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PHYSICAL REVIEW A VOLUME 3, NUMBER 2 FEBRUARY 1971

Quadrupole Crystalline Electric Field Shielding and Antishielding Factors at Some Rare-Earth and Heavy Ions

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(Received 3 August 1970)

We report the results of calculations of Sternheimer crystalline electric field shielding and antishielding factors for Pr^{3+}, Tm^{3+}, W^+, and Au^+ ions at all the core electronic sites, in addition to the unfilled valence electron site and the nuclear site of each ion. The calculations take into account the effect of polarization of all the closed shells within the ions, including the exchange interaction terms. Mann's relativistically corrected Hartree-Fock (HF) wave functions were used in the computations. Our calculations thus extend and improve upon the previous calculations by Sternheimer and others who did the computations for rare-earth ions at the location of the $4f$ electron and at the nuclear site only. Our values of shielding and antishielding factors λs at the location of the $4f$ electron and at the nuclear site for Pr^{3+} and Tm^{3+} ions agree well with previous calculations and measurements. The possibility of experimentally determining the quadrupole splittings of the atomic-core level by the recently developed technique of electron spectroscopy for chemical analysis (ESCA), which underlines the great significance of these calculations, is discussed.

I. INTRODUCTION

It has been of considerable interest to estimate the Sternheimer shielding parameters at the $4f$-electron site and the antishielding parameters at the nuclear site in rare-earth ions.[1-3] The electric field at any location within the ion is known in terms of these parameters when the field produced at the site of the ion by the ligands surrounding the ion and by other rare-earth ions in the crystal is given. However, the calculation of crystalline-electric field (CEF) parameters, defining the field, is a formidable task except for the simple cases of high-symmetry crystals.[4] Since the CEF parameter A_2^0 enters directly in the expression for the hyperfine energy splitting of nuclear levels, an experimental determination of A_2^0 was always sought. The spectroscopic measurements[5] gave information about A_2^0 coupled with the Sternheimer shielding parameter. Thus, an accurate knowledge of Sternheimer shielding is necessary to determine the value of A_2^0 from the experiments. Recent development of high-resolution techniques, such as electron spectroscopy for chemical analysis (ESCA)[6] has made it possible to measure very small splittings of the electronic energy levels of the order of 0.5 eV. It has been suggested by Sen[7] that the splitting of some $p_{3/2}$ electronic states should be measurable in some compounds of heavier elements. The splitting of $5p_{3/2}$ and $4p_{3/2}$ levels has recently been observed in compounds of Au, Th, U, Pu, and Np by Novakov and Hollander.[8] In view of these facts it seemed necessary to carry out calculations of the Sternheimer parameters for various electronic sites in rare-earth and heavy ions. We report here the Sternheimer parameters (to be denoted by λ) for W^+, Au^+, Pr^{3+}, and Tm^{3+} ions at all the core-electronic sites, as well as at the nuclear site of each ion. As a by-product of these calculations, electronic quadrupole polarizabilities[9] for the ions were obtained. These are also reported here.

For W^+ we have calculated $\lambda_{5d} = 0.110$ and λ_{nucl} (γ_∞ in Sternheimer's notation) $= -56.8$; for Au^+, $\lambda_{\text{nucl}} = -74.2$; for Pr^{3+}, λ_{4f} (σ_2 in Sternheimer's notation) $= 0.745$ and $\lambda_{\text{nucl}} = -84.8$; and for Tm^{3+}, $\lambda_{4f} = 0.601$ and $\lambda_{\text{nucl}} = -72.9$. The λ's here include the effect of polarization of all the cores, as well as exchange interaction terms. Mann's[10] relativistically corrected Hartree-Fock (HF) wave functions were used in all the calculations. The results for Pr^{3+} and Tm^{3+} compare well with other previous calculations[1,2] and with the measurements.[3]

It is shown from our calculation of the Sternheimer parameters that CEF could cause measurable splitting of $5p_{3/2}$ core levels in the cases studied, whereas the energy splitting of most of the lower $p_{3/2}$ levels is beyond the resolution of present instruments.

The internal-field gradient due to the CEF splitting of the unfilled valence electron shell or due to the covalent bonding orbitals, etc.[11] appears to be the primary cause of the splitting of the core-electronic levels lower than $n = 5$ and at least a partial cause of the splitting of the levels in the $n = 5$ shell. The calculations are now in progress to determine the internal electric field gradient and its shielding-antishielding parameters at various core-electronic sites, and these will be reported when available.

II. THEORY

In this section we will derive the general expressions for the CEF shielding and antishielding parameters and the quadrupole polarizability, following the same lines as Sternheimer [Ref. 1, Eqs. (1)–(37a)].

The potential energy of interaction between the CEF and a negative charge at a point (r, θ, ϕ) within an ion centered at the origin can be expressed as

$$V(r, \theta, \phi) = -\sum_{n} \sum_{m=-n}^{+n} A_n^m r^n \phi_n^m (\theta, \phi) , \qquad (1)$$

on the assumption that there is no overlap between the charge distribution of different ions. Here, A_n^m represent the lattice sums over the point charges and effective multipole moments in the surrounding ions. The functions ϕ_n^m are linear combinations of spherical harmonics Y_n^m and Y_n^{-m}. We shall concern ourselves here only with the term $-A_2^0 r^2 \phi_2^0$ of the expansion in Eq. (1), because this is the only term which could directly interact with the nuclear quadrupole moment or with the p electrons. We write this term explicitly as

$$V_R = -A_2^0 r^2 Y_2^0(\theta, \phi) . \qquad (2)$$

The contribution to the interaction energy due to V_R on an electron represented by wave function $v(n_e, l_e, m_e)$ can be written as

$$E_R = \int v^* V_R v \, d^3 r . \qquad (3)$$

The potential V_R interacts with all the electrons within the ion and this acts as a perturbation on them. The perturbed Schrödinger equation for an electron other than the one considered above, with wave function $u_0(n, l, m)$, is written in first order as

$$(H_0 - E_0) u_1 = (E_1 - H_1) u_0 , \qquad (4)$$

where H_0 is the unperturbed Hamiltonian and E_0 is the unperturbed-energy eigenvalue for the state nl, and $H_1 (= V_R)$ and E_1 are the corresponding first-order perturbation quantities. The wave function u_1 is the first-order perturbation in the zero-order wave function u_0. As usual with this type of calculation, we are taking u_0, u_1, v, etc. as r times the corresponding wave functions. We write

$$u_0(n, l, m) = u_0'(nl) Y_l^m , \qquad (5)$$

where u_0' is the radial part and Y_l^m is the angular part of u_0 with the corresponding normalizations being given by

$$\int_0^\infty u_0'^2 \, dr = 1 , \qquad (6)$$

$$\int Y_l^{m*} Y_l^m \, d\Omega = 1 . \qquad (7)$$

We note that

$$E_1 = \int u_0^2 H_1 \, d^3 r . \qquad (8)$$

It can then be seen from Eq. (4) that the angular part of u_1 is

$$Y_l^m Y_2^0 = (-1)^m \sum_{l_1 = |l-2|}^{l+2} (5/4\pi)^{1/2} [(2l+1)(2l_1+1)]^{1/2} \times \begin{pmatrix} l_1 & l & 2 \\ -m & m & 0 \end{pmatrix} \begin{pmatrix} l_1 & l & 2 \\ 0 & 0 & 0 \end{pmatrix} Y_{l_1}^m$$

$$= (5/4\pi)^{1/2} \sum_{l_1 = |l-2|}^{l+2} C^{(2)}(lm, l_1 m) Y_{l_1}^m , \qquad (9)$$

while the radial part u_1' is the solution of the inhomogeneous Schrödinger equation,

$$\left(\frac{d^2}{dr^2} + \frac{l_1(l_1+1)}{r^2} + V_0 - E_0 \right) u_1'(nl \rightarrow l_1) = u_0'(nl) (r^2 - \langle r^2 \rangle_{nl} \delta_{l l_1}) . \qquad (10)$$

In Eq. (9)

$$\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

is the usual Wigner 3-j symbol,[12]

$$C^{(2)}(lm, l_1 m) = (4\pi/5)^{1/2} \int Y_2^0 Y_{l_1}^{m*} Y_l^m \, d\Omega , \qquad (11)$$

where l_1 is an angular-momentum quantum number of u_1, V_0 is the effective potential originally introduced by Sternheimer[13] and obtainable directly from the unperturbed Schrödinger equation for u_0', viz.,

$$V_0 - E_0 = \frac{1}{u_0'} \frac{d^2 u_0'}{dr^2} - \frac{l(l+1)}{r^2} , \qquad (12)$$

described by Sternheimer,[13,14] and $\langle r^2 \rangle_{nl}$ is the expectation value of r^2 over $u_0(nl)$. The wave function u_1 corresponding to the change in angular momentum $l \rightarrow l_1$ could then be written as

$$u_1(nl \to l_1) = (5/\pi)^{1/2} A_2^0 C^{(2)}(lm, l_1 m) u_1'(nl \to l_1) Y_{l_1}^m , \tag{13}$$

with the condition that for $l = l_1$

$$\int_0^\infty u_0'(nl) u_1'(nl \to l)\, dr = 0. \tag{14}$$

Due to the perturbation we have the following interactions in addition to that defined by Eq. (3): (i) The overlap density $\rho^0(r)$ given by $\rho^0(r) r^2 = 2u_0^* u_1$ interacts with the charge density $\rho(r)$ given by $\rho(r) r^2 = v^* v$; and (ii) the overlap density $\rho^{ex}(r)$ given by $\rho^{ex}(r) r^2 = 2v^* u_1$ interacts with the charge density $\rho^D(r)$ given by $\rho^D(r) r^2 = v^* u_0$. The first is termed the direct Sternheimer addition and the second, the exchange Sternheimer addition, to E_R.

We shall now proceed to calculate both terms with one general approach. Let us rewrite our wave function u_1 as

$$u_1(n_1, l_1, m_1) = B u_1'(n_1 l_1) Y_{l_1}^{m_1} . \tag{15}$$

Its overlap with another wave function,

$$\omega(n, l, m) = \omega'(nl) Y_l^m , \tag{16}$$

we write generally as

$$\rho(r) r^2 = 2B u_1'(m_1 l_1) \omega'(nl) Y_{l_1}^{m_1 *} Y_l^m$$

$$= 2B u_1' \omega' \sum_{L=|l_1 - l|}^{l_1 + l} \left(\frac{2L+1}{4\pi} \right)^{1/2} \times C^{(L)}(l_1 m_1, lm) Y_L^{-m_1 + m} , \tag{17}$$

where

$$C^{(L)}(l_1 m_1, lm) = \left(\frac{4\pi}{2L+1} \right)^{1/2} \times \int Y_L^{m_1 - m} Y_{l_1}^{m_1 *} Y_l^m \, d\Omega . \tag{18}$$

The potential due to the charge density $\rho(r')$ at any point $\vec{r}$ is then given by

$$\Phi(\vec{r}) = \int d^3 r' \frac{\rho(r')}{|\vec{r} - \vec{r}'|} = \int d^3 r' \sum_{l'm'} \frac{4\pi}{2l'+1} \frac{r_<^{l'}}{r_>^{l'+1}} \rho(r') Y_{l'}^{m'}(r) Y_{l'}^{m' *}(r')$$

$$= 2B \sum_{l'm'} \frac{4\pi}{2l'+1} Y_{l'}^{m'}(r) \int_0^\infty dr' \frac{r_<^{l'}}{r_>^{l'+1}} u_1' \omega' \sum_{L=|l_1 - l|}^{l_1 + l} \left(\frac{2L+1}{4\pi} \right)^{1/2} C^L(l_1 m_1, lm)$$

$$\times \int d\Omega \, Y_L^{-m_1 + m}(r') Y_{l'}^{m' *}(r')$$

$$= 2B \sum_{L=|l_1 - l|}^{l_1 + l} \left(\frac{4\pi}{2L+1} \right)^{1/2} C^{(L)}(l_1 m_1, lm) Y_L^{-m_1 + m} \int_0^\infty dr' \frac{r_<^L}{r_>^{L+1}} u_1' \omega'$$

$$= 2B \sum_{L=|l_1 - l|}^{l_1 + l} \left(\frac{4\pi}{2L+1} \right)^{1/2} C^{(L)}(l_1 m_1, lm) Y_L^{-m_1 + m} F_L(r) , \tag{19}$$

where

$$F_L(r) = (1/r^{L+1}) \int_0^r u_1' \omega' r'^L \, dr' + r^L \int_r^\infty u_1' \omega' r'^{-L-1} \, dr' .$$

Let us first consider the direct perturbation term of the interaction energy defined in (i) following Eq. (14). In this case

$$B = (5/\pi)^{1/2} A_2^0 C^{(2)}(lm, l_1 m) , \tag{20}$$

$$\omega = u_0(n, l, m) , \tag{21}$$

$$u_1 = u_1(n, l_1, m) , \tag{22}$$

and therefore,

$$\Phi(r) = 2(5/\pi)^{1/2} A_2^0 C^{(2)}(lm, l_1 m) \times \sum_{L=|l_1 - l|}^{l_1 + l} C^{(L)}(l_1 m, lm) \left(\frac{4\pi}{2L+1} \right)^{1/2} Y_L^0 F_L(r) . \tag{23}$$

The quadrupolar part of this potential is that for which $L = 2$, and is

$$\Phi_2(r) = 4 A_2^0 [C^{(2)}(lm, l_1 m)]^2 Y_2^0 F_2(r) . \tag{24}$$

Higher moments of the potential Φ will be present in general but they will not interact either with p electrons or with the nuclear quadrupole moment. However, while considering the interaction of Φ with electrons having $l > 1$ one should, strictly speaking, consider also higher moments of Φ. In our calculations, we have not considered the latter. The interaction energy of $\Phi_2(r)$ with the electrons, represented by $v(n_e, l_e, m_e)$, could then be written as

$$E_2(n, l \to l_1, m) = \int v^* \Phi v \, d^3r$$
$$= 4A_2^0[C^{(2)}(lm, l_1m)]^2 \int_0^\infty dr\, v'^2 F_2(r)$$
$$\times \int d\Omega\, Y_2^0 Y_{l_e}^{m_e *} Y_{l_e}^{m_e} \ . \tag{25}$$

In order to obtain total E_2 due to a closed shell we must sum over all m values in Eq. (25) and multiply by 2 to take into account the two spin states for each m. If we define

$$C_{ll_1}^{(2)} = 8 \sum_{m=-l}^{+l} [C^{(2)}(lm, l_1m)]^2 , \tag{26}$$

then we find

$$E_2(nl \to l_1) = A_2^0 C_{ll_1}^{(2)} \int_0^\infty dr\, v'^2 F_2(r)$$
$$\times \int d\Omega\, Y_2^0 Y_{l_e}^{m_e *} Y_{l_e}^{m_e}$$
$$= (5/4\pi)^{1/2} A_2^0 C^{(2)}(l_e m_e, l_e m_e)$$
$$\times C_{ll_1}^{(2)} \int_0^\infty dr\, v'^2 F_2(r) \ . \tag{27}$$

Now in an exchange interaction, the overlap density is given by

$$\rho^{ex}(r) r^2 = 2(5/\pi)^{1/2} A_2^0 C^{(2)}(lm, l_1m)$$
$$\times u'(nl \to l_1) v'(n_e l_e) Y_{l_1}^{m *} Y_{l_e}^{m_e} , \tag{28}$$

and the potential due to ρ^{ex} at any point r [from Eq. (19)] is

$$\Phi^{ex}(r) = 2(5/\pi)^{1/2} A_2^0 C^{(2)}(lm, l_1m) \sum_{L=|l_1-l_e|}^{l_1+l_e} \left(\frac{4\pi}{2L+1}\right)^{1/2} C^{(L)}(l_1m, l_em_e) Y_L^{m_e-m} F_L(r) \ . \tag{29}$$

Thus the exchange energy can be written as

$$E^{ex}(n, l \to l_1, m) = -2(5/\pi)^{1/2} A_2^0 C^{(2)}(lm, l_1m) \sum_{L=|l_1-l_e|}^{l_1+l_e} \left(\frac{4\pi}{2L+1}\right)^{1/2} C^{(L)}(l_1m, l_em_e)$$
$$\times \int_0^\infty dr\, v'(n_e l_e) u_0'(nl) F_L(r) \int d\Omega\, Y_{l_e}^{m_e *} Y_L^{m_e-m} Y_l^m$$
$$= -2(5/\pi)^{1/2} A_2^0 C^{(2)}(lm, l_1m) \sum_{L=|l_1-l_e|}^{l_1+l_e} \left(\frac{4\pi}{2L+1}\right)^{1/2} C^{(L)}(l_1m, l_em_e)$$
$$\times \left(\frac{2L+1}{4\pi}\right)^{1/2} C^{(L)}(lm, l_em_e) \int_0^\infty dr\, v'(n_e l_e) u_0'(nl) F_L(r) \ . \tag{30}$$

The total exchange energy for a closed shell for the perturbation, $nl \to l_1$ is obtained by summing Eq. (30) over all m values. If we define,

$$C_L(nl \to l_1) = 4 \sum_{m=-l}^{l} C^{(2)}(lm, l_1m) C^{(L)}(l_1m, l_em_e) C^{(L)}(lm, l_em_e) / C^{(2)}(l_em_e, l_em_e) , \tag{31}$$

then

$$E^{ex}(nl \to l_1) = -(5/4\pi)^{1/2} A_2^0 C^{(2)}(l_em_e, l_em_e) \sum_{L=|l_1-l_e|}^{l_1+l_e} C_L(nl \to l_1) \int_0^\infty dr\, v'(n_e l_e) u_0'(nl) F_L(r) \ . \tag{32}$$

Also we can write E_R given by (3) as,

$$E_R = -A_2^0 \int d\Omega\, Y_{l_e}^{m_e *} Y_2^0 Y_{l_e}^{m_e} \int_0^\infty dr\, v'^2 r^2$$
$$= -(5/4\pi)^{1/2} A_2^0 C^{(2)}(l_em_e, l_em_e) \langle r^2 \rangle_{n_e l_e} \ . \tag{33}$$

Thus, the fractional change in the energy E_R due to the perturbation $l \to l_1$ of the nl shell is

$$\lambda_{nl \to l_1} = -(E_2 + E^{ex})/E_R = -(\lambda_{nl \to l_1}^D + \lambda_{nl \to l_1}^{ex}) ,$$

where

$$\lambda_{nl \to l_1}^D = C_{ll_1}^{(2)} \int_0^\infty dr \frac{v'^2 F_2(r)}{\langle r^2 \rangle_{n_e l_e}} \tag{34}$$

and

$$\lambda_{nl \to l_1}^{ex} = -\sum_{L=|l_1-l_e|}^{l_1+l_e} C_L(nl \to l_1)$$
$$\times \int_0^\infty dr \frac{v'(n_e l_e) u_0'(nl) F_L(r)}{\langle r^2 \rangle_{n_e l_e}} \ . \tag{35}$$

The total effect of V_R at any site $n_e l_e m_e$ will be

$$E = E_R(1 - \sum_n \sum_{l_1} \lambda_{nl \to l_1}) = E_R(1 - \lambda_{n_e l_e}) . \tag{36}$$

Let us now consider the effect of perturbation of the closed shells at the nuclear site. Since exchange-type terms do not have any physical meaning for the nuclear site, only the direct perturbation term, i.e.,

$$\lambda^{\text{nucl}}_{nl \to l_1} = C^{(2)}_{l l_1} \int_0^\infty dr \, \frac{v^2_{\text{nucl}} \left(r^{-3} \int_0^r u_0' u_1' r'^2 dr + r^2 \int_r^\infty u_0' u_1' r'^{-3} dr'\right)}{\langle r^2 \rangle_{\text{nucl}}} , \tag{37}$$

should be considered.

Assuming the nuclear wave function v_{nucl} to be a δ function, we get

$$\lambda^{\text{nucl}}_{nl \to l_1} = C^{(2)}_{l l_1} \int_0^\infty u_0' u_1' r^{-3} dr , \tag{38}$$

and the total Sternheimer nuclear antishielding factor is

$$\lambda_{\text{nucl}} = \sum_n \sum_{l_1} \lambda^{\text{nucl}}_{nl \to l_1} . \tag{39}$$

Similarly, the quadrupolar polarizability is written as

$$\alpha_q = \sum_n \sum_{l_1} \alpha^q_{nl \to l_1} = \sum_n \sum_{l_1} C^{(2)}_{l l_1} \int_0^\infty u_0' u_1' r^2 dr . \tag{40}$$

III. CALCULATIONS

The solution of the inhomogeneous Schrödinger equation [Eq. (10)] for u_1' is, in effect, the most significant part of the computations. The method of direct numerical integration was used in solving this equation. For this purpose, the differential equation [Eq. (10)] was written with the help of Eq. (12) as a difference equation (see Ref. 13), from which u_1' could easily be written as

$$\begin{aligned} u_1'(r+\delta) = u_1'(r) \left[2 + \delta^2 \left(\frac{l_1(l_1+1) - l(l+1)}{r^2} \right) \right] \\ + \frac{u_0'(r+\delta) - 2u_0'(r) + u_0'(r-\delta)}{u_0'(r)} \\ - u_1'(r-\delta) - u_0'(r)\delta^2 (r^2 - \langle r^2 \rangle_{nl} \delta_{l l_1}) . \end{aligned} \tag{41}$$

It can be seen from Eq. (41) that in order to determine u_1' completely one has to know the unperturbed wave functions $u_0'(nl)$ and the two boundary conditions on u_1'. Hartree-Fock $u_0'(nl)$ wave functions have recently been calculated by Mann[10] and we have used them throughout our work. The two boundary conditions are obviously $u_1' = 0$ at $r = 0$ and at $r = \infty$. However, it was found necessary to feed some more analytic information about u_1' to the computer in order to get a unique and consistent numerical solution of u_1'. It can be shown analytically that $u_1'(r) \to 0$ as r^{l+3} for the perturbation $l_1 = l + 2$ and $l_1 = l$, and as r^{l-1} for the perturbations $l_1 = l - 2$. For radial excitations ($l_1 = l$) one can even find analytically the constant of proportionality and an additional expansion coefficient of the u_1'. This additional information about u_1' has not been found of much use in calculations of Pr^{3+} and Tm^{3+} but for Au^+ and W^+ and for other ions of higher atomic number such information was indispensable. The Numerov method of numerical integration[15] did not show any great advantage over simple integration [direct use of Eq. (41)] and therefore only the latter was used. The variable mesh was employed for numerical integration purposes and the starting mesh size near $r = 0$ was reduced until consistency in u_1' output resulted. In general, the starting mesh size of the order of 0.0005 a.u. was found satisfactory for the cases studied. For angular excitations, only an outward integration of Eq. (41) was necessary. The proportionality constant relating to the known behavior of the u_1' wave function near $r = 0$ was adjusted until u_1' behaved properly at $r = \infty$. For radial excitation ($l_1 = l$), the outward integration of Eq. (41) was done up to $r = 0.05$ or $r = 0.1$ a.u., and inward integration from $r \simeq \infty$ to $r = 0.05$ or $r = 0.1$ a.u. (as the case may be) was done with many starting values of $u_1'(r)$ until it matched the former smoothly. For very large values of r, $u_1'(r)$, and $u_1'(r+\delta)$ are related by the following expression[14]:

$$u_1'(r+\delta) = u_1'(r) \, e^{-[N(r)]^{1/2} \delta} , \tag{42}$$

with

$$\begin{aligned} N(r) = \frac{u_0'(r+\delta) - 2u_0'(r) + u_0'(r-\delta)}{\delta^2 u_0'(r)} \\ + \frac{l'(l'+1) - l(l+1)}{r^2} - \frac{u_0'(r) r}{u_1'(r)} . \end{aligned} \tag{43}$$

For large r, N is a constant equal to $-E_0$.

Various angular integrals represented by the coefficient C in terms of the Wigner 3-j symbols[12] were evaluated in the computer. The total time taken for the calculations presented here by the central processing unit of the IBM-360-65 computer at the University of Manitoba in FORTRAN IV language was less than 12 min with an estimated efficiency of 70% (because of nonprofessional programming).

TABLE I. Shielding-antishielding factors at the different sites within the Pr^{3+} ion due to various perturbations. The first column gives the values of quadrupole polarizability α_q for different perturbations. Values of $\langle r^2 \rangle$ are in units of of a_H^2. The total was obtained after subtraction of the self-interaction terms from the sum.

Perturbation	$\alpha_q(Å^5)$	λ_{nucl}	λ_{2p}	λ_{3p}	λ_{3d}	λ_{4p}	λ_{4d}	λ_{4f}	λ_{5p}
$5p \to p$	0.327	-73.088	-1.531	-0.741	-1.262	-0.254	-0.330	-0.154	0.103
$5p \to f$	1.246	0.470	0.751	0.044	0.073	0.692	0.754	0.625	0.162
$5s \to d$	0.322	0.275	2.350	1.069	1.196	0.371	0.374	0.208	-0.019
$4d \to s$	0.002	- 0.024	-1.170	-0.432	-0.508	0.015	-0.040	-0.018	-0.001
$4d \to d$	0.002	- 2.693	-0.604	-0.206	-0.123	-0.007	0.040	-0.006	0.000
$4d \to g$	0.006	0.235	0.242	0.239	0.244	0.095	0.094	0.040	0.007
$4p \to p$	0.001	- 8.388	-0.136	-0.046	-0.103	0.026	-0.004	-0.002	0.001
$4p \to f$	0.003	0.171	0.133	0.244	0.235	0.059	0.074	0.030	0.004
$4s \to d$	0.002	0.043	0.565	0.242	0.277	-0.009	0.037	0.020	0.003
$3d \to s$	0.000	- 0.020	-0.229	0.007	-0.046	-0.002	-0.002	-0.001	0.000
$3d \to d$	0.000	- 0.317	-0.050	-0.006	0.022	0.000	0.001	0.000	0.000
$3d \to g$	0.000	0.090	0.072	0.021	0.029	0.002	0.002	0.001	0.000
$3p \to p$	0.000	- 1.486	-0.012	0.015	-0.004	0.001	0.000	0.000	0.000
$3p \to f$	0.000	0.079	0.090	0.020	0.038	0.002	0.002	0.001	0.000
$3s \to d$	0.000	0.046	0.185	-0.007	0.043	0.003	0.002	0.001	0.000
$2p \to p$	0.000	- 0.244	0.014	0.001	0.000	0.000	0.000	0.000	0.000
$2p \to f$	0.000	0.036	0.006	0.000	0.001	0.000	0.000	0.000	0.000
$2s \to d$	0.000	0.027	-0.001	0.000	0.001	0.000	0.000	0.000	0.000
$1s \to d$	0.000	0.011	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Total	1.911	-84.777	0.642	0.458	0.113	0.980	0.995	0.745	0.216
$\langle r^2 \rangle$			0.0106	0.0883	0.0720	0.5138	0.6126	1.3479	3.737
$(1-\lambda)\langle r^2 \rangle$			0.004	0.048	0.064	0.010	0.616	0.344	2.922

IV. RESULTS AND DISCUSSION

The results are presented for Pr^{3+}, Tm^{3+}, W^+, and Au^+ in Tables I, II, III, and IV, respectively.

In the calculation of total λ_{nl}, the self-interaction terms have been subtracted. The self-interaction term arises because when $n_e l_e m_e = nlm$, the electron interacts with its own perturbation. We call

TABLE II. Shielding-antishielding factors at different sites within the Tm^{+3} ion due to various perturbations. The first column gives the values of quadrupole polarizability α_q for different perturbations. Values $\langle r^2 \rangle$ are in units of a_H^2. The total was obtained after the subtraction of the self-interaction terms from the sum.

Perturbation	$\alpha_q(Å^5)$	λ_{nucl}	λ_{2p}	λ_{3p}	λ_{3d}	λ_{4p}	λ_{4d}	λ_{4f}	λ_{5p}
$5p \to p$	0.154	-64.487	-1.394	-0.677	-1.166	-0.238	-0.325	-0.189	0.079
$5p \to f$	0.520	0.573	1.497	-0.703	-0.513	0.568	0.558	0.491	0.148
$5s \to d$	0.131	0.221	1.889	0.910	1.018	0.350	0.360	0.236	-0.017
$4d \to s$	0.000	- 0.013	-0.890	-0.358	-0.419	0.011	-0.041	-0.027	-0.001
$4d \to d$	0.001	- 2.080	-0.449	-0.155	-0.098	-0.006	0.033	-0.006	0 000
$4d \to g$	0.002	0.184	0.191	0.188	0.193	0.072	0.074	0.039	0.004
$4p \to p$	0.000	- 6.411	-0.105	-0.036	-0.082	0.020	-0.003	-0.002	0.001
$4p \to f$	0.001	0.142	0.105	0.199	0.191	0.048	0.064	0.033	0.003
$4s \to d$	0.001	0.379	0.470	0.215	0.245	-0.008	0.035	0.024	0.002
$3d \to s$	0.000	- 0.014	-0.195	0.007	-0.042	-0.002	-0.002	-0.001	0.000
$3d \to d$	0.000	- 0.239	-0.035	-0.004	0.017	0.000	0.001	0.000	0.000
$3d \to g$	0.000	0.073	0.057	0.016	0.024	0.002	0.001	0.001	0.000
$3p \to p$	0.000	- 1.154	-0.010	0.012	-0.003	0.001	0.000	0.000	0.000
$3p \to f$	0.000	0.065	0.074	0.017	0.032	0.002	0.002	0.001	0.000
$3s \to d$	0.000	0.036	0.170	-0.007	0.042	0.003	0.003	0.001	0.000
$2p \to p$	0.000	- 0.200	0.011	0.000	0.000	0.000	0.000	0.000	0.000
$2p \to f$	0.000	0.030	0.005	0.000	0.001	0.000	0.000	0.000	0.000
$2s \to d$	0.000	0.022	0.000	0.000	0.001	0.000	0.000	0.000	0.000
$1s \to d$	0.000	0.010	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Total	0.810	-72.863	1.388	-0.381	-0.559	0.812	0.753	0.601	0.181
$\langle r^2 \rangle$			0.0076	0.0600	0.0473	0.3397	0.3848	0.7062	2.7272
$(1-\lambda)\langle r^2 \rangle$			-0.003	0.083	0.074	0.064	0.095	0.282	2.233

TABLE III. Shielding-antishielding factors at different sites within the W^+ ion due to various perturbations. The first column gives the values of quadrupole polarizability α_q for different perturbations. Values of $\langle r^2 \rangle$ are in units of a_H^2. The total was obtained after subtraction of the self-interaction terms from the sum.

Perturbation	α_q(Å^5)	$\lambda_{\rm nucl}$	λ_{2p}	λ_{3p}	λ_{3d}	λ_{4p}	λ_{4d}	λ_{4f}	λ_{5p}	λ_{5d}
$5p \to p$	0.047	-47.591	-1.000	-0.469	-0.833	-0.152	-0.222	-0.176	0.058	-0.007
$5p \to f$	0.136	0.448	-0.309	1.416	1.251	0.385	0.435	0.353	0.060	0.044
$5s \to d$	0.053	0.205	1.579	0.774	0.866	0.308	0.320	0.266	-0.014	0.018
$4f \to p$	0.069	0.014	3.061	-3.858	-3.181	0.021	-0.221	-0.088	0.113	0.048
$4f \to f$	0.004	- 1.840	-1.659	-0.792	-0.486	-0.108	-0.037	0.088	0.002	0.000
$4f \to h$	0.005	0.208	0.207	0.187	0.193	0.100	0.099	0.074	0.013	0.004
$4d \to s$	0.000	- 0.030	-0.719	-0.303	-0.355	0.008	-0.039	-0.038	-0.001	0.000
$4d \to d$	0.000	- 1.743	-0.364	-0.122	-0.076	-0.005	0.027	-0.006	0.000	0.000
$4d \to g$	0.000	0.161	0.169	0.166	0.172	0.063	0.067	0.049	0.004	0.001
$4p \to p$	0.000	- 5.574	-0.091	-0.030	-0.071	0.017	-0.003	-0.003	0.001	0.000
$4p \to f$	0.000	0.124	0.084	0.183	0.174	0.045	0.063	0.047	0.003	0.001
$4s \to d$	0.000	0.060	0.435	0.202	0.230	-0.007	0.035	0.035	0.002	0.001
$3d \to s$	0.000	- 0.013	-0.183	0.007	-0.041	-0.002	-0.002	-0.002	0.000	0.000
$3d \to d$	0.000	- 0.213	-0.030	-0.004	0.015	0.000	0.001	0.000	0.000	0.000
$3d \to g$	0.000	0.067	0.052	0.015	0.022	0.001	0.001	0.001	0.000	0.000
$3p \to p$	0.000	- 1.041	-0.009	0.011	-0.003	0.001	0.000	0.000	0.000	0.000
$3p \to f$	0.000	0.059	0.068	0.016	0.030	0.002	0.002	0.001	0.000	0.000
$3s \to d$	0.000	- 0.023	0.161	-0.007	0.040	0.003	0.003	0.002	0.000	0.000
$2p \to p$	0.000	- 0.184	0.011	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$2p \to f$	0.000	0.028	0.005	0.000	0.001	0.000	0.000	0.000	0.000	0.000
$2s \to d$	0.000	0.021	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000
$1s \to d$	0.000	0.009	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Total	0.314	-56.848	1.465	-2.612	-2.051	0.670	0.524	0.598	0.221	0.110
$\langle r^2 \rangle$			0.0065	0.0507	0.0396	0.2793	0.3053	0.4159	1.9397	4.3548
$(1-\lambda)\langle r^2 \rangle$			-0.003	0.183	0.121	0.092	0.145	0.167	1.511	3.876

the corresponding term in Eq. (26) the self-interaction term. The self-interaction term is then $(2\sum_{m=-l}^{l} m)^{-1}$ times the total term given by Eq. (27), and is present only when $n_e l_e = nl$. The self-interaction terms correspond to unphysical situations and are to be subtracted from the final results. However, all results include the exchange-interaction energy term $\lambda_{nl\text{-}l_1}^{\rm ex}$, which was often found comparable to, and sometimes even dominant over, the direct term $\lambda_{nl\text{-}l_1}^{D}$.[16] The comparison of the results obtained here with some of the available estimates is shown in Table V. One can see that we have not obtained very different results even though we used better wave functions[10] than those used by other workers, confirming that it is not necessary to know the core-electron wave functions very accurately for this type of calculation.

The results $\lambda_{\rm nucl} = -56.8$ for tungsten, and $\lambda_{\rm nucl} = -74.2$ for gold have been obtained.

We shall now see if the energy splitting of any of the $p_{3/2}$ state or any other electronic state, due to the crystalline electric field, could be measured. The energy splitting of an $np_{3/2}$ state could be written as[7]

$$\Delta E_{np_{3/2}} = A_2^0 (1 - \lambda_{np}) \langle r^2 \rangle_{np} [\langle 3\cos^2\theta - 1 \rangle_{j=3/2, m_j=\pm 3/2} - \langle 3\cos^2\theta - 1 \rangle_{j=3/2, m_j=\pm 1/2}] \ . \qquad (44)$$

Phillips and Grodzins[17] have given the values of field gradients in the compounds WS_2 at the nucleus of the tungsten ion as -2.0×10^{18} V/cm^2, i.e.,

$$4A_2^0 (1 - \lambda_{\rm nucl}) = 2.0\times 10^{18}\ {\rm V/cm^2} \ .$$

Therefore we have $A_2^0 \simeq 0.875\times 10^{16}$ V/cm^2. The square-bracketed term in Eq. (44) is $\frac{4}{5}$. Also, it can be seen from Table III that among the p states, the maximum value of $(1-\lambda_{np})\langle r^2 \rangle_{np}$ is $1.51\ a_H^2$ for the $5p$ state. Thus, $\Delta E_{5p_{3/2}} \simeq 0.3$ eV, which is at the threshold of resolution of the best instruments available at present.

Let us study another case, namely, $PrCl_3$. Hutchings and Ray[4] have calculated $A_2^0 = 2.35\times 10^{-3}$ a.u. at the Pr^{3+}-ion site in $PrCl_3$. For $5p$ states in Pr^{3+} we find $(1-\lambda_{5p})\langle r^2 \rangle_{5p} = 2.92 a_H^2$ from Table I. This gives $\Delta E_{5p3/2} = 0.15$ eV. In $PrBr_3$, we find that $\Delta E_{5p3/2} \simeq 0.3$ eV. These values are not far from being measurable. Higher values of A_2^0 are possible in some compounds of the ions studied. One can, therefore, conclude that at least a part of the splitting of $O_{\rm III}$ lines in gold[8] could be caused by the CEF. The $\Delta E_{4p_{3/2}}$ for Pr^{3+}, Tm^{3+}, and W^+ came out to be less than one tenth of $\Delta E_{5p_{3/2}}$. For Au^+, $\Delta E_{4p_{3/2}}$ was greater than $\Delta E_{5p_{3/2}}$. Thus, one should look forward to the internal electric field as the partial or total cause of splitting of $N_{\rm III}$ and $O_{\rm III}$ lines. The internal electric field gradient is the

TABLE IV. Shielding-antishielding factors at different sites within the Au^+ ion due to various perturbations. The first column gives the values of quadrupole polarizability α_q for different perturbations. Values of $\langle r^2 \rangle$ are in units of a_H^2. The total was obtained after the subtraction of the self-interaction terms from the sum.

Perturbation	α_q(Å^5)	λ_{nucl}	λ_{2p}	λ_{3p}	λ_{3d}	λ_{4p}	λ_{4d}	λ_{4f}	λ_{5p}	λ_{5d}
$5d \rightarrow s$	2.295	0.422	-13.459	-5.935	-6.779	-1.508	-1.642	-1.459	0.341	0.166
$5d \rightarrow d$	0.568	-30.724	-7.217	-3.162	-2.412	-1.194	-0.797	-0.943	-0.061	0.194
$5d \rightarrow g$	1.032	0.522	0.517	0.520	0.517	0.547	0.544	0.518	0.289	0.123
$5p \rightarrow p$	0.018	-36.206	-0.753	-0.350	-0.628	-0.118	-0.172	-0.160	0.047	-0.007
$5p \rightarrow f$	0.059	0.254	-0.380	1.019	0.866	0.391	0.430	0.398	0.065	0.049
$5s \rightarrow d$	0.024	-0.689	1.602	0.706	0.811	0.261	0.281	0.265	-0.012	0.019
$4f \rightarrow p$	0.003	-0.071	0.430	-0.668	-0.555	-0.060	-0.109	-0.102	0.009	0.007
$4f \rightarrow f$	0.001	-1.024	-0.910	-0.400	-0.231	-0.046	-0.022	0.050	0.002	0.000
$4f \rightarrow h$	0.001	0.172	0.171	0.150	0.157	0.072	0.073	0.064	0.008	0.003
$4d \rightarrow s$	0.000	-0.010	-0.647	-0.276	-0.321	0.007	-0.040	-0.050	-0.002	-0.001
$4d \rightarrow d$	0.000	-1.331	-0.274	-0.092	-0.063	-0.004	0.022	-0.005	0.000	0.001
$4d \rightarrow g$	0.000	0.144	0.151	0.147	0.152	0.055	0.060	0.054	0.004	0.002
$4p \rightarrow p$	0.000	-4.722	-0.077	-0.026	-0.060	0.015	-0.002	-0.004	0.001	0.000
$4p \rightarrow f$	0.000	0.111	0.072	0.167	0.158	0.042	0.061	0.055	0.004	0.001
$4s \rightarrow d$	0.000	0.055	0.402	0.189	0.216	-0.007	0.036	0.043	0.003	0.001
$3d \rightarrow s$	0.000	-0.012	-0.173	0.006	-0.039	-0.002	-0.003	-0.003	0.000	0.000
$3d \rightarrow d$	0.000	-0.192	-0.027	-0.004	0.013	0.000	0.001	0.000	0.000	0.000
$3d \rightarrow g$	0.000	0.062	0.048	0.014	0.020	0.001	0.001	0.001	0.000	0.000
$3p \rightarrow p$	0.000	-0.938	-0.009	0.010	-0.002	0.001	0.000	0.000	0.000	0.000
$3p \rightarrow f$	0.000	0.054	0.063	0.014	0.028	0.002	0.002	0.002	0.000	0.000
$3s \rightarrow d$	0.000	0.022	0.177	-0.008	0.044	0.003	0.003	0.003	0.000	0.000
$2p \rightarrow p$	0.000	-0.170	0.010	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$2p \rightarrow f$	0.000	0.026	0.004	0.000	0.001	0.000	0.000	0.000	0.000	0.000
$2s \rightarrow d$	0.000	0.019	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000
$1s \rightarrow d$	0.000	0.009	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Total	4.001	-74.217	-20.281	-7.983	-8.105	-1.552	-1.277	-1.274	0.679	0.510
$\langle r^2 \rangle$			0.0056	0.0435	0.0336	0.2310	0.2437	0.2814	1.4510	2.8340
$(1-\lambda)\langle r^2 \rangle$			0.119	0.391	0.306	0.590	0.555	0.640	0.466	1.389

electric field gradient caused by CEF split electronic levels of the unfilled valence shell. Preliminary calculations in this direction are encouraging, giving the correct ratio of energy splitting of the $4p_{3/2}$ and $5p_{3/2}$ levels in gold.[8]

Briefly, we describe the procedures of our treatment of the unfilled valence shell. Instead of considering the potential energy of interaction as in

TABLE V. Comparison of the present and previous estimates of quadrupole polarizability α_q antishielding factors λ_{nucl} at the nuclear site and the shielding factors λ_{4f} for Pr^{3+} and Tm^{3+} ions and λ_{5d} for W^+ and Au^+ ions.

	α_q(Å^5)		λ_{nucl}		λ_{4f} or λ_{5d}		
Ion	Present estimate	Previous estimates	Present estimate	Previous estimates	Present estimate	Previous estimates	Site
Pr^{3+}	1.911	1.731[a] 1.752[b]	-84.78	-72.61[a] -80.82[b]	0.745	0.672[a] 0.70[b]	4*f*
Tm^{3+}	0.810	0.729[a] 0.718[b]	-72.86	-64.54[a] -74.16[b]	0.601	0.545[a] 0.59[b] 0.34 - 0.71[c]	4*f*
W^+	0.314		-56.85		0.110		5*d*
Au^+	4.001		-74.22		0.510		5*d*

[a] Reference 2(a); the estimates do not include contributions from terms with $n < 4$.

[b] Reference 2(b); the estimates do not include contribution from terms with $n < 4$.

[c] References 3(a) and 3(b).

Eq. (1), we start by writing the potential energy due to charge distribution of density $\rho(\vec{r}\,')$ at any point $\vec{r}$ as

$$\phi(r) = -\int [\rho(r')/|\vec{r}-\vec{r}\,'|]\, d^3r' \ . \qquad (45)$$

Now, $\rho(r')$ is written in terms of the wave function u_l of an open-shell electron, and the quadrupolar part $\phi_2(r)$ of Eq. (45) is substituted for H_1 in Eq. (4). The result is a slight modification of the angular part of u_1 [Eq. (9)] and a change in the inhomogeneous Schrödinger equation [Eq. (10)]. In Eq. (10), r^2 and $\langle r^2\rangle_{nl}$ are replaced by

$$K(r) = r^{-3}\int_0^r u_l'^2 r'^2\, dr' + r^2 \int_r^\infty u_l'^2 r'^{-3}\, dr' \ , \qquad (46)$$

and $\langle K(r)\rangle_{nl}$, respectively. With these modifications in the basic formulation of the problem, the shielding and antishielding factors for internal electric field are computed easily. Details of the calculations of the effect of the internal electric field on the energy splitting of core-electronic levels will be reported when available.

ACKNOWLEDGMENTS

The authors wish to thank Dr. B. S. Bhakar in the Department of Physics of the University of Manitoba for many helpful discussions and Dr. R. M. Sternheimer of Brookhaven National Laboratory for important correspondence. Acknowledgments are also due to the National Research Council of Canada for financial support of this work and for financial assistance to two of us (R. P. G. and B. K. R.).

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