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Shielding of Crystal Fields at Rare-Earth Ions*

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In connection with the interpretation of the spectra of the salts of rare-earth ions, the appropriate shielding factors σ_2, σ_4, and σ_6 have been calculated for Pr^{3+} ($Z=59$) and Tm^{3+} ($Z=69$). The shielding factor σ_k measures the effective reduction of the $A_k{}^q r^k Y_{kq}$ term of the crystal potential at the location of the $4f$ shell which is produced by the more external $5s$ and $5p$ electrons of the rare earths (and also to a smaller extent by the inner core electrons). The values of σ_4 and σ_6 were found to be small, i.e., of order 0.1. Thus σ_4 is weakly shielding ($\sigma_4=0.091$ for Pr^{3+}), while σ_6 gives a small antishielding ($\sigma_6=-0.040$ for Pr^{3+}). A previous calculation of σ_2 has been improved by including the effect of the $4s$, $4p$, and $4d$ subshells. The resulting values of σ_2 are in reasonable agreement with experiment. Finally, an angular factor which arises in the evaluation of the direct and exchange terms of σ_k has been expressed in terms of 3-j and 6-j symbols involving the various angular momenta of the problem.

I. INTRODUCTION

THE shielding of crystal fields at rare-earth ions in ionic solids has been the subject of a number of investigations, both experimental[1] and theoretical.[2–4] The shielding is provided primarily by the $5s$ and $5p$ shells of the rare-earth ion, which are essentially external to the $4f$ electrons whose quadrupole coupling with the nucleus is measured. The crystal field at the location of the ion can be written (for C_{3h} or D_{3h} symmetry)[5] as follows:

$$V_{\mathrm{cr}}=A_2{}^0r^2Y_{20}(\theta,\varphi)+A_4{}^0r^4Y_{40}(\theta,\varphi)+A_6{}^0r^6Y_{60}(\theta,\varphi)+\tfrac{1}{2}A_6{}^6[Y_{66}(\theta,\varphi)+Y_{66}{}^*(\theta,\varphi)],\quad(1)$$

where $Y_{kq}(\theta,\varphi)$ is the normalized spherical harmonic, the $A_k{}^q$ are constants determined by the distribution of ions in the lattice, i.e., by the appropriate lattice sums, r is the distance from the rare-earth nucleus, and θ and φ are the angles with respect to one of the principal axes of the crystal.

Equation (1) gives the potential of the crystal field produced by all of the charges external to the ion considered. In order to obtain the actual effective potential acting at the location of the $4f$ electrons, it is necessary to introduce the shielding parameters σ_2, σ_4, and σ_6, which have been extensively discussed in Refs. 1–4. Thus the effective crystal potential at the location of the $4f$ electron is given by

$$V_{4f}=A_2{}^0r^2(1-\sigma_2)Y_{20}(\theta,\varphi)+A_4{}^0r^4(1-\sigma_4)Y_{40}(\theta,\varphi)+A_6{}^0r^6(1-\sigma_6)Y_{60}(\theta,\varphi)+\tfrac{1}{2}A_6{}^6r^6(1-\sigma_6)\times[Y_{66}(\theta,\varphi)+Y_{66}{}^*(\theta,\varphi)].\quad(2)$$

Both from the experiments[1] and from the calculations,[2–4] it is found that σ_2 is large throughout the rare-earth region, of the order of 0.7 to 1.0, and there is also good experimental evidence that σ_2 decreases somewhat with increasing Z in going from cerium ($Z=58$; $\sigma_2\sim1.0$) to ytterbium ($Z=70$; $\sigma_2\sim0.65$). As an example of the theoretical results obtained, one of us (R.M.S.) has previously calculated[6] the following values: $\sigma_2(\mathrm{Pr}^{3+})\cong 0.60$ and $\sigma_2(\mathrm{Tm}^{3+})\cong0.48$. This calculation includes exchange effects, but does not include the (small) shielding effect of the inner shells (in particular, those with principal quantum number $n=4$). As shown below (Sec. III), upon taking into account the effect of the $n=4$ subshells, the preceding values are increased to $\sigma_2(\mathrm{Pr}^{3+})\cong0.67$ and $\sigma_2(\mathrm{Tm}^{3+})\cong0.55$.

The main purpose of the present paper is to give the results of calculations of the shielding factors σ_4 and σ_6 for the Pr^{3+} and Tm^{3+} ions. These calculations are completely analogous to the previous work on the parameter σ_2, which was published in Ref. 6. In the same manner as in Ref. 6, we have included both the direct terms and the exchange terms (with the $4f$ electrons) in the determination of σ_4 and σ_6. In connection with the exchange terms, it is necessary to evaluate a coefficient C_E, analogous to $C(nl\rightarrow l',L)$ of Ref. 6 [see Eq. (37)], which expresses the result of summing over the magnetic quantum numbers and integrating over the angular variables. An expression for C_E in terms of 3-j and 6-j symbols has been obtained in the present paper. In view of the high angular momenta

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[1] D. T. Edmonds, Phys. Rev. Letters **10**, 129 (1963); R. G. Barnes, R. L. Mössbauer, E. Kankeleit, and J. M. Poindexter, *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); D. L. Uhrich, D. J. Genin, and R. G. Barnes, *ibid.* **166**, 261 (1968).

[2] G. Burns, Phys. Rev. **128**, 2121 (1962); J. Chem. Phys. **42**, 377 (1965).

[3] C. J. Lenander and E. Y. Wong, J. Chem. Phys. **38**, 2750 (1963); D. K. Ray, Proc. Phys. Soc. (London) **82**, 47 (1963).

[4] R. E. Watson and A. J. Freeman, Phys. Rev. **133**, A1571 (1964); **139**, A1606 (1965); R. M. Sternheimer, *ibid.* **146**, 140 (1966); M. N. Ghatikar, A. K. Raychaudhuri, and D. K. Ray, Proc. Phys. Soc. (London) **86**, 1235 (1965).

[5] R. J. Elliott and K. W. H. Stevens, Proc. Phys. Soc. (London) **A64**, 205 (1951); Proc. Roy. Soc. (London) **A215**, 437 (1952).

[6] R. M. Sternheimer, Phys. Rev. **146**, 140 (1966). See Eqs. (49) and (50).

involved for $k=4$ and $k=6$ (where k is the multipolarity of the term in the external potential V_{cr}), such an expression for C_E is almost indispensable. The principal result of the calculations is that σ_4 and σ_6 are small, of the order of 0.05 to 0.10, i.e., considerably smaller than σ_2.

In addition to the calculations of σ_4 and σ_6, we have also obtained values for the (small) terms of σ_2 which are due to the excitation of the $4s$, $4p$, and $4d$ shells of Pr^{3+} and Tm^{3+}. As indicated above, these terms are much smaller than the dominant σ_2 contribution which is due to the excitations of the $5s$ and $5p$ electrons.

In Sec. II, we obtain the basic equations for σ_k and the relevant perturbed radial wave functions $u_1'(nl\rightarrow l')_k$ for $k=4$ and $k=6$. We also present the resulting values of the various terms of σ_4 and σ_6 for both Pr^{3+} and Tm^{3+}. It is shown that the total values of σ_4 and σ_6 are the result of a considerable amount of cancellation between the direct and the exchange terms. For σ_6, the exchange terms actually predominate and give rise to a small net antishielding of the external potential $A_6^0r^6Y_{60}(\theta,\varphi)$.

In Sec. III, we give the details of the calculation of the terms $\Delta\sigma_2(4s, 4p, 4d)$ ($k=2$) arising from the excitation of the $n=4$ subshells, for both Pr^{3+} and Tm^{3+}.

Section IV is devoted to the derivation of an expression for the "angular" coefficients C_D and C_E (which enter into σ_k) in terms of 3-j and 6-j symbols. As indicated by the subscript, C_D is a coefficient analogous to C_E, but pertaining to the direct terms of σ_k. C_D has been previously denoted by $c(nl\rightarrow l')$ or $C_{ll'}^{(2)}$ for the special case $k=2$.

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

II. CALCULATIONS OF THE SHIELDING FACTORS σ_4 AND σ_6

The derivation of the equations for the shielding factor σ_k in the general case $k>2$ follows exactly the same lines as the derivation for the case $k=2$, which was given in Ref. 6 [see Eqs. (1)–(24) for the direct terms, and Eqs. (25)–(38) for the exchange terms]. The only difference is that the external perturbation $\propto Y_{20}r^2$ is now replaced by $Y_{k0}r^k$. We note that in the present discussion (Sec. II) we shall restrict ourselves to the $Y_{40}r^4$ and $Y_{60}r^6$ terms of the external potential V_{cr} [Eq. (1)], i.e., we shall not consider the term $\frac{1}{2}A_6^6r^6(Y_{66}+Y_{66}^*)$. In Sec. IV, it will be shown that the shielding (or antishielding) factor σ_{kq} pertaining to the external potential $A_k^qr^kY_{kq}$ is independent of the magnetic quantum number q, i.e., $\sigma_{kq}=\sigma_{k0}\equiv\sigma_k$. Thus the same parameter σ_6 applies to the Y_{60}, Y_{66}, and Y_{66}^* terms [see Eq. (2)].

The radial part of the perturbed wave function (times r), to be denoted by $u_1'(nl\rightarrow l')_k$, is determined by the equation

$$\left[-\frac{d^2}{dr^2}+\frac{l'(l'+1)}{r^2}+V_0-E_0\right]u_1'(nl\rightarrow l')_k =u_0'(nl)[r^k-\langle r^k\rangle_{nl}\delta_{ll'}], \quad (3)$$

and moreover, for $l'=l$, by the orthogonality condition

$$\int_0^\infty u_0'(nl)u_1'(nl\rightarrow l)_k dr=0. \quad (4)$$

The notation is the same as in Ref. 6, except that l_1 has been replaced by l'. Thus u_0' is r times the radial part of the unperturbed wave function of the core electron considered (with quantum numbers nl, excited to states with azimuthal quantum number l'). The normalization of u_0' is given by

$$\int_0^\infty u_0'^2dr=1. \quad (5)$$

In Eq. (3), the function V_0-E_0 ($V_0=$effective potential, $E_0=$unperturbed energy) is obtained directly from u_0' by a procedure previously described by Sternheimer[7]:

$$V_0-E_0=(1/u_0')(d^2u_0'/dr^2)-[l(l+1)/r^2]. \quad (6)$$

We now consider the direct term of σ_k to be denoted by $\sigma_{k,D}$. This term is caused by the interaction of the overlap density $2u_0u_1$ with the $4f$ electron density. Here u_0 and u_1 refer to the *complete* wave functions (to zero and first order, respectively) times r, i.e., the products of radial functions and functions of θ. In the same manner as in Ref. 6, we have suppressed the (obvious) dependence on φ, which accounts for the absence of the factor $(2\pi)^{-1/2}$ in both u_0 and u_1. Correspondingly, the integration over φ is not carried out explicitly. Moreover, the functions $Y_{lm}(\theta,\varphi)$ are replaced by the Θ_l^m which are functions of θ only and are normalized to 1.

Referring to Eq. (12) of Ref. 6, we find that $2u_0u_1$ can be written as follows:

$$2u_0(nlm)u_1(nl\rightarrow l')_k=(4/R^{k+1})I_{ll'}^{k(m)}u_0'u_1'(nl\rightarrow l')_k \times\Theta_l^m\Theta_{l'}^m, \quad (7)$$

where

$$I_{ll'}^{k(m)}\equiv\int_0^\pi P_k\Theta_l^m\Theta_{l'}^m\sin\theta d\theta=c^{(k)}(lm;l'm), \quad (8)$$

where $c^{(k)}(lm;\, l'm)$ is a special case of the coefficient $c^{(k)}(lm;l'm')$ of Condon and Shortley.[8]

The P_k part of the potential due to the density (7) is given by

$$V_k(nlm)=(8/R^{k+1})[c^{(k)}(lm;l'm)]^2P_k(\cos\theta) \times\left[(1/r^{k+1})\int_0^r u_0'u_1'r'^kdr'+r^k\int_r^\infty u_0'u_1'r'^{-k-1}dr'\right], \quad (9)$$

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[7] R. M. Sternheimer, Phys. Rev. **96**, 951 (1954); **105**, 158 (1957); **115**, 1198 (1959).

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

where P_k is the Legendre polynomial

$$P_k=[4\pi/(2k+1)]^{1/2}Y_{k0}.$$

In the same manner as in Ref. 6, an additional factor of 2 arises in going from Eq. (7) to (9), since all energies are expressed in Rydberg units $e^2/2a_H$ in the present work.

The function in the square brackets of Eq. (9) will be denoted by $f_k(r)$. The remainder of the derivations of $\sigma_{k,D}$ proceeds in the same manner as for σ_2 [Ref. 6, Eqs. (14)–(21)]. We thus obtain

$$\sigma_{k,D}=C_{ll'}^{(k)}\left(\int_0^\infty v_{4f}'^2 f_k(r)\,dr/\langle r^k\rangle_{4f}\right), \tag{10}$$

where v_{4f}' is r times the radial part of the $4f$ wave function, normalized according to

$$\int_0^\infty v_{4f}'^2 dr=1; \tag{11}$$

$\langle r^k\rangle_{4f}$ is the expectation value of r^k over $v_{4f}'^2$, and $C_{ll'}^{(k)}$ (which will also be denoted by C_D) is completely analogous to $C_{ll'}^{(2)}$ of Ref. 6 [see Eq. (37a)], namely,

$$C_D=C_{ll'}^{(k)}=8\sum_{m=-l}^{l}[c^{(k)}(lm;l'm)]^2. \tag{12}$$

The integral of Eq. (10) will be denoted by K_D.

For relatively low values of l and l', i.e., for $l\leq 3$, $l'\leq 3$, the expression of Eq. (12) can be evaluated directly from the tables of $c^{(k)}(lm;l'm)$ given in Ref. 8. For higher values of l and l', the following expression, to be derived in Sec. IV, can be used:

$$C_D=C_{ll'}^{(k)}=\frac{8(2l+1)(2l'+1)}{2k+1}\begin{pmatrix} l' & k & l\\ 0 & 0 & 0\end{pmatrix}^2, \tag{13}$$

where

$$\begin{pmatrix} l' & k & l\\ 0 & 0 & 0\end{pmatrix}$$

is the usual 3-j symbol, as tabulated for example by Rotenberg *et al.*[9]

The derivation of the exchange terms $\sigma_{k,E}$ proceeds in the same manner as for $k=2$, where the exchange term has been denoted by ζ_2 [Ref. 6, see Eqs. (25)–(37)]. Thus instead of Eqs. (36a) and (37) of Ref. 6, we now obtain

$$\sigma_{k,E}(nl\rightarrow l';L)=-\frac{C_E(nl\rightarrow l';l_e;L)_k K_E(nl\rightarrow l';L)_k}{\langle r^k\rangle_{4f}}, \tag{14}$$

where the coefficient $C_E(nl\rightarrow l';\ l_e;\ L)_k$ (also to be denoted simply by C_E) is given by

$$C_E\equiv C_E(nl\rightarrow l';l_e;L)_k=4\sum_{m=-l}^{l}c^{(k)}(lm;l'm)\,c^{(L)}(lm;l_em_e)\,c^{(L)}(l'm;l_em_e)/c^{(k)}(l_em_e;l_em_e)\,. \tag{15}$$

In Eqs. (14) and (15), the notation is essentially the same as in Ref. 6. Thus l_e and m_e are the quantum numbers of the $4f$ electron; we note that $C_E(nl\rightarrow l';\ l_e;\ L)_k$ is independent of the magnetic quantum number m_e. L denotes the multipolarity of the exchange interaction with the $4f$ electron (there is usually more than one L value for a given $nl\rightarrow l'$ excitation). The coefficients $c^{(L)}(lm;\ l_em_e)$ and $c^{(L)}(l'm;\ l_em_e)$ with $m\neq m_e$ are examples of the general Condon-Shortley coefficient[8] $c^{(L)}(lm;\ l'm')$, defined as follows[10]:

$$c^{(L)}(lm;l'm')=[2/(2L+1)]^{1/2}\int_0^\pi \Theta_L^{m-m'}\times\Theta_l^m\Theta_{l'}^{m'}\sin\theta d\theta. \tag{16}$$

In Eqs. (14) and (15), the additional subscript k in $C_E(nl\rightarrow l';l_e;L)_k$ and $K_E(nl\rightarrow l';\ L)_k$ indicates the multipolarity of the external (crystal) potential. The integral $K_E(nl\rightarrow l';\ L)_k$ is defined in exactly the same way as in Ref. 6 [see Eqs. (32) and (34)]:

$$K_E(nl\rightarrow l';L)_k\equiv\int_0^\infty u_0'(nl)v_{4f}'G(r)\,dr, \tag{17a}$$

where

$$G(r)\equiv(1/r^{L+1})\int_0^r u_1'(nl\rightarrow l')_k v_{4f}'r'^L dr' +r^L\int_r^\infty u_1'(nl\rightarrow l')_k v_{4f}'r'^{-L-1}dr'. \tag{17b}$$

The only dependence of $K_E(nl\rightarrow l',\ L)_k$ on k arises from the fact that the perturbed wave function $u_1'(nl\rightarrow l')_k$ which enters into G was obtained with the appropriate k value [see Eq. (3)].

In the same manner as for C_D [Eq. (12)], C_E can be

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[9] M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, Jr., *The 3-j and 6-j Symbols* (The Technology Press, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1959).

[10] We note that in Ref. 6, Eq. (28), $P_L^{m-m_1}$ should be replaced by $[2/(2L+1)]^{1/2}\Theta_L^{m-m_1}$. In the subsequent calculations leading to Eqs. (38) and (38a), the correct expression for $c^{(L)}(lm;\ l_1m_1)$ was used.

TABLE I. The coefficients $C_D(nl\rightarrow l')_k$ and $C_E(nl\rightarrow l';\,l_e;\,L_i)_k$ pertaining to the $(nl\rightarrow l')$ excitation produced by an external potential $A_k{}^q r^k Y_{kq}(\theta,\varphi)$ [see Eqs. (20) and (23)]; l_e is the azimuthal quantum number of the valence electron. For the exchange term C_E, the value of L_i is listed in parentheses after each coefficient.

$(nl\rightarrow l';\,l_e)$	k	C_D	$C_E(L_1)$	$C_E(L_2)$	$C_E(L_3)$
$(nf\rightarrow h;\,p)$	2	16/3	40/27(4)		
$(nf\rightarrow h;\,d)$	2	16/3	40/63(3)	80/99(5)	
$(nd\rightarrow g;\,f)$	2	144/35	12/49(1)	24/49(3)	300/539(5)
$(nf\rightarrow h;\,f)$	2	16/3	20/63(2)	40/77(4)	700/1287(6)
$(ns\rightarrow g;\,f)$	4	8/9	4/7(3)		
$(np\rightarrow f;\,f)$	4	32/27	88/105(2)	8/63(4)	
$(np\rightarrow h;\,f)$	4	40/27	4/21(2)	40/63(4)	
$(nd\rightarrow d;\,f)$	4	80/63	44/49(1)	176/441(3)	100/4851(5)
$(nd\rightarrow g;\,f)$	4	800/693	40/49(1)	40/539(3)	1200/5929(5)
$(nd\rightarrow i;\,f)$	4	200/99	200/693(3)	700/1089(5)	
$(ns\rightarrow i;\,f)$	6	8/13	4/7(3)		
$(np\rightarrow h;\,f)$	6	144/169	36/35(2)	4/91(4)	
$(np\rightarrow j;\,f)$	6	168/169	28/39(4)		

evaluated from Eq. (15) for $l\leq 3$ and $l'\leq 3$ using the tables of Ref. 8. For higher[11] l' it is necessary to calculate the appropriate $c^{(k)}$ and $c^{(L)}$ coefficients by integration over the spherical harmonics [Eq. (16)]. This procedure becomes very laborious for the large values of l' (up to $l'=7$) involved in the present work. For this reason, we have obtained the following expression for C_E, which will be derived in Sec. IV:

$$C_E(nl\rightarrow l';\,l_e;\,L)_k=4(-1)^L(2l+1)(2l'+1)\begin{pmatrix} l & k & l' \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l & L & l_e \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l' & L & l_e \\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix} k & l_e & l_e \\ L & l & l'\end{Bmatrix}\Big/\begin{pmatrix} l_e & k & l_e \\ 0 & 0 & 0\end{pmatrix}, \tag{18}$$

where the 3-j symbols

$$\begin{pmatrix} \alpha & \beta & \gamma \\ 0 & 0 & 0\end{pmatrix}$$

and the 6-j symbol

$$\begin{Bmatrix} k & l_e & l_e \\ L & l & l'\end{Bmatrix}$$

can be obtained from the tables of Rotenberg *et al.*[9]

In a recent paper[12] on atomic quadrupole shielding and antishielding factors,[13] a table of values of $C_E(nl\rightarrow l';\,l_e;\,L)_k$ for $k=2$ was presented. These values had been obtained by using Eq. (15) with $m_e=0$. We have verified all of these results by means of Eq. (18). The table of Ref. 12 is almost complete for $k=2$, i.e., all cases with $l\leq 3$ and $l_e\leq 3$ were evaluated, with the exception of the following four combinations: $(nl\rightarrow l';\,l_e)=(nf\rightarrow h;\,p)$, $(nf\rightarrow h;\,d)$, $(nd\rightarrow g;\,f)$, and $(nf\rightarrow h;\,f)$. These four sets of C_E values (usually with several L values, labeled L_i) have now been calculated by means of (18).

In addition, we have, of course, obtained the relevant values of $C_E(nl\rightarrow l';\,l_e;\,L_i)_k$ for $k=4$ and $k=6$. The corresponding values of $C_D=C_{ll'}{}^{(k)}$ have also been calculated from Eqs. (12) and (13). The combined list of the C_D and C_E coefficients obtained in the present work is given in Table I. After each $C_E(L_i)$ value, the angular momentum L_i is listed in parentheses, in the same manner as in Table II of Ref. 12.

The calculation of the radial wave functions $u_1'(nl\rightarrow l')_4$ and $u_1'(nl\rightarrow l')_6$ from Eq. (3) was carried out in the same manner as in our previous work.[6,12,13] We used the CDC-6600 program described in Ref. 12 [see the discussion after Eq. (20)]. We note that in the present case, since $u_1'(nl\rightarrow l')_k$ behaves as $r^{l'+1}$ near $r=0$, the proper boundary condition for the computer program is: $u_1'=0$ at $r=0$.

Equation (3) was solved for the following cases for both Pr^{3+} and Tm^{3+}: (a) For $k=4$: $5s\rightarrow g$, $5p\rightarrow f$, and $5p\rightarrow h$; (b) for $k=6$: $5s\rightarrow i$, $5p\rightarrow h$, and $5p\rightarrow j$. In addition, in order to obtain an estimate of the contribution of the inner shells, we have obtained $u_1'(4d\rightarrow d)_4$,

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[11] Note that in all practical cases, l (= quantum number of the unperturbed wave function) never exceeds 3, corresponding to a $4f$ or $5f$ shell.

[12] R. M. Sternheimer, Phys. Rev. **164**, 10 (1967). See Table II.

[13] R. M. Sternheimer, Phys. Rev. **80**, 102 (1950); **84**, 244 (1951); **95**, 736 (1954); **105**, 158 (1957).

TABLE II. Values of $\Gamma_D(nl\rightarrow l')_4$, $\Gamma_E(nl\rightarrow l')_4$, and the total $\Gamma(nl\rightarrow l')_4$ (in units $a_H{}^4$) for the various modes of excitation $(5s\rightarrow l')_4$ and $(5p\rightarrow l')_4$ of the Pr^{3+} ion ($k=4$). The last two columns of the table give the values of the P_4 polarizability $\alpha_4{}^{(i)}$ in units $a_H{}^9$ for two choices of the external potential (see text). Concerning Tables II–VI we note that, in contrast to Γ_D and Γ_E, the values of σ_4 and σ_6 given in the last row of the tables are dimensionless.

Excitation	Γ_D	Γ_E	Γ(total)	$\alpha_4{}^{(1)}$	$\alpha_4{}^{(2)}$
$(5s\rightarrow g)_4$	0.1240	−0.0703	0.0537	115.87	115.31
$(5p\rightarrow f)_4$	0.6041	−0.5166	0.0875	997.6	973.1
$(5p\rightarrow h)_4$	0.1986	−0.0817	0.1169	746.4	722.0
Sum	0.9267	−0.6686	0.2581	1859.9	1810.4
σ_4	0.3264	−0.2355	0.0909	···	···

$u_1'(4d\rightarrow g)_4$, and $u_1'(4d\rightarrow i)_4$ for the Pr^{3+} ion. In the same manner as in Ref. 6, we used the Hartree wave functions of Ridley[14] for the $5s$ and $5p$ electrons.

It was pointed out by Burns[2] that a considerable part of the induced charge distribution $\propto u_0'u_1'$ is located outside a sphere of radius equal to the distance to the nearest-neighbor ion. This distance will be denoted by R. For the case of the PrCl_3 lattice,[15] which may be regarded as fairly typical, R is $2.94\text{Å}=5.57a_H$. If one assumes that the dominant part of the P_k-type potential ($k=4$ or 6) is due to the nearest neighbors, as is probably the case,[2] then we must replace the factor $r^kY_{k0}(\theta,\varphi)/R^{k+1}$ in the perturbing potential [cf. Eq. (1)] by $R^kY_{k0}(\theta,\varphi)/r^{k+1}$ for $r\geqq R$. The result of this replacement is to multiply the term r^k on the right-hand side of Eq. (3) by R^{2k+1}/r^{2k+1}, i.e., for $k=4$, r^4 is changed to R^9/r^5, and for $k=6$, r^6 becomes R^{13}/r^7 for $r\geqq R$. We note that for $5s$ and $5p$ electrons, we do not have to concern ourselves with the corresponding change of the average $\langle r^k\rangle_{nl}$ in Eq. (3), since for all cases with $k=4$ or 6, $l'\neq l$, so that $\delta_{ll'}=0$.

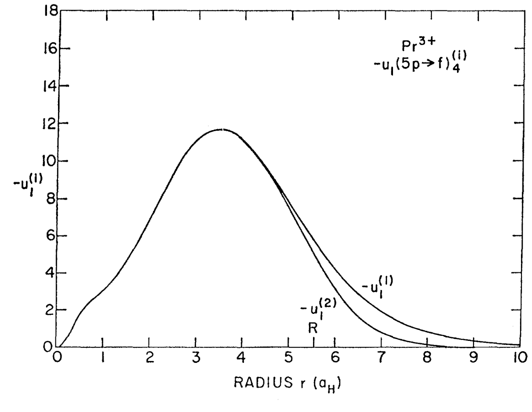

FIG. 1. The perturbed functions $u_1(5p\rightarrow f)_4{}^{(i)}$ for Pr^{3+} (with $k=4$) for two choices of the external perturbation. Here and in Figs. 2 and 4, $u_1{}^{(1)}$ pertains to $R\rightarrow\infty$ and $u_1{}^{(2)}$ pertains to a cutoff radius $R=5.57a_H$ (see text). We note that in all of the figures (Figs. 1–5), the primes have been omitted from u_0' and u_1' for simplicity of notation; e.g., $u_1(5p\rightarrow f)_4{}^{(i)}$ of Fig. 1 is the same as the radial function $u_1'(5p\rightarrow f)_4{}^{(i)}$ discussed in the text.

In the present work, the effect of the cutoff at $r=R$ has been tested for all of the perturbed wave functions obtained for the Pr^{3+} ion. These functions will be denoted by $u_1'(nl\rightarrow l')_k{}^{(1)}$ for $R\rightarrow\infty$, i.e., no cutoff [Eq. (3) with r^k for all r], and by $u_1'(nl\rightarrow l')_k{}^{(2)}$ for $R=5.57a_H$, i.e., Eq. (3) with r^k replaced by R^{2k+1}/r^{k+1} for $r\geqq R$.

The resulting wave functions $u_1'(nl\rightarrow l')_k{}^{(i)}$ ($i=1$, 2) for Pr^{3+} and $u_1'(nl\rightarrow l')_k$ for Tm^{3+} have been tabulated in a separate paper.[16]

In Figs. 1 and 2, we show two sets of perturbed wave functions for Pr^{3+}, namely $u_1'(5p\rightarrow f)_4{}^{(i)}$and $u_1'(5p\rightarrow h)_4{}^{(i)}$. We note that in all cases, u_1' is negative and does not change sign throughout the range of r. In addition, the functions $u_1'(5p\rightarrow f)_4{}^{(i)}$ have a slight edge and an inflection point near $r=0.9a_H$. The same behavior, both as regards the sign of u_1' and the inflection region, has been previously noticed[17] for the functions $u_1'(5p\rightarrow f)_2$ of Pr^{3+} and Tm^{3+} pertaining to the calculation of σ_2 (see Tables I and II of Ref. 17). The function $u_1'(5p\rightarrow f)_2$ for Tm^{3+} is shown in Fig. 3. The existence of the inflection region is related to the presence of nodes of the unperturbed function $u_0'(5p)$ in the same region of r. In this connection, we note that whereas $u_1'(5p\rightarrow f)_2$ has no zeros, the corresponding function $u_1'(5s\rightarrow d)_2$ has two nodes at small r (at $r=0.31a_H$ and $1.04a_H$ for Pr^{3+}),[17] which reflect the existence of the nodes of $u_0'(5s)$, although the number of nodes of the two functions is evidently not the same.

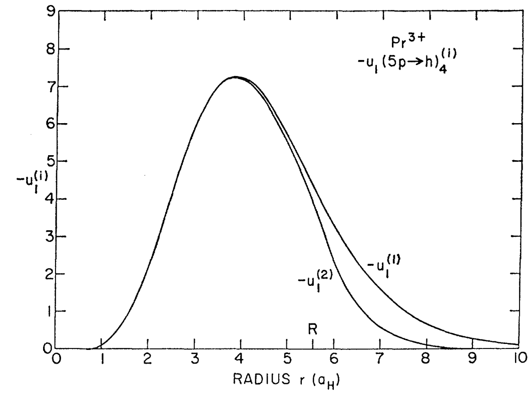

FIG. 2. The perturbed wave functions $u_1(5p\rightarrow h)_4{}^{(i)}$ for Pr^{3+} (with $k=4$) for two choices of the external perturbation ($i=1$ and 2).

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[14] E. C. Ridley, Proc. Cambridge Phil. Soc. **56**, 41 (1960).

[15] M. T. Hutchings and D. K. Ray, Proc. Phys. Soc. (London) **81**, 663 (1963). See Table 4.

[16] Tables of the perturbed wave functions $u_1'(nl\rightarrow l')_k$ obtained in the present work are given in a supplementary paper, Document No. 10047, ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C. (unpublished). A copy may be secured by citing the Document number and by remitting $6.25 for photoprints or $2.50 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[17] R. M. Sternheimer, ADI Auxiliary Publications Project, Document No. 8800, Library of Congress, Washington, D.C. (unpublished).

It should be pointed out that for all of the perturbed wave functions $u_1'(nl \to l')_k$ obtained in the present work (see Figs. 1–5), the sign of $u_1'(nl \to l')_k$ in the external region is the same as that of $u_0'(nl)$, in accordance with the fact that the corresponding P_k-type polarizability must be positive [Eqs. (24) and (35)], i.e., the product $u_0'u_1'$ is positive for large r. Thus the functions $u_1'(5s \to l')_k$ are positive for large r, whereas the functions $u_1'(5p \to l')_k$ for Pr^{3+} and Tm^{3+} are negative at large r, and in fact negative throughout the range of r for $l' \geqq 3$ (see Refs. 16 and 17, and Figs. 1–4).

Figure 2 shows that for $(5p \to h)_4$, the inflection region noted above in Figs. 1 and 3 has completely disappeared. The absence of an inflection region for the perturbations with $l' > 3$ arises from the overwhelming predominance of the centrifugal potential $l'(l'+1)/r^2$ near $r=0$ for large l'. In fact, Figs. 1, 2, and 4 show that u_1' is practically zero for r up to $\sim 1a_H$ in all cases with $l' > 3$, as a result of the $r^{l'+1}$ dependence of u_1' near $r=0$.

As an example of the results obtained for $k=6$, we show in Fig. 4 the functions $u_1'(5p \to h)_6{}^{(i)}$ for the Pr^{3+} ion.

Figures 1, 2, and 4 show clearly the influence of the cutoff at $r=R$ in the perturbing potential. For $k=4$ the cutoff effect is relatively unimportant even at large r. By way of contrast, this effect is much more pronounced for $k=6$, obviously as a result of the more drastic cutoff factor R^{13}/r^{13}, as compared to R^9/r^9 for $k=4$.

On the other hand, as will be discussed below, the effect of the change of u_1' on the $\sigma_{k,D}$ and $\sigma_{k,E}$ terms is practically negligible ($<0.5\%$ in all cases). This result arises from the fact that the $4f$ wave function v_{4f}' is completely internal to the region ($r \gtrsim 4a_H$) where the changes of u_1' take place. Thus the effect on the radial integrals of Eqs. (10) and (17a) is almost unnoticeable.

The second feature exhibited in Figs. 1, 2 and 4 is the large magnitude of the maximum of $u_1'(nl \to l')_k$ in all cases, namely of the order of 10 for $k=4$ and ~ 100 for $k=6$, when the $5p$ electrons are considered. These large values are due mainly to the presence of the factor r^k in Eq. (3), which also explains why the maxima are larger for $k=6$ than for $k=4$. For two cases with the same nl ($=5p$) and the same k, the maximum is larger for the case with the lower l' value, as a result of the smaller centrifugal term $l'(l'+1)/r^2$ which permits the function u_1' to grow to larger values [e.g., 11.7 for $(5p \to f)_4$ of Pr^{3+}, as compared to 7.3 for $(5p \to h)_4$].

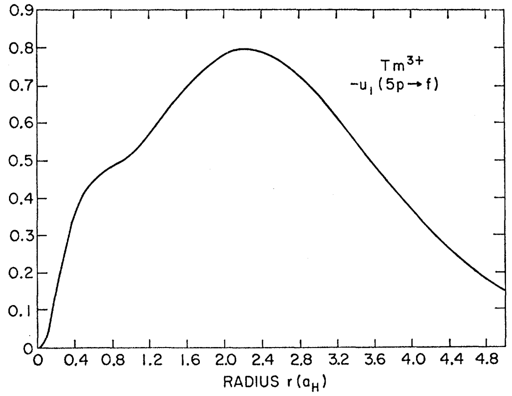

FIG. 3. The perturbed wave function $u_1(5p \to f)_2$ for Tm^{3+} ($k=2$) pertaining to the calculation of the shielding factor σ_2 and the quadrupole polarizability α_q.

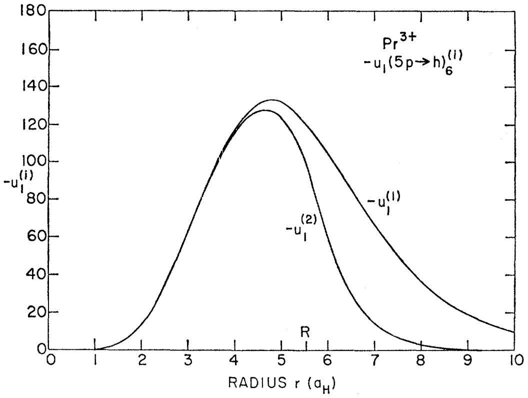

FIG. 4. The perturbed wave functions $u_1(5p \to h)_6{}^{(i)}$ for Pr^{3+} for two choices of the external perturbation.

In order to present our results on the various terms of $\sigma_{k,D}$ and $\sigma_{k,E}$ for Pr^{3+} and Tm^{3+}, we will introduce a simplifying notation in connection with Eqs. (10) and (14). This notation is similar to that previously used in Ref. 12.

Thus Eq. (10) will be rewritten as follows:

$$\sigma_{k,D} = \Gamma_D / \langle r^k \rangle_{4f}, \tag{19}$$

where Γ_D is the (normalized) electrostatic interaction energy between the perturbed density $\propto u_0'u_1'$ and the $4f$ electron density $v_{4f}'^2$. Γ_D is given by

$$\Gamma_D = C_D K_D, \tag{20}$$

where $C_D = C_{ll'}{}^{(k)}$ [see Eq. (12)] and

$$K_D \equiv \int_0^\infty v_{4f}'^2 f_k(r)\,dr = \int_0^\infty \Bigg[(1/r^{k+1}) \int_0^r u_0'u_1'r'^k dr' + r^k \int_r^\infty u_0'u_1'r'^{-k-1} dr' \Bigg] v_{4f}'^2 dr. \tag{21}$$

In the same manner as in the calculations of σ_2 in Ref. 6, we used the Hartree-Fock $4f$ wave functions v_{4f}' obtained by Freeman and Watson.[18]

For the exchange terms $\sigma_{k,E}$ [Eqs. (14)–(17)], we write

$$\sigma_{k,E} = \Gamma_E / \langle r^k \rangle_{4f}, \tag{22}$$

where

$$\Gamma_E = -C_E K_E, \tag{23}$$

with C_E given by Eq. (15) or (18), and K_E given by Eqs. (17a) and (17b). For the sake of simplicity, in

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[18] A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962); and (private communication).

TABLE III. Values of $\Gamma_D(nl\rightarrow l')_4$, $\Gamma_E(nl\rightarrow l')_4$, and the total $\Gamma(nl\rightarrow l')_4$ (in units $a_H{}^4$) for the various modes of excitation $(5s\rightarrow l')_4$ and $(5p\rightarrow l')_4$ of the Tm^{3+} ion ($k=4$). The last column of the table gives the values of the P_4 polarizability α_4 in units $a_H{}^9$.

Excitation	Γ_D	Γ_E	Γ(total)	α_4
$(5s\rightarrow g)_4$	0.0437	−0.0238	0.0199	27.43
$(5p\rightarrow f)_4$	0.2056	−0.1740	0.0316	262.94
$(5p\rightarrow h)_4$	0.0696	−0.0277	0.0419	199.45
Sum	0.3189	−0.2255	0.0934	489.82
σ_4	0.2987	−0.2112	0.0875	⋯

Eqs. (19)–(23), we have suppressed the parentheses that describe the particular term of $\sigma_{k,D}$ or $\sigma_{k,E}$ that is being considered, i.e., $(nl\rightarrow l')_k$ for $\sigma_{k,D}$ and $(nl\rightarrow l';\, n_el_e;\, L_i)_k$ for $\sigma_{k,E}$. The double integrals of Eqs. (17a) and (21) were obtained by using the CDC-6600 computer program previously described in Ref. 12 (see p. 15).

In addition to the terms of $\sigma_{k,D}$ and $\sigma_{k,E}$ ($k=4$ and 6), we have also calculated corresponding (P_4- and P_6-type) polarizabilities, which are given by

$$\alpha_k{}^{(i)}(nl\rightarrow l')=C_{ll'}{}^{(k)}\int_0^\infty u_0'(nl)\,u_1'(nl\rightarrow l')_k{}^{(i)}r^k dr \qquad (\text{in units } a_H{}^{2k+1}), \quad (24)$$

where $\alpha_k{}^{(i)}(nl\rightarrow l')$ pertains to a particular excitation $[(nl\rightarrow l')_k]$ of the $5s$ or $5p$ shell. As would be expected, since the integrand for $\alpha_k{}^{(i)}$ depends strongly on the external regions of the ion, $\alpha_k{}^{(i)}$ will be appreciably smaller for the choice $i=2$ of the Pr^{3+} wave functions ($R=5.57a_H$) than for $i=1$ ($R\rightarrow\infty$) (see Figs. 1, 2, 4). This effect is most pronounced for the $5p$ electrons, and with $k=6$.

The results obtained for $k=4$ for Pr^{3+} and Tm^{3+} are presented in Tables II and III, respectively. These tables include only the (dominant) terms arising from the excitation of the $5s$ and $5p$ shells. Table IV gives the corresponding results for the $4d$ electron of Pr^{3+}. In each case, the term of σ_4 is obtained by dividing the entry marked "Sum" by the value of $\langle r^4\rangle_{4f}$, which is $2.839a_H{}^4$ for Pr^{3+} and $1.068a_H{}^4$ for Tm^{3+}, from the wave functions of Freeman and Watson.[18] The values of α_4 are given in units of $a_H{}^9$.

The results of Tables II and III show that for both Pr and Tm, there is considerable cancellation of the direct and exchange terms of σ_4. The final total values of σ_4 are quite small, of the order of 0.1, and shielding (positive). The effect of the inner shells ($n\leq 4$) is unimportant, as shown by the very small value of $\sum_{l'}\sigma_4(4d\rightarrow l')$, namely -0.0060 (see Table IV). For the P_4 polarizability, the effect of $4d$ is completely negligible ($0.724a_H{}^9$ as compared to $\sim 1860a_H{}^9$ for $5s$ and $5p$). The effect of taking $R=5.57a_H$, although noticeable, is not important for $k=4$, since the total α_4 is reduced by only 2.7% (from 1860 to $1810a_H{}^9$).

We note that the Γ_E values listed in Tables II–IV (and also in Tables V and VI below) represent, in general, a sum over several contributions with different L_i (see Table I). Thus we have

$$\Gamma_E(nl\rightarrow l';\, n_el_e)_k \equiv \sum_{L_i}\Gamma_E(nl\rightarrow l';\, n_el_e;\, L_i)_k, \quad (25)$$

in complete analogy to Eqs. (34) and (37) of Ref. 12. Of course, in Eq. (25), $n_el_e=4f$. The individual terms $\Gamma_E(L_i)_k$ for each mode of excitation are listed in the tables of Ref. 16. These tables also give the values of Γ_D and Γ_E for both functions $u_1'(nl\rightarrow l')_k{}^{(1)}$ and $u_1(nl\rightarrow l')_k{}^{(2)}$ for Pr^{3+}, where the superscripts (1) and (2) refer to the two choices $R\rightarrow\infty$ and $R=5.57a_H$, respectively. As mentioned above, the two types of functions u_1' lead to practically the same Γ_D and $\Gamma_E(L_i)$ values, the maximum difference being 0.4%. The results listed in Tables II and V for Pr pertain to $R\rightarrow\infty$. For Tm (Tables III and VI), we have carried out the calculations only for $R\rightarrow\infty$, i.e., using Eq. (3) without modification at large r.

Tables V and VI give the corresponding results for $k=6$, i.e., the terms Γ_D and Γ_E pertaining to the parameter σ_6. The terms of σ_6 (direct, exchange, and the total σ_6) listed in the last row are obtained by dividing the corresponding entries in the preceding row (marked "Sum") by $\langle r^6\rangle_{4f}$, which equals[18] $16.02a_H{}^6$ for Pr^{3+} and $3.657a_H{}^6$ for Tm^{3+}. It is seen from Tables V and VI that both for Pr and Tm, the exchange terms of σ_6 are somewhat larger than the direct (shielding) terms. Thus one obtains a small net antishielding effect for the total σ_6, which is -0.040 for Pr^{3+} and -0.043 for Tm^{3+}.

The last two columns of Table V and the last column of Table VI give the results for the P_6 polarizability α_6 in units $a_H{}^{13}$ [see Eq. (24)]. For the present case ($k=6$), the decrease of α_6 in changing from case $i=1$ ($R\rightarrow\infty$) to case $i=2$ ($R=5.57a_H$) for Pr is more pronounced than for $k=4$, obviously on account of the larger power of r involved in Eq. (24). The decrease is from 2.807×10^5 to 2.264×10^5 $a_H{}^{13}$, or a reduction of 19.3%, as compared to 2.7% for $k=4$ (see Table II).

TABLE IV. Values of $\Gamma_D(4d\rightarrow l')_4$, $\Gamma_E(4d\rightarrow l')_4$, and the total $\Gamma(4d\rightarrow l')_4$ (in units $a_H{}^4$) for the modes of excitation of the $4d$ shell of the Pr^{3+} ion ($k=4$). The last column of the table gives the values of the P_4 polarizability α_4 in units $a_H{}^9$.

Excitation	Γ_D	Γ_E	Γ(total)	α_4
$(4d\rightarrow d)_4$	−0.00803	0.00079	−0.00724	0.2772
$(4d\rightarrow g)_4$	0.01356	−0.02847	−0.01491	0.2140
$(4d\rightarrow i)_4$	0.00995	−0.00492	0.00503	0.2324
Sum	0.01548	−0.03260	−0.01712	0.7236
σ_4	0.0055	−0.0115	−0.0060	⋯

TABLE V. Values of $\Gamma_D(nl\to l')_6$, $\Gamma_E(nl\to l')_6$, and the total $\Gamma(nl\to l')_6$ (in units $a_H{}^6$) for the various modes of excitation $(5s\to l')_6$ and $(5p\to l')_6$ of the Pr^{3+} ion ($k=6$). The last two columns of the table give the values of the P_6 polarizability $\alpha_6{}^{(i)}$ in units $a_H{}^{13}$ for two choices of the external potential (see text).

Excitation	Γ_D	Γ_E	Γ(total)	$\alpha_6{}^{(1)}$	$\alpha_6{}^{(2)}$
$(5s\to i)_6$	0.1050	−0.1584	−0.0534	9615	9062
$(5p\to h)_6$	0.4238	−1.0403	−0.6165	1.458×10^5	1.183×10^5
$(5p\to j)_6$	0.2096	−0.1809	0.0287	1.253×10^5	0.990×10^5
Sum	0.7384	−1.3796	−0.6412	2.807×10^5	2.264×10^5
σ_6	0.0461	−0.0861	−0.0400	⋯	⋯

In order to summarize the results of the present calculations, we note that from Tables II and III, the theoretical values of σ_4 are as follows:

$$\sigma_4(\mathrm{Pr}^{3+})\cong+0.091, \tag{26}$$

$$\sigma_4(\mathrm{Tm}^{3+})\cong+0.088, \tag{27}$$

where we have not included the small contribution of the $n=4$ subshells, which is of the order of 0.005 to 0.01, as shown by the results of Table IV for Pr^{3+} $(4d\to l')$.

Similarly from Tables V and VI, we obtain

$$\sigma_6(\mathrm{Pr}^{3+})\cong-0.040, \tag{28}$$

$$\sigma_6(\mathrm{Tm}^{3+})\cong-0.043. \tag{29}$$

These results for σ_4 and σ_6 are considerably smaller than the previously calculated values of σ_2 for the same ions [see Ref. 6, Eqs. (49) and (50)]. In Sec. III, it will be shown that the inner shells 4*s*, 4*p*, and 4*d* give rise to a σ_2 contribution which is $\Delta\sigma_2=+0.069$ for Pr^{3+} and $+0.061$ for Tm^{3+}. The previous results, pertaining to 5*s* and 5*p* alone, were $\sigma_2(\mathrm{Pr}^{3+})=0.603$ and $\sigma_2(\mathrm{Tm}^{3+})=0.484$.

Thus our present theoretical values of σ_2 [including $\Delta\sigma_2(4s, 4p, 4d)$] are as follows:

$$\sigma_2(\mathrm{Pr}^{3+})=0.603+0.069=0.672, \tag{30}$$

$$\sigma_2(\mathrm{Tm}^{3+})=0.484+0.061=0.545. \tag{31}$$

The final calculated values of σ_2, σ_4, and σ_6 for the two ions are presented in Table VII.

TABLE VI. Values of $\Gamma_D(nl\to l')_6$, $\Gamma_E(nl\to l')_6$, and the total $\Gamma(nl\to l')_6$ (in units $a_H{}^6$) for the various modes of excitation $(5s\to l')_6$ and $(5p\to l')_6$ of the Tm^{3+} ion ($k=6$). The last column of the table gives the values of the P_6 polarizability α_6 in units $a_H{}^{13}$.

Excitation	Γ_D	Γ_E	Γ(total)	α_6
$(5s\to i)_6$	0.0260	−0.0390	−0.0130	1430
$(5p\to h)_6$	0.1074	−0.2605	−0.1531	2.619×10^4
$(5p\to j)_6$	0.0522	−0.0441	0.0081	2.258×10^4
Sum	0.1856	−0.3436	−0.1580	5.020×10^4
σ_6	0.0508	−0.0940	−0.0432	⋯

It is of interest to compare the present values of σ_4 and σ_6 [Eqs. (26)–(29)] with those previously calculated by Burns.[2] Thus the function denoted by Burns as $-\langle F(r)\rangle$ (see Table I of the first paper in Ref. 2) corresponds to our $\Gamma_D(nl\to l')_k$. We note that for Pr^{3+} with $k=4$, whereas the terms due to $5s\to g$ and $5p\to h$ are in reasonable agreement with our determinations (e.g., 0.0992 versus 0.1240 for $5s\to g$), there is a large discrepancy for $5p\to f$ (−0.0109 as compared to our result +0.6041). In as much as the sign of $u_1'(5p\to f)_4$ (see Fig. 1) is negative throughout and therefore the same as the sign of $u_0'(5p)$ at large r, the $5p\to f$ direct term must necessarily give a shielding, i.e., a positive contribution to σ_4, in disagreement with the result of Ref. 2. Moreover, in view of the comparable magnitudes of $u_1'(5p\to f)_4$ and $u_1'(5p\to h)_4$ in the regions of their outermost maxima, one expects that the values of $\Gamma_D(5p\to f)_4$ and $\Gamma_D(5p\to h)_4$ will differ by a relatively small factor, as is indeed found in our calculations (see Table II). Thus it can be concluded that the result of Ref. 2 for $\Gamma_D(5p\to f)_4$ of Pr^{3+} is probably in error.

An important point of difference between our calculations and those of Ref. 2 concerns the fact that we have consistently included the exchange terms $\sigma_{k,E}$ [Eqs. (22) and (23)], whereas these terms were neglected by Burns.[2] However, our results (Tables II–VI) show that the exchange terms cannot by any means be neglected, since their contribution is of the same order as that of the direct terms in all cases. In fact, for $k=6$ the exchange terms predominate and lead to a small antishielding of the $Y_{6q}r^6$ part of the external field. Moreover, for $k=4$, if we were to include only the direct terms, we would obtain a shielding factor $\sigma_{4,D}$ several times larger than the final value σ_4 including the ex-

TABLE VII. Calculated values of σ_2, σ_4, and σ_6 for the Pr^{3+} and Tm^{3+} ions.

Ion	Pr^{3+}	Tm^{3+}
σ_2	0.672	0.545
σ_4	0.091	0.088
σ_6	−0.040	−0.043

TABLE VIII. Values of $\sigma_D(nl\to l')_2$, $\sigma_E(nl\to l')_2$, and the total $\sigma(nl\to l')_2$ for the various modes of excitation $(4s\to l')_2$, $(4p\to l')_2$, and $(4d\to l')_2$ of the Pr^{3+} ion ($k=2$). The last column of the table gives the values of the quadrupole polarizability α_q in units 10^{-2} Å^5.

Excitation	σ_D	σ_E	σ(total)	$10^2\alpha_q$/Å^5
$(4s\to d)_2$	0.0361	−0.0096	0.0265	0.192
$(4p\to f)_2$	0.0493	−0.0134	0.0359	0.323
$(4d\to g)_2$	0.0611	−0.0155	0.0456	0.711
$(4p\to p)_2$	−0.0018	−0.0005	−0.0023	0.080
$(4d\to d)_2$	−0.0075	−0.0006	−0.0081	0.253
$(4d\to s)_2$	−0.0375	0.0084	−0.0291	0.222
Total	0.0997	−0.0312	0.0685	1.781

change terms (e.g., 0.326 as compared to 0.091 for Pr^{3+}; see Table II).

As concerns the comparison with experiment, it has been pointed out by Burns (second paper in Ref. 2, pp. 384–387) that the calculated values $(1-\sigma_k)\langle r^k\rangle_{4f}A_k{}^q$ can be brought into reasonable agreement with the experimental crystal-field splittings $V_k{}^q$, provided that the extended nature of the neighboring negative ions (e.g., Cl^- or Br^-) is taken into account. If this is done, one obtains fairly good agreement with the magnitudes of $V_4{}^0$ and $V_6{}^0$, and their approximate constancy in going through the rare-earth series (from Pr^{3+} to Er^{3+}). In these estimates, Burns assumed that σ_4 and σ_6 are small, of the order of a few percent. In the present work, we have confirmed the fact that these parameters are of order 0 to 0.1, although, as pointed out above, the smallness of σ_4 arises mainly from the near cancellation of the direct and exchange terms, which was not considered in Ref. 2.

III. CALCULATIONS OF $\Delta\sigma_2(4s, 4p, 4d)$

As mentioned above, in addition to the work on σ_4 and σ_6, we have also carried out calculations pertaining to the shielding factor σ_2 which acts on the P_2r^2 part of the crystal potential [see Eq. (1)]. Values of $\sigma_2(\mathrm{Pr}^{3+})$ and $\sigma_2(\mathrm{Tm}^{3+})$ have been previously published in Ref. 6. However, these results were based only on the $5s\to d$, $5p\to p$, and $5p\to f$ perturbations, and thus did not include the effect of the inner ($n\leq 4$) shells of the ions. Since the σ_2 terms decrease rapidly with decreasing principal quantum number n, it is expected that we will have to consider only the $n=4$ subshells, i.e., the effect of the $n\leq 3$ shells is probably negligible. This conclusion is indeed borne out by the results of the present calculations for $n=4$, which show that the $n=4$ term is already quite small compared to the $n=5$ term, the ratio of the two terms being $\sim$0.12.

The six perturbations involved for $4s$, $4p$, and $4d$ are the following: $4s\to d$, $4p\to f$, $4d\to g$, $4p\to p$, $4d\to d$, and $4d\to s$.

We used again the wave functions of Ridley[14] for the core electrons ($4s$, $4p$, $4d$) and the $4f$ Hartree-Fock wave function of Freeman and Watson.[18] For $4s\to d$, $4p\to f$, and $4d\to g$, the solution of Eq. (3) could be directly obtained from the CDC-6600 computer program, which has been used in Ref. 12 and in the present calculations of σ_4 and σ_6. For the remaining three types of perturbation, namely, $4p\to p$, $4d\to d$, and $4d\to s$, it was necessary to carry out an outward integration (starting at $r=0$) on a desk computer, and to match the resulting functions with the results of several inward integrations carried out on the Brookhaven IBM-7094 using an older machine program, previously employed in the calculation of the ionic antishielding factors[19] $\gamma_\infty(nl\to l')$.

The resulting functions $u_1'(nl\to l')_2$ for both Pr^{3+} and Tm^{3+} are presented in the tables of Ref. 16. The integrals K_D and K_E of Eqs. (17a) and (21) were obtained by means of the computer program mentioned above (in Sec. II). The appropriate values of C_D and $C_E(L_i)$ are listed in Ref. 12, Table II, except for $nd\to g$, where the values are given in Table I of the present paper. The individual terms $\Gamma_E(L_i)$ are listed in Ref. 16. Upon combining these terms, we obtain the total $\Gamma_E(nl\to l')_2$ [see Eq. (25)].

In Tables VIII and IX, we give the individual terms $\sigma_D(nl\to l')_2$ and $\sigma_E(nl\to l')_2$ of σ_2, which are defined as follows [see Eqs. (19) and (22)]:

$$\sigma_D(nl\to l')_2=\Gamma_D(nl\to l')_2/\langle r^2\rangle_{4f}, \tag{32}$$

$$\sigma_E(nl\to l')_2=\Gamma_E(nl\to l')_2/\langle r^2\rangle_{4f}. \tag{33}$$

The value of $<r^2\rangle_{4f}$ is $1.088a_H{}^2$ for Pr^{3+} and $0.646a_H{}^2$ for Tm^{3+}. The next-to-last column of the tables gives the total (direct + exchange) terms $\sigma(nl\to l')_2$, i.e.,

$$\sigma(nl\to l')_2\equiv\sigma_D(nl\to l')_2+\sigma_E(nl\to l')_2. \tag{34}$$

We note that the exchange terms σ_E have been previously denoted by ζ_2 for the external ($5s$ and $5p$) shells (see Tables III and IV of Ref. 6.).

It can be seen from Tables VIII and IX that both for Pr^{3+} and Tm^{3+}, the $4s\to d$, $4p\to f$, and $4d\to g$ modes provide a weak shielding which is appreciably larger than the small antishielding produced by the other three excitation modes. Thus the resulting total $\Delta\sigma_2$ (bottom row) is positive (shielding) and small, namely $+0.069$ for Pr^{3+} and $+0.061$ for Tm^{3+}. These results

TABLE IX. Values of $\sigma_D(nl\to l')_2$, $\sigma_E(nl\to l')_2$, and the total $\sigma(nl\to l')_2$ for the various modes of excitation $(4s\to l')_2$, $(4p\to l')_2$, and $(4d\to l')_2$ of the Tm^{3+} ion ($k=2$). The last column of the table gives the values of the quadrupole polarizability α_q in units 10^{-2} Å^5.

Excitation	σ_D	σ_E	σ(total)	$10^2\alpha_q$/Å^5
$(4s\to d)_2$	0.0395	−0.0104	0.0291	0.063
$(4p\to f)_2$	0.0458	−0.0124	0.0334	0.092
$(4d\to g)_2$	0.0498	−0.0125	0.0373	0.171
$(4p\to p)_2$	−0.0026	0.0002	−0.0024	0.024
$(4d\to d)_2$	−0.0078	0.0016	−0.0062	0.064
$(4d\to s)_2$	−0.0395	0.0094	−0.0301	0.039
Total	0.0852	−0.0241	0.0611	0.453

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[19] H. M. Foley, R. M. Sternheimer, and D. Tycko, Phys. Rev. **93**, 734 (1954). R. M. Sternheimer, Phys. Rev. **130**, 1423 (1963); **132**, 1637 (1963); **159**, 266 (1967).

have been used above in Eqs. (30) and (31) to obtain the best theoretical values of σ_2 for the two ions.

The last column of Tables VIII and IX lists the contributions to the quadrupole polarizability α_q $(=\alpha_2)$ arising from the $n=4$ subshells. α_q is given in units Å^5 rather than $a_H{}^5$, in order to make possible a direct comparison with the results of Ref. 6 (Tables I and II) for the 5*s* and 5*p* terms.

In view of Eq. (24), $\alpha_q/\text{Å}^5$ is given by

$$(\alpha_q/\text{Å}^5)=0.0415C_{ll'}{}^{(2)}\int_0^\infty u_0'(nl)u_1'(nl\rightarrow l')_2 r^2 dr, \tag{35}$$

where $0.0415=(a_H/\text{Å})^5=(0.5292)^5$, and $\alpha_q \equiv \alpha_q(nl\rightarrow l')$.

For Pr^{3+}, the total $\alpha_q(4s, 4p, 4d)=0.0178\,\text{Å}^5$ can be compared with the term due to 5*s* and 5*p*, namely $\alpha_q(5s, 5p)=1.713\,\text{Å}^5$. For Tm^{3+}, we find $\alpha_q(4s, 4p, 4d)=0.00453\,\text{Å}^5$, as compared to $\alpha_q(5s, 5p)=0.724\,\text{Å}^5$. Thus the inner shells contribute $\lesssim 1\%$ of the total α_q. This was to be expected from our previous results on dipole and quadrupole polarizabilities.[20]

In connection with Tm^{3+}, we have not considered the effect of the shielding of 4*f* by the other 4*f* electrons present in the same subshell. For Tm^{3+}, there are altogether twelve 4*f* electrons, which is equivalent to two 4*f* electron holes. Thus, detailed questions of the coupling of the two holes (*jj*, *ls*, or intermediate coupling) will enter into the calculations. We note that nonlinear shielding within the 4*f* shell has been considered by Freeman and Watson.[21] In any case, we still expect that any effects within the 4*f* shell will be appreciably smaller than the $5s+5p$ terms calculated in Ref. 6, which probably give rise to the dominant contribution to $\sigma_2(\text{Tm}^{3+})$.

We note that the direct terms of $\Delta\sigma_2(4s, 4p, 4d)$ for Pr^{3+} and Tm^{3+} have been previously calculated by Ghatikar *et al.*[22] Their results are in reasonable agreement with the present values of $\sigma_D(nl\rightarrow l')_2$, although they are systematically lower [e.g., 0.025 as compared to 0.0361 for $4s\rightarrow d$ of Pr^{3+}; 0.038 as compared to 0.0458 for $4p\rightarrow f$ of Tm^{3+}]. A similar systematic trend is also observed for the values of Ref. 22 pertaining to the 5*s* and 5*p* shells (e.g., 0.505 as compared to our value 0.576 for $5p\rightarrow f$ of Pr^{3+}; see Ref. 6, Table I). We believe that this difference arises mainly from the use of Ridley's 4*f* wave function in Ref. 22. Since this function is appreciably more external than the Hartree-Fock function of Ref. 18, it will give a larger $\langle r^2\rangle_{4f}$, thus leading to smaller values of the $\sigma_D(nl\rightarrow l')_2$ terms [see Eq. (32)].

It should be pointed out that Ghatikar *et al.*[22] did not include the exchange terms $\sigma_E(nl\rightarrow l')_2$ for any of their calculated perturbations. As is seen from the present work and from Ref. 6, these terms give rise to a small net antishielding in all cases, thus reducing the values of σ_2. Hence the two effects (use of Ridley's $\langle r^2\rangle_{4f}$ and neglect of exchange terms) tend to compensate each other to some extent, and as a result our final values of $\sigma_2(\text{Pr}^{3+})=0.672$ and $\sigma_2(\text{Tm}^{3+})=0.545$ [Eqs. (30) and (31)] differ only by small amounts from those of Ref. 22, namely 0.70 for Pr^{3+} and 0.59 for Tm^{3+}. Both sets of values are also in reasonable agreement with the previous theoretical estimates of Lenander and Wong[3] and of Ray.[3] Moreover, the above results are in general agreement with the order of magnitude of the experimental values[1] and their trend toward a decrease of σ_2 with increasing *Z* in going through the rare-earth region, i.e., from Pr to Tm.

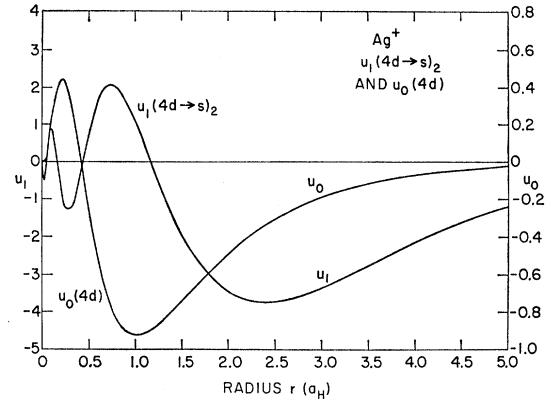

FIG. 5. The perturbed wave function $u_1(4d\rightarrow s)_2$ and the 4*d* function $u_0(4d)$ for Ag$^+$. The left-hand ordinate scale pertains to u_1; the right-hand scale pertains to u_0.

In connection with the perturbations $u_1'(4d\rightarrow s)_2$ for Pr^{3+} and Tm^{3+} which have been obtained in the present work (see Tables VIII and IX), it is of interest to consider the corresponding wave function $u_1'(4d\rightarrow s)_2$ for the Ag$^+$ ion. This function, which was obtained some time ago (in 1962), is shown in Fig. 5, together with the zero-order Hartree-Fock wave function[23] $u_0'(4d)$ used in the calculations. It is seen that $u_1'(4d\rightarrow s)_2$ has altogether four nodes, the same number as a 5*s* function. At large *r*, u_0' and u_1' have the same sign, resulting in a positive quadrupole polarizability α_q [Eq. (35)]. One finds that $\alpha_q(4d\rightarrow s)$ is very considerably larger for Ag$^+$ than for Pr^{3+} or Tm^{3+}, as would be expected from the external character of the Ag$^+$ $u_1'(4d\rightarrow s)$ function and from its large magnitude in the external region[16] (maximum $=-3.74$ at $r=2.4a_H$ for Ag$^+$, as compared to -0.095 at $r=1.4a_H$ for Pr^{3+} and -0.039 at $r=1.15a_H$ for Tm^{3+}). Thus the value of $\alpha_q(4d\rightarrow s)$ is 1.021 Å^5 for Ag$^+$, as compared to $2.22\times10^{-3}\,\text{Å}^5$ for Pr^{3+} and $0.39\times10^{-3}\,\text{Å}^5$ for Tm^{3+}.

In principle, the function $u_1'(4d\rightarrow s)$ could be employed to obtain the contribution $\gamma_\infty(4d\rightarrow s)$ to the quadrupole shielding (or antishielding) factor by means of the equation

$$\gamma_\infty(4d\rightarrow s)=(8/5)\int_0^\infty u_0'(4d)u_1'(4d\rightarrow s)r^{-3}dr. \tag{36}$$

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[20] R. M. Sternheimer, Phys. Rev. **96**, 951 (1954); **107**, 1565 (1957); **115**, 1198 (1959); **127**, 1220 (1962).

[21] R. E. Watson and A. J. Freeman, Phys. Rev. **133**, A1571 (1964); **139**, A1606 (1965).

[22] M. N. Ghatikar, A. K. Raychaudhuri, and D. K. Ray, Proc. Phys. Soc. (London) **86**, 1235 (1965).

[23] B. H. Worsley, Proc. Roy. Soc. (London) **A247**, 390 (1958).

However, in actual practice, the value of $\gamma_\infty(4d\to s)$ given by Eq. (36) is not reliable, on account of the large variations and changes of sign (3 nodes) of $u_1'(4d\to s)$ in the region near $r=0$ which is the most heavily weighted (factor r^{-3} in the integrand). Thus one must use the alternative expression

$$\gamma_\infty(4d\to s)=(8/5)\int_0^\infty u_0'(4d)v_1'(4d\to s)r^2dr, \qquad (37)$$

involving the function $v_1'(4d\to s)$ pertaining to the $-QP_2(\cos\theta)/r^3$ potential produced by the nuclear quadrupole moment Q. The appropriate equation which determines $v_1'(4d\to s)$ is

$$[-(d^2/dr^2)+V_0-E_0]v_1'(4d\to s)=u_0'(4d)/r^3. \qquad (38)$$

This equation was previously[24] solved for the case of Ag$^+$, with the result that $\gamma_\infty(4d\to s)=+1.211$, i.e., a relatively small shielding effect, as compared to the total antishielding factor[6,19] $\gamma_\infty(\mathrm{Ag}^+)=-34.9$.

It may be remarked that the inability of an equation of the type of (36) to give a reliable value of $\gamma_\infty(nl\to l')$ has also been previously noticed[17] for the perturbation $u_1'(5s\to d)$ for Pr^{3+}. In this case, the rapid variation and the large number of nodes of $u_0'(5s)$ near $r=0$ coupled with the weighting factor r^{-3} in the integrand make it impossible to obtain a reliable value of $\gamma_\infty(5s\to d)$ by means of $u_1'(5s\to d)$. On the other hand, the corresponding integral in terms of $v_1'(5s\to d)$ [cf. Eq. (37)] does not suffer from these defects and yields the expected small shielding, i.e., $\gamma_\infty(5s\to d)=+0.58$ (see Ref. 17, pp. 3–4).

IV. DERIVATION OF THE ANGULAR COEFFICIENTS C_D AND C_E

In this section, we shall derive Eqs. (13) and (18) for the angular coefficients C_D and C_E for the case where we have a single electron outside closed shells. We denote the quantum numbers of this electron by l_em_e. The determinantal wave function $\Psi_{l_em_e}{}^{(0)}$ satisfies

$$\mathcal{H}\Psi_{l_em_e}{}^{(0)}=\mathcal{E}^{(0)}\Psi_{l_em_e}{}^{(0)}, \qquad (39)$$

where

$$\mathcal{H}_0=\sum_{i=1}^{N}(p_i^2/2m)+\sum_{i=1}^{N}V_0(r_i). \qquad (40)$$

$\Psi_{l_em_e}{}^{(0)}$ is a single determinant with electron l_em_e outside closed shells, and V_0 is the central field in which the electrons are assumed to move. The ion is subject to a perturbation

$$\mathcal{H}_1=\tfrac{1}{2}a\sum_{i=1}^{N}r_i{}^k[Y_{kq}(\hat{r}_i)+Y_{kq}{}^*(\hat{r}_i)], \qquad (41)$$

as a result of the external crystalline field acting on the ion. In Eq. (41), a denotes the constant $A_k{}^q$ of Secs. I and II, pertaining to a single term (k,q) of the potential V_{cr} [Eq. (1)]. We must, in calculating matrix elements of $\mathcal{H}_1$, take into account the fact that $\mathcal{H}_0$ is not the exact Hamiltonian, in that we have neglected the Coulomb interaction between electrons. This perturbation is (in Rydberg units)

$$V_c=\sum_{i>j}^{N}(2/r_{ij})-\sum_{i=1}^{N}(2Z/r_i)-\sum_{i=1}^{N}V_0(r_i). \qquad (42)$$

We consider the effect of $\mathcal{H}_1$ on the wave function. We have

$$(\mathcal{H}_0+\mathcal{H}_1)\Psi=\mathcal{E}\Psi, \qquad (43)$$

or, upon writing

$$\Psi=\Psi_{l_em_e}{}^{(0)}+\Psi_{l_em_e}{}^{(1)}, \qquad (44)$$

$$\mathcal{E}=\mathcal{E}^{(0)}+\mathcal{E}^{(1)}, \qquad (45)$$

we obtain

$$(\mathcal{H}_0-\mathcal{E}^{(0)})\Psi_{l_em_e}{}^{(1)}=(\mathcal{E}^{(1)}-\mathcal{H}_1)\Psi_{l_em_e}{}^{(0)}. \qquad (46)$$

The first-order perturbed wave functions $\Psi_{l_em_e}{}^{(1)}$ may be written

$$\Psi_{l_em_e}{}^{(1)}=\sum_{nlm,l'm'}\Psi^{(1)}(nlm\to l'm'), \qquad (47)$$

where $\Psi^{(1)}(nlm\to l'm')$ is a determinant identical to $\Psi_{l_em_e}{}^{(0)}$, except that the single-electron wave function $\psi_0(nlm)$ is replaced by the perturbed function

$$\psi_1(nlm\to l'm')_k=(1/r)\,du_1'(nl\to l')_kY_{l'm'}, \qquad (48)$$

where $u_1'(nl\to l')_k$ satisfies Eq. (3), and the constant d is given by

$$\begin{aligned}d&=\tfrac{1}{2}a\int Y_{lm}(Y_{kq}+Y_{kq}{}^*)Y_{l'm'}{}^*d\hat{r}\\&=\tfrac{1}{2}a(-1)^{m'}\left[\frac{(2l+1)(2l'+1)(2k+1)}{4\pi}\right]^{1/2}\begin{pmatrix}l'&k&l\\0&0&0\end{pmatrix}\\&\quad\times\left[\begin{pmatrix}l'&k&l\\-m'&q&m\end{pmatrix}+(-1)^q\begin{pmatrix}l'&k&l\\-m'&-q&m\end{pmatrix}\right],\end{aligned} \qquad (49)$$

where we have used Eq. (4.6.3) of Edmonds's book[25] on angular momentum. (We shall make constant use of this expression in what follows.)

We wish to calculate the matrix elements of the perturbation $\mathcal{H}_1+V_c$ to first order in $\mathcal{H}_1$. We have

$$\begin{aligned}\langle\Psi_{l_em_e'}\,|\,\mathcal{H}_1+V_c\,|\,\Psi_{l_em_e}\rangle&\approx\langle\Psi_{l_em_e'}{}^{(0)}\,|\,\mathcal{H}_1\,|\,\Psi_{l_em_e}{}^{(0)}\rangle\\&\quad+\langle\Psi_{l_em_e'}{}^{(1)}\,|\,V_c\,|\,\Psi_{l_em_e}{}^{(0)}\rangle+\langle\Psi_{l_em_e'}{}^{(0)}\,|\,V_c\,|\,\Psi_{l_em_e}{}^{(1)}\rangle.\end{aligned} \qquad (50)$$

The first term gives the unscreened contribution of the crystalline field perturbation, while the second and third give the effects of screening. The matrix elements of the operators can be evaluated using the prescriptions

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[24] R. M. Sternheimer, Phys. Rev. **159**, 266 (1967). See Sec. III.

[25] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, N.J., 1957).

of Ref. 8, p. 173, for the handling of determinants. We have

$$\begin{aligned}\langle \Psi_{l_e m_e'}{}^{(0)} \mid \mathcal{H}_1 \mid \Psi_{l_e m_e}{}^{(0)} \rangle &= \tfrac{1}{2}a \int \psi_0{}^*(l_e m_e'; \mathbf{r}) r^k (Y_{kq}+Y_{kq}{}^*) \psi_0(l_e m_e; \mathbf{r})\, d\mathbf{r} \\ &= \tfrac{1}{2}a \langle r^k \rangle (-1)^{m_e'} \left[\frac{(2l_e+1)^2(2k+1)}{4\pi}\right]^{1/2} \begin{pmatrix} l_e & k & l_e \\ 0 & 0 & 0 \end{pmatrix} \\ &\quad \times \left[\begin{pmatrix} l_e & k & l_e \\ -m_e' & q & m_e \end{pmatrix} + (-1)^q \begin{pmatrix} l_e & k & l_e \\ -m_e' & -q & m_e \end{pmatrix}\right]. \qquad (51)\end{aligned}$$

In evaluating the matrix elements of V_c, we need consider only the two-electron part $(2/r_{ij})$ of the perturbation. We find a sum of direct and exchange terms:

$$\begin{aligned}&\langle \Psi_{l_e m_e'}{}^{(1)} \mid \sum_{i>j}^{N} (2/r_{ij}) \mid \Psi_{l_e m_e}{}^{(0)} \rangle \\ &\quad = 2 \sum_{nlm,l'm'} \iint \psi_1{}^*(nlm \to l'm'; \mathbf{r}_1) \psi_0{}^*(l_e m_e'; \mathbf{r}_2) (2/r_{12}) \psi_0(nlm; \mathbf{r}_1) \psi_0(l_e m_e; \mathbf{r}_2)\, d\mathbf{r}_1 d\mathbf{r}_2 \\ &\quad - \sum_{nlm,l'm'} \iint \psi_1{}^*(nlm \to l'm'; \mathbf{r}_1) \psi_0{}^*(l_e m_e'; \mathbf{r}_2) (2/r_{12}) \psi_0(nlm; \mathbf{r}_2) \psi_0(l_e m_e; \mathbf{r}_1)\, d\mathbf{r}_1 d\mathbf{r}_2. \qquad (52)\end{aligned}$$

The factor 2 in the direct terms results from a summation over spins. Such a factor does not occur for the exchange terms, which are present only between electrons of the same spin. We also find for the third term of Eq. (50)

$$\begin{aligned}\langle \Psi_{l_e m_e'}{}^{(0)} \mid V_c \mid \Psi_{l_e m_e}{}^{(1)} \rangle &= 2 \sum_{nlm,l'm'} \iint \psi_0{}^*(l_e m_e'; \mathbf{r}_1) \psi_0{}^*(nlm; \mathbf{r}_2) (2/r_{12}) \psi_0(l_e m_e; \mathbf{r}_1) \psi_1(nlm \to l'm'; \mathbf{r}_2)\, d\mathbf{r}_1 d\mathbf{r}_2 \\ &\quad - \sum_{nlm,l'm'} \iint \psi_0{}^*(l_e m_e'; \mathbf{r}_1) \psi_0{}^*(nlm; \mathbf{r}_2) (2/r_{12}) \psi_0(l_e m_e; \mathbf{r}_2) \psi_1(nlm \to l'm'; \mathbf{r}_1)\, d\mathbf{r}_1 d\mathbf{r}_2. \qquad (53)\end{aligned}$$

Using the expansion

$$2/r_{12} = 8\pi \sum_{k'q'} \left(\frac{1}{2k'+1}\right) \left(\frac{r_<{}^{k'}}{r_>{}^{k'+1}}\right) Y_{k'q'}{}^*(1)\, Y_{kq}(2), \qquad (54)$$

and Eqs. (48) and (49), we find for the direct term of Eq. (52),

$$\begin{aligned}&16\pi \sum_{nlm,l'm',k'q'} d \left[\iint u_1{}'(nl \to l'; r_1) u_0{}'^2(n_e l_e; r_2) u_0{}'(nl; r_1) \left(\frac{r_<{}^{k'}}{r_>{}^{k'+1}}\right) dr_1 dr_2\right] \\ &\qquad \times (2k'+1)^{-1} \left[\int Y_{l'm'}{}^* Y_{k'q'}{}^* Y_{lm} d\Omega\right] \left[\int Y_{l_e m_e'}{}^* Y_{k'q'} Y_{l_e m_e} d\Omega\right], \qquad (55)\end{aligned}$$

which, upon substituting the value of d and evaluating the integrals over spherical harmonics in terms of 3-j symbols, becomes

$$\begin{aligned}&16\pi \sum_{nlm,l'm',k'q'} \tfrac{1}{2}a (-1)^{m_e'+q'} \frac{(2l+1)(2l'+1)(2l_e+1)(2k+1)^{1/2}}{(4\pi)^{3/2}} \\ &\qquad \times \left[\iint u_1{}'(nl \to l'; r_1) u_0{}'^2(n_e l_e; r_2) u_0{}'(nl; r_1) \left(\frac{r_<{}^{k'}}{r_>{}^{k'+1}}\right) dr_1 dr_2\right] \\ &\qquad \times \begin{pmatrix} l' & k' & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_e & k' & l_e \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & k & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & k' & l \\ -m' & -q' & m \end{pmatrix} \begin{pmatrix} l_e & k' & l_e \\ -m_e' & q' & m_e \end{pmatrix} \\ &\qquad \times \left[\begin{pmatrix} l' & k & l \\ -m' & q & m \end{pmatrix} + (-1)^q \begin{pmatrix} l' & k & l \\ -m' & -q & m \end{pmatrix}\right]. \qquad (56)\end{aligned}$$

Upon using the result [Ref. 9, Eq. (1.14)],

$$\sum_{mm'}\begin{pmatrix} l' & k' & l \\ -m' & -q' & m \end{pmatrix}\begin{pmatrix} l' & k & l \\ -m' & q & m \end{pmatrix}=\frac{\delta_{q',-q}\delta_{k'k}}{2k+1}, \tag{57}$$

we find for the direct term

$$\begin{aligned}&\tfrac{1}{2}a\langle r^k\rangle(-1)^{m_e}\left[\frac{(2l_e+1)^2(2k+1)}{4\pi}\right]^{1/2}\begin{pmatrix} l_e & k & l_e \\ 0 & 0 & 0 \end{pmatrix}\left[\begin{pmatrix} l_e & k & l_e \\ -m_e' & q & m_e \end{pmatrix}+(-1)^q\begin{pmatrix} l_e & k & l_e \\ -m_e' & -q & m_e \end{pmatrix}\right]\\ &\qquad\times 4\sum_{nll'}\begin{pmatrix} l' & k & l \\ 0 & 0 & 0 \end{pmatrix}^2\left[\frac{(2l+1)(2l'+1)}{2k+1}\right]\langle r^k\rangle^{-1}\\ &\qquad\times\iint u_1'(nl\rightarrow l';r_1)u_0'^2(n_el_e;r_2)u_0'(nl;r_1)(r_<^{k'}/r_>^{k'+1})dr_1dr_2. \end{aligned}\tag{58}$$

An identical contribution is found for the direct terms of (53), so that the factor of 4 becomes 8. We note that this result is proportional to the matrix element of the unscreened term.

The exchange terms are evaluated similarly. We find for the second term of (52)

$$\begin{aligned}&-8\pi\sum_{nlm,l'm',k'q'}d\left[\iint u_1'(nl\rightarrow l';r_1)u_0'(n_el_e;r_1)u_0'(nl;r_2)u_0'(n_el_e;r_2)(r_<^{k'}/r_>^{k'+1})dr_1dr_2\right]\\ &\qquad\times(2k'+1)^{-1}\left[\int Y_{l'm'}{}^*Y_{k'q'}{}^*Y_{l_em_e}d\Omega\right]\left[Y_{l_em_e'}{}^*Y_{k'q'}Y_{lm}d\Omega\right]\\ &=-8\pi\sum_{nlm,l'm',k'q'}\tfrac{1}{2}a(-1)^{m_e'+q'}K_E(nl\rightarrow l';k')\frac{(2l+1)(2l'+1)(2l_e+1)}{(4\pi)^{3/2}}(2k+1)^{1/2}\\ &\qquad\times\begin{pmatrix} l' & k & l \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l' & k' & l_e \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l_e & k' & l \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l' & k' & l_e \\ -m' & -q' & m_e \end{pmatrix}\begin{pmatrix} l_e & k' & l \\ -m_e' & q' & m \end{pmatrix}\\ &\qquad\times\left[\begin{pmatrix} l' & k & l \\ -m' & q & m \end{pmatrix}+(-1)^q\begin{pmatrix} l' & k & l \\ -m' & -q & m \end{pmatrix}\right], \end{aligned}\tag{59}$$

where K_E is defined by Eq. (17a). We can perform the summation over m, m', and q' by using Eq. (2.20) of Ref. 9. We thus find for the exchange terms of (52)

$$\begin{aligned}&\tfrac{1}{2}a\langle r^k\rangle(-1)^{m_e}\left[\frac{(2l_e+1)^2(2k+1)}{4\pi}\right]^{1/2}\begin{pmatrix} l_e & k & l_e \\ 0 & 0 & 0 \end{pmatrix}\left[\begin{pmatrix} l_e & k & l_e \\ -m_e' & q & m_e \end{pmatrix}+(-1)^q\begin{pmatrix} l_e & k & l_e \\ -m_e' & -q & m_e \end{pmatrix}\right]\\ &\qquad\times(-2)\sum_{nll',k'}(-1)^{l+l'+k'}\frac{K_E}{\langle r^k\rangle}(2l+1)(2l'+1)\\ &\qquad\times\begin{pmatrix} l' & k & l \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l' & k' & l_e \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l_e & k' & l \\ 0 & 0 & 0 \end{pmatrix}\begin{Bmatrix} l_e & k & l_e \\ l' & k' & l \end{Bmatrix}\Big/\begin{pmatrix} l_c & k & l_e \\ 0 & 0 & 0 \end{pmatrix}. \end{aligned}\tag{60}$$

A similar contribution appears in Eq. (53).

Upon combining these results and using the symmetry properties of the 3-j and 6-j symbols, we find that the effect of the perturbation of the wave function by $\mathcal{H}_1$ results in a screening of the crystalline field, and that we may replace $\mathcal{H}_1$ by

$$\begin{aligned}\mathcal{H}_1\rightarrow\tfrac{1}{2}ar^k(Y_{kq}+Y_{kq}{}^*)&\left\{1+8\sum_{nll'}\begin{pmatrix} l' & k & l \\ 0 & 0 & 0 \end{pmatrix}^2\left[\frac{(2l+1)(2l'+1)}{2k+1}\right]\langle r^k\rangle^{-1}\int_0^\infty v_{4f}'^2f_kdr\right.\\ &\left.-4\sum_{nll'}(-1)^{l+l'+k'}\frac{K_E}{\langle r^k\rangle}(2l+1)(2l'+1)\begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l & k' & l_e \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l' & k' & l_e \\ 0 & 0 & 0 \end{pmatrix}\begin{Bmatrix} k & l_e & l_e \\ k' & l & l' \end{Bmatrix}\Big/\begin{pmatrix} l_e & k & l_e \\ 0 & 0 & 0 \end{pmatrix}\right\}. \end{aligned}\tag{61}$$

These are the angular coefficients mentioned in Sec. II. Note that they depend only on k and not on q, as we might have anticipated on symmetry grounds. The angular momentum k' is identical with the multipolarity L of Sec. II. Furthermore, we remark that in all practical cases considered here, we have $k=$even, and hence in the expression for C_E, $(-1)^{l+l'+k'}=(-1)^{k'}=(-1)^L$, as given in Eq. (18).

V. SUMMARY AND DISCUSSION

The main purpose of the present paper has been to obtain values of the rare-earth shielding (or antishielding) factors σ_4 and σ_6 with an accuracy comparable to that of the previous calculations of σ_2 of Ref. 6. In the same manner as in our previous work,[6,7,13,19] we have integrated directly the inhomogeneous equation satisfied by the various radial perturbed wave functions $u_1'(nl\rightarrow l')_k$, which describe the excitation of the $5s$ and $5p$ electrons by the crystal field. The calculations of the $u_1'(nl\rightarrow l')_k$ were performed on the Brookhaven CDC-6600 computer. In view of the large angular momenta l' involved for $k=4$, and especially for $k=6$, the calculations would have been prohibitively long on a desk computer, except for the consideration of a few special cases, e.g., a single mode of excitation for each k value for one of the ions. Instead, we were able to carry through the entire calculation of σ_4 and σ_6 for both Pr^{3+} and Tm^{3+}, involving a total of 21 perturbed wave functions, in a reasonable amount of time, i.e., about three months. Some of the resulting wave functions are shown in Figs. 1–4.

Concerning σ_4 and σ_6, it was found that both of these quantities are small (of the order of 0.1), which is in contrast to the large values of σ_2 which have been previously determined both experimentally[1] and theoretically.[2–4] Moreover, it was found that the exchange terms $\sigma_{k,E}$ of σ_k play a progressively more important role with increasing k.

Thus taking the case of Pr^{3+} as an example, we have from Ref. 6 [Eq. (49)] and from Table II of the present paper

$$\sigma_{2,D}=0.678+0.100=0.778, \tag{62}$$

$$\sigma_{2,E}=-0.075-0.031=-0.106, \tag{63}$$

so that the ratio

$$\xi_2\equiv-\sigma_{2,E}/\sigma_{2,D}=0.106/0.778=0.136. \tag{64}$$

In a similar fashion, from Tables II and V, we find for the corresponding ratios ξ_k for $k=4$ and $k=6$ (for Pr^{3+})

$$\xi_4\equiv-\sigma_{4,E}/\sigma_{4,D}=0.236/0.326=0.724, \tag{65}$$

$$\xi_6\equiv-\sigma_{6,E}/\sigma_{6,D}=0.086/0.046=1.87. \tag{66}$$

The increase of ξ_k with k demonstrates the necessity of including the exchange terms of σ_k for $k=4$ and $k=6$, as has been discussed extensively in Sec. II.

Our final results for σ_4 and σ_6 agree qualitatively with the previous conclusions of Burns,[2] namely that these shielding factors are small, i.e., of the order of 0.1 or less. Thus the presence of σ_4 and σ_6 in the theoretical expressions for the crystal-field parameters, namely $(1-\sigma_k)A_k{}^q\langle r^k\rangle_{4f}$ will not materially affect the comparison with experiment. As shown by Burns,[2] the theoretical values are too small, unless the extended nature of the neighboring (negative) ions is taken into account in the calculation of $A_4{}^0$, $A_6{}^0$, and $A_6{}^6$.

In addition to the calculations of σ_4 and σ_6, we have also made an improvement of the earlier determinations[6] of σ_2 by evaluating the contributions of the $4s$, $4p$, and $4d$ subshells for both Pr^{3+} and Tm^{3+}. This work involves a total of 12 perturbed wave functions (see Tables VIII and IX). The resulting change $\Delta\sigma_2(4s,\ 4p,\ 4d)$ of σ_2 amounts to about 12% of the previously determined $(5s+5p)$ dominant term.

The resulting total σ_2 values, namely 0.67 for Pr^{3+} and 0.55 for Tm^{3+} [see Eqs. (30) and (31)] are in reasonable agreement with experiment, although both seem to be somewhat low. Thus, from the recent tabulation of Blok and Shirley,[26] we find that the corresponding experimentally derived values are ~1.0 for Pr^{3+} and 0.68 for Tm^{3+}. The experimental value for Pr^{3+} is about 1.5 times our theoretical result, and the experimental decrease of σ_2 with increasing Z is more pronounced than the similar trend shown by our calculations. The (rather small) discrepancies between theory and experiment may arise from the neglect of two effects not included in the present ionic model: (1) the covalent bonding of the $4f$ or $5s$ and $5p$ electrons of the rare earths with the electrons of the neighboring ions[27]; (2) the charge distribution of the ligand ions (e.g., the Cl^- ions in PrCl_3).[28]

Finally, in Sec. IV of this paper, we have obtained simple formulas for the angular coefficients $C_D(nl\rightarrow l')_k$ and $C_E(nl\rightarrow l';\ l_e;\ L_i)_k$ which enter into the expressions for $\sigma_{k,D}$ and $\sigma_{k,E}$, respectively [see Eqs. (19)–(23)]. These formulas are convenient for the present work, since they are evaluated much more easily than the equivalent expressions, Eqs. (12) and (15), which involve complicated sums over the magnetic quantum number m pertaining to nl. The present expressions for C_D and C_E involve the (3-j) and (6-j) symbols, for which values have been conveniently tabulated.[9]

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[26] J. Blok and D. A. Shirley, Phys. Rev. **143**, 278 (1966). See Table I.

[27] C. K. Jørgensen, R. Pappalardo, and H. H. Schmidtke, J. Chem. Phys. **39**, 1422 (1963); J. D. Axe and G. Burns, Phys. Rev. **152**, 331 (1966); R. E. Watson and A. J. Freeman, *ibid.* **156**, 251 (1967).

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