamma_\infty(nl \rightarrow l \pm 2)$ is a simple linear function of the principal quantum number n : $\gamma_\infty(nl \rightarrow l') = an + b$, where the coefficients a and b depend on l and l' only (but not on n), and are inversely proportional to Z .

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