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Sternheimer Shielding-Antishielding; Rare-Earth Ions

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Sternheimer shielding-antishielding parameters pertinent to the quadrupole perturbations outside an ion (λ), as well as within the ion owing to an unfilled 4f shell (R), have been calculated for rare-earth ions La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Pm^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, Lu^{3+}, Sm^{2+}, and Eu^{2+}. Hartree–Fock–Slater-type ionic wave functions have been used. The value of λ_0 varies smoothly from -65.82 for La^{3+} to -58.49 for Yb^{3+}, whereas that of R_0 (without exchange) varies from 0.081 for Ce^{3+} to 0.128 for Yb^{3+}. The calculation of Sternheimer parameters for Sm^{2+} and Eu^{2+} with $\lambda_0=-73.28$ and $R_0=0.124$ for Sm^{2+} shows that their dependence on the charge of the ions is appreciable. Sternheimer parameters are reported also for the core-electron sites.

I. INTRODUCTION

The present investigation is carried out in an attempt to understand the role played by core electrons of an ion in modifying a perturbation,[1] particularly at the core-electron sites. The structures and shapes of the x-ray emission lines[2] and of photoemitted core electrons[3,4] are affected by the environment. The potential due to environment is modified by the electron cloud of the ion in a rather complicated way. However, as Sternheimer[1] showed for the first time, the repercussion of electron cloud on the perturbing potential could be accounted for by linear parameters, now known as Sternheimer parameters. Most of the work in the past[5–7] was done on the calculation of Sternheimer parameters either at the nuclear site (λ_0, R_0) or at the valence electron site λ_{val}. With the availability of very-high-resolution tools to probe the structure of the inner-shell electron-vacancy energy levels it has become necessary to know the Sternheimer parameters for the core-electron sites.[2,8] For Pr^{3+}, Tm^{3+}, W^{+}, and Au^{+}, Sternheimer parameters (λ) pertinent to quadrupole perturbing potential outside the ion, at all the electronic as well as the nuclear sites, have been reported.[9] More important for the inner-electron sites for ions in solids are the Sternheimer parameters (R) relevant to perturbation originating from the unfilled valence-electron shells.[4,10] In principle, the calculations of R_{nl} are not very different from that of λ_{nl} parameters.

A better and faster numerical code has been developed to calculate the Sternheimer parameters. The Hartree–Fock–Slater free-ion wave functions used in the present work were obtained using a Desclaux[11] computer program. The Hartree–Fock ionic wave functions used were computed using the Froese–Fischer code.[12] (The wave functions used in an earlier work[9] were atomic Hartree–Fock type, as reported by Mann.[13]) In the present paper, Sternheimer parameters are reported for the tripositive rare-earth ions La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Pm^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, and Lu^{3+}, and dipositive ions Sm^{2+} and Eu^{2+} using Hartree–Fock–Slater (HFS) wave functions, and for La^{3+} using Hartree–Fock (HF) wave functions. For La^{3+}, $\lambda_0(\text{HFS}) = -65.82$ and $\lambda_0(\text{HF}) = -59.5$, and for Lu^{3+}, $\lambda_0(\text{HFS}) = -61.39$, have been calculated. The parameter $R_0 = 0.081$ (without exchange) for Ce^{3+} has been obtained with HFS wave functions. The HF calculation for R_0 has not yet been completed.

Recent measurements of λ_0 for the Li^{+} ion in lithium fluoride[14] have confirmed the view that the use of free-ion wave functions for calculating the Sternheimer parameters is inadequate; $|1-\lambda_0|$ for Li^{+} in LiF was measured as 3.4, as against 0.75 obtained theoretically for the Li^{+} free ion. Calculation of Sternheimer parameters for ions in compounds, rather than merely for free ions, seems warranted.

II. THEORY

Sternheimer's method[5] of directly solving the perturbed inhomogeneous Schrödinger equation is used here. In this section a brief account of the method is presented for the quadrupole perturbing potential. We consider the effect of the perturbing quadrupole potential of the form $Af(r)Y_2^0(\theta, \phi)$ on the nuclear and electronic sites of an ion directly and via the closed electronic shells. If the perturbing potential source lies outside an ion, say crystal potential in solids, then $f(r)$ has the simple form r^2, but if it originates from the perturbed valence-electron shell then $f(r)$ has a form involving the wave functions of the valence electrons (and the wave functions of various other electrons when we consider the exchange interactions in addition). We show the Sternheimer effect schematically in Fig. 1.

The perturbing potential is considered to originate from a charge distribution $\omega(1)$. The direct interaction of $w(1)$ with a point at the perturbed site could be written as

$$H_1(3)=\langle w(1)|\frac{e^2}{r_{13}}(1-P_{13})|w(1)\rangle, \qquad (1)$$

where P_{13} is the the operator which interchanges coordinates 1 with coordinates 3 and accounts for the exchange interaction. The expectation value of H_1 over $v(3)$ gives the perturbation energy of the site

$$E_1=\langle v|H_1|v\rangle. \qquad (2)$$

The charge distribution $w(1)$ interacts with the closed-shell electrons $u_0(2)$ in a similar way. The wave equation for an unperturbed function u_0,

$$H_0u_0=E_0u_0, \qquad (3)$$

is considered after introducing the perturbation $H_1(2)$, and is solved for u_1 in the perturbed function u_0+u_1 from the usual second perturbation theory relation

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

We have $E_1=\langle u_0|H_1|u_0\rangle$ and $\langle u_1|u_0\rangle=0$. The charge distribution u_0+u_1 interacts with $v(3)$ via

$$H_1'(3)=\langle u_0+u_1|\frac{e^2}{r_{23}}(1-P_{23})|u_0+u_1\rangle. \qquad (5)$$

The term $\langle u_0|(e^2/r_{23})(1-P_{23})|u_0\rangle$ summed over all electrons in a closed shell vanishes. Out of the remaining two terms the leading term $2\langle u_0|(e^2/r_{23})(1-P_{23})|u_1\rangle$ is of second order. The expectation value of H_1' over $v(3)$ gives the Sternheimer perturbation energy of the site:

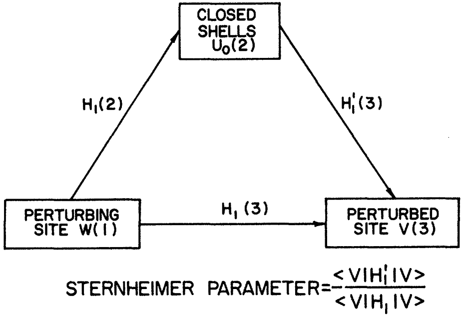

FIG. 1. Schematic diagram showing Sternheimer effect.

$$E_1'=\sum_{\text{all core electrons}}\langle v|H_1'|v\rangle. \qquad (6)$$

The Sternheimer parameter is defined as

$$R=-E_1'/E_1, \qquad (7)$$

in order to write the total perturbed energy of the site as

$$E_1(1-R). \qquad (8)$$

We shall consider only the direct quadrupole part of the Hamiltonian H_1 [Eq. (1)]:

$$H_1=e^2\langle w'|\frac{r_<^2}{r_>^3}|w'\rangle\langle Y_{l_w}^{m_w}|Y_2^0|Y_{l_w}^{m_w}\rangle Y_2^0$$
$$\equiv Af(r)Y_2^0, \qquad (9)$$

where we have written $w=w'(r)Y_{l_w}^{m_w}(\theta,\phi)$ with $w'(r)$ as r times the radial wave function of the perturbing site. Then

$$E_1=A\langle v'|f(r)|v'\rangle\langle Y_{l_v}^{m_v}|Y_2^0|Y_{l_v}^{m_v}\rangle, \qquad (10)$$

where $v=v'(r)Y_{l_v}^{m_v}$. We define $u_1=Bu_1'(r)Y_{l_1}^{m_1}$ and $u_0=u_0'(r)Y_l^m$, and write Eq. (4) as

$$(H_0-E_0)Bu_1'(r)Y_{l_1}^{m_1}(\theta,\phi)$$
$$=-A[f(r)Y_2^0-\langle u_0'|f(r)|u_0'\rangle\langle lm|Y_2^0|lm\rangle$$
$$\times u_0'(r)Y_l^m(\theta,\phi)$$

or

$$\left[-\frac{\hbar^2}{2m_e}\left(\frac{d^2}{dr^2}-\frac{l_1(l_1+1)}{r^2}\right)+V_0-E_0\right]Bu_1'Y_{l_1}^{m_1} \qquad (11)$$
$$=-A\sum_{L=|l-2|}^{l+2}(Lm|Y_2^0|lm)Y_L^m$$
$$\times[f(r)-\langle u_0'|f(r)|u_0'\rangle\delta_{Ll}]u_0'.$$

There are as many solutions of this equation as there are allowed values of L, i.e., $l_1=|l-2|$ to $l+2$, taken in steps of 2. Separating angular and radial parts,

$$BY_{l_1}^{m_1}=-\frac{2m_e}{\hbar^2}A(Lm|Y_2^0|lm)Y_l^m\Big|_{L=|l-2|\text{ to }l+2} \qquad (12)$$

and

$$\left[-\left(\frac{d^2}{dr^2}-\frac{l_1(l_1+1)}{r^2}\right)+\frac{2m_e}{\hbar^2}(V_0-E_0)\right]u_1'(l_1)$$
$$=u_0'(l)[f(r)-\langle u_0'|f(r)|u_0'\rangle\delta_{l_1l}]. \qquad (13)$$

Following Sternheimer this equation could be solved numerically by substituting V_0-E_0 from the radial wave equation of unperturbed u_0:

$$\left[-\frac{\hbar^2}{2m_e}\left(\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}\right)+V_0\right]u_0'=E_0u_0'$$

or

$$\frac{2m_e}{\hbar^2}(V_0-E_0)=\frac{1}{u_0'}\frac{d^2u_0'}{dr^2}-\frac{l(l+1)}{r^2}\,. \tag{14}$$

The perturbation Hamiltonian H_1' [Eq. (5)] becomes

$$H_1'=-\frac{2m_e}{\hbar^2}\,2Ae^2\sum_{L=|l-2|}^{l+2}(Lm|Y_2^0|lm)\left((lm|Y_2^0|Lm)\langle u_0'|\frac{r_<^2}{r_>^3}|u_1'\rangle Y_2^0-\sum_{kq}(lm|Y_k^qP_{23}|Lm)\langle u_0'|\frac{r_<^k}{r_>^{k+1}}P_{23}|u_1'\rangle Y_k^{q*}\right), \tag{15}$$

and the perturbed energy E_1' due to a closed shell nl becomes

$$E_1'(nl)=-\frac{2m_e}{\hbar^2}\,2Ae^2\sum_{m=-l}^{l}\left(2\sum_L(Lm|Y_2^0|lm)^2\langle v'|\langle u_0'|\frac{r_<^2}{r_>^3}|u_1'\rangle|v'\rangle(l_vm_v|Y_2^0|l_vm_v)\right.$$

$$\left.-\sum_L(Lm|Y_2^0|lm)\sum_{kq}(lm|Y_k^q|l_vm_v)(l_vm_v|Y_k^q|Lm)\langle v'|\langle u_0'|\frac{r^k}{r_>^{k+1}}|v'\rangle|u_1'\rangle\right). \tag{16}$$

TABLE I. α_q and λ parameters for the rare-earth ions at various sites. For La^{3+} the HF calculations are shown in parentheses.

Ion \ Site	Nucl.	$2p$	$3p$	$3d$	$4p$	$4d$	$5p$	$4f$	α_q (Å^5)
La^{3+} λ	−65.82	2.446	−0.582	−0.689	1.123	1.016	0.234		1.390
	(−59.42)	(2.145)	(+0.489)	(+0.381)	(0.990)	(0.904)	(0.184)		(1.499)
$\langle r^2\rangle$		0.01135	0.09554	0.07813	0.54933	0.64398	3.33319		
		(0.01147)	(0.09640)	(0.07930)	(0.56184)	(0.67396)	(3.58413)		
Ce^{3+} λ	−64.84	2.534	−0.749	−0.851	1.106	1.002	0.234	0.722	1.255
$\langle r^2\rangle$		0.01092	0.09140	0.07440	0.52311	0.60901	3.20378	1.06878	
Pr^{3+} λ	−63.99	2.618	−0.904	−1.001	1.089	0.987	0.234	0.719	1.139
$\langle r^2\rangle$		0.01052	0.08753	0.07093	0.49900	0.57733	3.08609	0.99613	
Na^{3+} λ	−63.23	2.695	−1.045	−1.137	1.071	0.971	0.234	0.714	1.037
$\langle r^2\rangle$		0.01014	0.08390	0.06771	0.47674	0.54845	2.97814	0.93315	
Pm^{3+} λ	−62.55	2.765	−1.170	−1.259	1.053	0.954	0.233	0.706	0.947
$\langle r^2\rangle$		0.00978	0.08049	0.06471	0.45611	0.52199	2.87845	0.87783	
Sm^{3+} λ	−61.94	2.825	−1.279	−1.365	1.034	0.936	0.232	0.697	0.867
$\langle r^2\rangle$		0.00944	0.07729	0.06191	0.43693	0.49764	2.78587	0.82874	
Eu^{3+} λ	−61.38	2.874	−1.371	−1.455	1.015	0.918	0.230	0.686	0.796
$\langle r^2\rangle$		0.00912	0.07429	0.05930	0.41906	0.47515	2.69950	0.78481	
Gd^{3+} λ	−60.87	2.912	−1.447	−1.529	0.995	0.899	0.228	0.674	0.731
$\langle r^2\rangle$		0.00881	0.07145	0.05684	0.40235	0.45430	2.61861	0.74520	
Tb^{3+} λ	−60.40	2.939	−1.506	−1.587	0.975	0.880	0.225	0.660	0.673
$\langle r^2\rangle$		0.00852	0.06878	0.05454	0.38670	0.43493	2.54259	0.70927	
Dy^{3+} λ	−59.97	2.953	−1.549	−1.631	0.956	0.861	0.223	0.646	0.621
$\langle r^2\rangle$		0.00824	0.06625	0.05238	0.37202	0.41687	2.47094	0.67651	
Ho^{3+} λ	−59.56	2.956	−1.577	−1.660	0.936	0.842	0.219	0.632	0.573
$\langle r^2\rangle$		0.00798	0.06387	0.05035	0.35821	0.40001	2.40324	0.64648	
Er^{3+} λ	-59.18	2.949	−1.591	−1.676	0.916	0.823	0.216	0.617	0.530
$\langle r^2\rangle$		0.00772	0.06161	0.04844	0.34520	0.38423	2.33911	0.61886	
Tm^{3+} λ	−58.82	2.931	−1.593	−1.681	0.897	0.804	0.212	0.603	0.490
$\langle r^2\rangle$		0.00748	0.05947	0.04663	0.33294	0.36942	2.27824	0.59336	
Yb^{3+} λ	−58.49	2.905	−1.585	−1.676	0.878	0.785	0.208	0.588	0.454
$\langle r^2\rangle$		0.00726	0.05744	0.04493	0.32135	0.35551	2.22037	0.56972	
Lu^{3+} λ	−61.39	−2.453	0.182	0.267	0.557	0.614	0.102	0.635	0.349
$\langle r^2\rangle$		0.00704	0.05552	0.04331	0.31038	0.34241	2.16524	0.54776	
Sm^{2+} λ	−73.28	1.905	−0.327	−0.557	0.976	0.867	0.204	0.584	1.092
$\langle r^2\rangle$		0.00944	0.07729	0.06190	0.44017	0.50499	3.05852	0.96779	
Eu^{2+} λ	−72.60	1.913	−0.384	−0.615	0.957	0.849	0.201	0.578	0.998
$\langle r^2\rangle$		0.00912	0.07428	0.05928	0.42198	0.48174	2.96099	0.90981	

TABLE II. Various contributions to α_q and λ's for Pr^{3+}. The exchange contributions are shown in parentheses. Figures not in parentheses are total (direct + exchange) values. Those contributions which are zero are not shown for clarity.

Perturbation \ Site	λ_0	λ_{2p}	λ_{3p}	λ_{3d}	λ_{4p}	λ_{4d}	λ_{5p}	λ_{4f}	α_q (Å^5)
$5p \to f$	0.530	1.898	−1.585	−1.452	0.710	0.663	0.184	0.521	0.783
		(−0.624)	(0.058)	(−0.292)	(0.233)	(0.052)	(−0.184)	(−0.114)	
$5p \to p$	−52.862	−0.907	−0.446	−0.804	−0.138	−0.190	0.050	−0.114	0.138
		(2.593)	(0.440)	(0.203)	(0.146)	(0.063)	(0.073)	(0.033)	
$5s \to d$	0.172	2.309	1.001	1.130	0.350	0.357	−0.017	0.243	0.205
		(1.254)	(−0.208)	(−0.201)	(−0.104)	(−0.058)	(−0.145)	(−0.042)	
$4d \to g$	0.226	0.234	0.231	0.232	0.091	0.070	0.008	0.042	0.005
		(0.003)	(−0.010)	(−0.007)	(−0.034)	(−0.026)	(−0.002)	(−0.014)	
$4d \to d$	−2.514	−0.480	−0.176	−0.109	−0.004	0.034		−0.007	0.002
		(0.734)	(0.044)	(0.164)	(0.023)	(0.051)	(−0.001)		
$4d \to s$	−0.021	−1.117	−0.419	−0.490	0.014	−0.040	−0.002	−0.030	0.001
		(−0.644)	(0.118)	(0.111)	(0.126)	(0.040)	(−0.001)	(0.009)	
$4p \to f$	0.169	0.130	0.239	0.234	0.048	0.053	0.005	0.036	0.003
		(0.019)	(−0.002)	(0.009)	(−0.048)	(−0.044)	(−0.001)	(−0.013)	
$4p \to p$	−8.011	−0.108	−0.039	−0.091	0.020	−0.003	0.001	−0.002	0.001
		(0.394)	(0.065)	(0.032)	(0.028)	(0.003)	(0.001)		
$4s \to d$	0.082	0.573	0.244	0.279	−0.009	0.039	0.004	0.029	0.002
		(0.284)	(−0.058)	(−0.053)	(−0.104)	(−0.040)	(−0.001)	(−0.010)	
$3d \to g$	0.089	0.071	0.021	0.023	0.002	0.002		0.001	
		(−0.007)	(−0.008)	(−0.008)					
$3d \to d$	−0.316	−0.039	−0.005	0.019		0.001			
		(0.106)	(−0.001)	(0.031)		(0.001)			
$3d \to s$	−0.020	−0.229	0.007	−0.042	−0.002	−0.002		−0.001	
		(−0.116)	(0.081)	(0.042)	(0.001)				
$3p \to f$	0.079	0.089	0.017	0.028	0.002	0.002		0.001	
		(−0.005)	(−0.017)	(−0.019)	(−0.001)				
$3p \to p$	−1.474	−0.009	0.012	−0.003	0.001				
		(0.073)	(0.017)	(0.006)	(0.001)				
$3s \to d$	0.047	0.185	−0.007	0.044	0.003	0.003		0.001	
		(0.077)	(−0.077)	(−0.040)	(−0.001)				
$2p \to f$	0.036	0.005		0.001					
		(−0.005)		(−0.001)					
$2p \to p$	−0.241	0.012	0.001						
		(0.016)		(−0.001)					
$2s \to d$	0.026	−0.001	0.001	0.001					
		(−0.017)		(−0.001)					
$1s \to d$	0.011								
Total	−63.990	2.618	−0.904	−1.001	1.089	0.987	0.234	0.719	1.139
		(4.134)	(0.441)	(−0.025)	(0.265)	(0.041)	(−0.261)	(−0.154)	
$\langle r^2 \rangle$		0.01052	0.08753	0.07093	0.49900	0.57733	3.08609	0.99613	
$(1-\lambda)\ \langle r^2 \rangle$		−0.017	0.167	0.142	−0.044	0.008	2.363	0.279	

The total perturbed energy E_1' is obtained by summing $E_1'(nl)$ over all n and l values of the closed shells, and the Sternheimer parameter from the definition given in Eq. (7).

When the perturbed site is the nucleus, the exchange term in Eq. (16) has no physical meaning and the Sternheimer parameter has the simple expression

$$R_0 = \frac{8m_e}{\hbar^2} \sum_{nl} \sum_{m} \sum_{L} \frac{(Lm\,|\,Y_2^0\,|\,lm)^2 \langle u_0'\,|\,r^{-3}\,|\,u_1'\rangle}{\langle w'\,|\,r^{-3}\,|\,w'\rangle} . \tag{17}$$

If the perturbing source is simply the crystal potential, then (quadrupole term only) $f(r) = r^2$ in Eq. (9) and the Sternheimer parameter is

$$\lambda_0 = \frac{8m_e}{\hbar^2} \sum_{nl} \sum_{m} \sum_{L} (Lm\,|\,Y_2^0\,|\,lm)^2 \langle u_0'\,|\,r^{-3}\,|\,u_1'\rangle . \tag{18}$$

As a by-product we obtain the quadrupole polarizability α_q of the ion from the calculated u_1':

$$\alpha_q = \frac{8m_e}{\hbar^2} e^2 \sum_{nl} \sum_{m} \sum_{L} (Lm\,|\,Y_2^0\,|\,lm)^2 \langle u_0'\,|\,r^2\,|\,u_1'\rangle . \tag{19}$$

III. COMPUTATION

The unperturbed wave functions used in the present investigation are Hartree–Fock–Slater type.[11] For La^{3+}, closed shell Hartree–Fock type[12] wave functions have also been used to compare the HFS results. HFS as well as HF functions are calculated in the convenient equally spaced logarithmic mesh,[15] $\rho=\ln(cr)$; c is a constant to select the mesh size and was set at approximately $50\times Z$ (Z is atomic number). The Numerov method of solving eigenvalue differential equations is very efficient and for its use it is convenient to define a new function $\bar{u}(r)=u'(r)/r^{1/2}$. The wave equation [Eq. (13)] then becomes (in atomic units)

$$\left(-\frac{d^2}{d\rho^2}+(l_1+\tfrac{1}{2})^2+V_0-E_0\right)\bar{u}_1(l_1) = r^2\bar{u}_0(l)\left[f(r)-\langle u_0'|f(r)|u_0'\rangle\,\delta_{l_1 l}\right]. \qquad (20)$$

We found that for heavier ions it is more reliable and convenient to use $V_0(r)$ and E_0 obtainable from the same program giving u_0, than to use Eq. (14) for V_0-E_0. For the cases $l_1\neq l$, it was only necessary to carry out outward integration of this equation. Near $r=0$, $u_1'\propto r^{l_1+1}$, and the constant of proportionality was adjusted by iteration until u_1' behaved properly at large r. The satisfactory iteration condition is simply to bring the slope of u_1' at large r to zero. Three to four iterations were enough to get a well behaved u_1'.

For the cases $l_1=l$ we first tried the procedure used for obtaining the atomic functions u_0',[15] i.e., integrated outward up to the classical turning point and then used the "tail procedure." The iteration condition was set $\langle u_1'|u_0'\rangle=0$. Although the iteration condition was easily achieved, u_1' was not smooth through the point where the tail procedure took over We gave prime importance to the orthogonality condition $\langle u_1'|u_0'\rangle=0$ in developing the new iteration scheme. The following method was found satisfactory. The outward integration was carried out up to the middle of logarithmic mesh (variable ρ) in the same way as for the cases of $l_1\neq l$ with proportionality constant x. To start inward integration it is necessary to know the value of $\bar{u}_1$ at the last three points of the mesh. At large r all the quantities in Eq. (20) are sufficiently stationary or small to permit us to write it as

$$\frac{d^2\bar{u}_1(l_1)}{d\rho^2}=N\bar{u}_1(l_1),$$

with

$$N=(l_1+\tfrac{1}{2})^2+(V_0-E_0)-(1/\bar{u}_1) \times\left\{r^2\bar{u}_0\left[f(r)-\langle u_0'|f(r)|u_0'\rangle\,\delta_{l_1 l}\right]\right\}.$$

TABLE III. The R parameters for the rare-earth ions at various sites. The exchange part of H_1 in Eq. (1) is not considered. The exchange interaction of the function u_0+u_1 with the site is included.

Ion \ Site		Nucl.	$2p$	$3p$	$3d$	$4p$	$4d$	$5p$	$4f$
Ce^{3+}	R	0.081	0.263	0.213	0.234	0.224	0.249	0.222	
	$\langle F^2\rangle$		0.05882	0.34263	0.29128	0.54828	0.53166	0.22493	0.47779
Pr^{3+}	R	0.092	0.254	0.205	0.226	0.217	0.241	0.217	0.294
	$\langle F^2\rangle$		0.06279	0.36112	0.30660	0.56673	0.54946	0.22680	0.49550
Nd^{3+}	R	0.100	0.245	0.199	0.219	0.210	0.234	0.211	0.285
	$\langle F^2\rangle$		0.06670	0.37899	0.32137	0.58442	0.56662	0.22862	0.51251
Pm^{3+}	R	0.107	0.237	0.193	0.213	0.204	0.227	0.205	0.276
	$\langle F^2\rangle$		0.07054	0.39633	0.33569	0.60148	0.58325	0.23041	0.52894
Sm^{3+}	R	0.112	0.229	0.188	0.207	0.198	0.221	0.199	0.268
	$\langle F^2\rangle$		0.07434	0.41324	0.34964	0.61804	0.59944	0.23218	0.54489
Eu^{3+}	R	0.116	0.222	0.183	0.202	0.193	0.214	0.193	0.260
	$\langle F^2\rangle$		0.07809	0.42977	0.36328	0.63418	0.61528	0.23393	0.56044
Gd^{3+}	R	0.119	0.216	0.179	0.197	0.188	0.209	0.187	0.253
	$\langle F^2\rangle$		0.08180	0.44598	0.37664	0.64995	0.63081	0.23565	0.57565
Tb^{3+}	R	0.122	0.209	0.175	0.192	0.183	0.203	0.181	0.246
	$\langle F^2\rangle$		0.08549	0.46190	0.38976	0.66542	0.64607	0.23736	0.59055
Dy^{3+}	R	0.124	0.203	0.171	0.188	0.179	0.198	0.175	0.239
	$\langle F^2\rangle$		0.08915	0.47757	0.40267	0.68061	0.66111	0.23906	0.60519
Ho^{3+}	R	0.126	0.198	0.168	0.184	0.174	0.194	0.169	0.233
	$\langle F^2\rangle$		0.09278	0.49302	0.41539	0.69557	0.67594	0.24074	0.61959
Er^{3+}	R	0.127	0.192	0.164	0.180	0.170	0.189	0.163	0.228
	$\langle F^2\rangle$		0.09639	0.50828	0.42795	0.71032	0.69060	0.24241	0.63379
Tm^{3+}	R	0.128	0.187	0.161	0.177	0.167	0.185	0.158	0.222
	$\langle F^2\rangle$		0.09999	0.52335	0.44036	0.72489	0.70510	0.24408	0.64780
Yb^{3+}	R	0.128	0.182	0.158	0.173	0.163	0.181	0.152	0.217
	$\langle F^2\rangle$		0.10356	0.53826	0.45264	0.73929	0.71946	0.24573	0.66164
Sm^{2+}	R	0.124	0.229	0.196	0.214	0.198	0.221	0.175	0.270
	$\langle F^2\rangle$		0.06898	0.38546	0.32583	0.59000	0.57286	0.22301	0.50734
Eu^{2+}	R	0.128	0.221	0.190	0.208	0.193	0.215	0.170	0.262
	$\langle F^2\rangle$		0.07283	0.40278	0.34015	0.60729	0.58969	0.22459	0.52390

The solution is

$$\bar{u}_1 \propto e^{-\sqrt{N}\rho}.$$

The values of $\bar{u}_1$ at the last three points were determined from this relation within a proportionality constant y, and the inward integration was carried out up to the middle of the mesh. The Raphson method of iteration of the multiple variable equation[16] was used for adjusting x and y such that the solution is orthogonal to u_0 and is continuous. Continuity of slope was automatically achieved by this procedure. For $l_1 \neq l$ we tried the method used for $l_1 = l$ but with orthogonality criterion replaced by continuity of slope $\bar{u}_1$ at the matching point. The results thus obtained were the same as using only the outward integration method, but the number of iterations needed were usually two and rarely three. We therefore adopted this procedure.

Angular integrals were computed in the computer as in an earlier work.[9] A check was made by hand calculation for a few random cases, and by comparison with already known integrals.[5]

The total time taken, for the results reported in this paper (including the calculation of u_0') was 20 min on IBM-360-65 computer at the University of Manitoba.

IV. RESULTS

The free-ion λ parameters for rare earths are presented in Table I. Various contribution to λ are shown in Table II for the case of Pr^{3+}. The R parameters are given in Table III and the various contributions to R for Pr^{3+} are shown in Table IV. $\langle F^2\rangle$ is $\langle v'|\langle w'|r_<^2/r_>^3|w'\rangle|v'\rangle$. The self-interaction terms[9] have been substracted from sites where applicable. The parameters λ_0, R_0, and λ_{4f} as functions of atomic number Z are plotted in Figs. 2, 3, and 4, respectively. The smooth variation of these parameters against Z is apparent from the figures. The $4f$ shell is completely filled for Lu^{3+} and therefore its perturbation due to external potential is essential to include with other perturbations. This gives rise to the displacement of the point for Lu^{3+} from the smooth curves.[17]

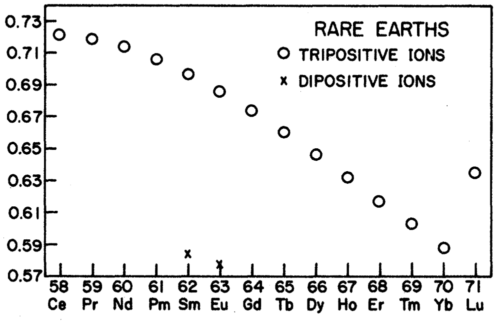

FIG. 3. Parameter λ_{4f} as a function of atomic number Z for the rare-earth ions.

In a previous paper[9] we reported λ's for Pr^{3+} and Tm^{3+} ions. There is appreciable difference between those results and the ones calculated here (Table V). This is because, in that paper, we used atomic wave functions for the ions since good ionic wave functions were not available to us.

The importance of the Sternheimer parameters at the core-electron sites has been shown[10] to lie in the calculation of the inner-shell vacancy energy levels. The parameters R_{4f} signify the role played by closed shells on the interaction of two $4f$ electrons, and could be useful in calculating multiplet energies of the free ions with more than one electron in the open shell.

In Table V we compare the results calculated here with existing experimental and theoretical values. To get experimental values, knowledge of the quadrupole moment of the ions' nuclei is generally required. Since the quadrupole moments Q are not known with great certainty the results cannot be taken very seriously. The ratio $\rho \equiv (1-\lambda_0)/$

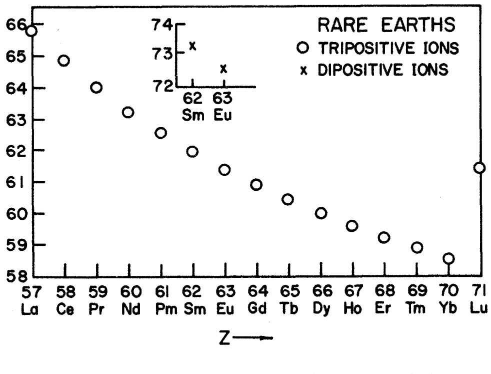

FIG. 2. Parameter $-\lambda_0$ shown as a function of the atomic number Z for the rare-earth ions.

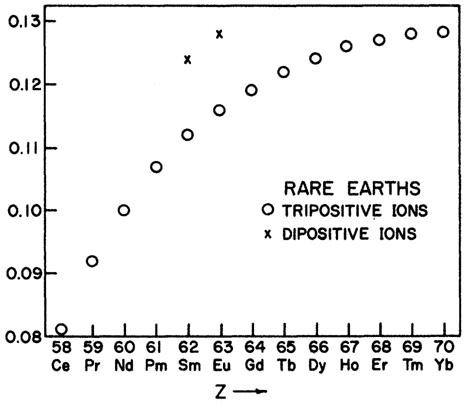

FIG. 4. Sternheimer parameter R_0 vs atomic number Z for the rare-earth ions.

$(1-\lambda_{4f})(1-R_0)$ or $\alpha \equiv (1-\lambda_0)/(1-\lambda_{4f})$, is the measurable quantity and not the individual Sternheimer parameters. The experimental ratio α, therefore, is compared with its theoretical value in the table.

It is hoped that the nature of the Z dependence of various Sternheimer parameters shown in Figs. 2–4 and Tables I and III will help extrapolation of the parameters for various other ions.

The comparison of the results of Sm^{3+} and Eu^{3+} with those of Sm^{2+} and Eu^{2+} shows that the Sternheimer parameters are sensitive to the ionic charge. This introduces complications when we realize that experimentally the parameters are measured in compounds, and the wave functions of the outermost shells ($5p$ and $5s$) contributing most significantly to the shielding-antishielding may be appreciably distorted owing to overlap with the negative ligand ions. Then the ion potential function appropriate to the physical situation will be different from the free-ion potential $V_0(r)$ used in Eq. (20). For free ions, an orbital energy E_0 is easily defined as the energy required to remove the electron to infinity in field free space. It seems desirable that E_0 be redefined for ions in a compound before substituting in Eq. (20). It ap-

TABLE IV. Various contributions to R's for Pr^{3+}. The exchange part of H_1 in Eq. (1) is not considered. The contributions to R's due to the exchange interaction of the function u_0+u_1 with the site are shown in the parantheses. The figures not in parentheses are total (direct + exchange) values. Those contributions which are zero are not shown for clarity.

Site Perturbation	Nucl.	$2p$	$3p$	$3d$	$4p$	$4d$	$5p$	$4f$
$5p \to f$	0.007	0.015	−0.005	−0.004	0.044	0.048	0.122	0.065
		(−0.003)		(−0.002)	(0.005)	(−0.001)	(−0.122)	(−0.014)
$5p \to p$	0.516	0.009	0.006	0.011	0.008	0.011	−0.036	0.012
		(−0.027)	(−0.007)	(−0.003)	(−0.007)	(−0.004)	(−0.048)	(−0.004)
$5s \to d$	0.003	0.044	0.027	0.029	0.034	0.041	−0.011	0.051
		(0.024)	(−0.006)	(−0.005)	(−0.011)	(−0.008)	(−0.162	(−0.010)
$4d \to g$	0.040	0.043	0.059	0.057	0.067	0.061	0.069	0.069
		(0.001)	(−0.003)	(−0.002)	(−0.027)	(−0.023)	(−0.008)	(−0.022)
$4d \to d$	0.064	0.014	0.006	−0.002		−0.005)	−0.001	0.003
		(−0.022)	(−0.001)	(−0.012)	(−0.004)	(−0.008)	(0.003)	(0.001)
$4d \to s$	−0.014	−0.122	−0.075	−0.082	0.008	−0.043	−0.050	−0.066
		(−0.063)	(0.018)	(0.016)	(0.106)	(0.043)	(0.013)	(0.023)
$4p \to f$	0.032	0.025	0.071	0.066	0.047	0.061	0.066	0.077
		(0.004)	(−0.001)	(0.003)	(−0.047)	(−0.050)	(−0.009)	(−0.027)
$4p \to p$	0.185	0.001	−0.003	0.002	−0.002	0.001	−0.002	0.001
		(−0.013)	(−0.006)	(−0.002)	(−0.003)		(−0.001)	
$4s \to d$	0.014	0.130	0.077	0.084	−0.008	0.049	0.050	0.068
		(0.067)	(−0.019)	(−0.017)	(−0.108)	(−0.049)	(−0.013)	(−0.023)
$3d \to g$	0.067	0.054	0.020	0.022	0.006	0.006	0.003	0.005
		(−0.006)	(−0.008)	(−0.008)	(−0.001)	(−0.001)		(−0.001)
$3d \to d$	−0.147	−0.016	−0.003	0.011	0.001	0.003	0.001	
		(0.051)	(−0.001)	(0.017)		(0.002)		(−0.001)
$3d \to s$	−0.019	−0.146	0.007	−0.038	−0.009	−0.010	−0.004	−0.009
		(−0.070)	(0.078)	(0.038)	(0.003)	(0.001)	(0.001)	(0.002)
$3p \to f$	0.054	0.064	0.016	0.026	0.008	0.007	0.004	0.007
		(−0.004)	(−0.016)	(−0.018)	(−0.001)	(−0.001)		(−0.002)
$3p \to p$	−0.591	−0.007	0.007	−0.001	0.002		0.001	
		(0.026)	(0.009)	(0.004)	(0.001)			
$3s \to d$	0.030	0.133	−0.007	0.042	0.011	0.011	0.005	0.011
		(0.056)	(−0.078)	(−0.039)	(−0.003)	(−0.002)	(−0.001)	(−0.002)
$2p \to f$	0.035	0.005	0.001	0.001				
		(−0.005)		(−0.001)				
$2p \to p$	−0.223	0.011	0.001					
		(0.015)		(−0.001)				
$2s \to d$	0.025	−0.001	0.001	0.001				
		(−0.017)		(−0.001)				
$1s \to d$	0.011							
Total	0.092	0.254	0.205	0.226	0.217	0.241	0.217	0.294
		(0.015)	(−0.042)	(−0.033)	(−0.096)	(−0.101)	(−0.347)	(−0.080)
$\langle F^2 \rangle$		0.06279	0.36112	0.30660	0.56673	0.54946	0.22680	0.49550
$(1-R)\ \langle F^2 \rangle$		0.047	0.287	0.237	0.444	0.417	0.178	0.350

TABLE V. Comparison of present work with existing theoretical and experimental works.

Ion \ Parameter	R_0		λ_0		λ_{4f}		$\alpha = (1-\lambda_0)/(1-\lambda_{4f})$	
	This work	Other works	This work	Other works	This work	Other works	This work	Experimental
La^{3+}			−65.82 −59.42[e]	−68[a] −76[a]				−300 ± 40[b,c,d] ± 550[d]
Ce^{3+}	0.081		−64.84	−71[a] −73.5[g]	0.722		237	
Pr^{3+}	0.092	0.1308[h]	−63.99	−105[i]	0.706	0.41[j] 0.25[j]	221	
		0.200[m]		−16.37[l] −80.9[h] −84.8[k] −80.82[m]		0.524[l] 0.59[m] 0.672[n] 0.745[k]		
Nd^{3+}	0.100		−63.23	−65[o]	0.714	0.792[o]		
Eu^{3+}	0.116		−61.38		0.686		200	300 ± 40[b,c]
Gd^{3+}	0.119		−60.87		0.674		200	193 ± 40[b,c]
Dy^{3+}	0.124		−59.97		0.646		172	262 ± 30[c]
Ho^{3+}	0.126		−59.56		0.632		165	208[f]
Tm^{3+}	0.128	0.1296[h]	−58.82	−61.5[i]	0.603	0.70[m]	151	250[p]
		0.150[m]		−75.3[h] −74.16[m]		0.545[n] 0.601[k]		
Yb^{3+}	0.128		−58.49	−79[a]	0.588		144	
Lu^{3+}			−61.39		0.635		171	140 ± 20[b,c]

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pears at this stage that future efforts on Sternheimer effect need be concentrated on the calculation of shielding-antishielding parameters for ions in solids than for free ions. The concept of using linear Sternheimer parameters, Eq. (8), is questionable[7] and needs reexamination. Nevertheless it will remain of interest to know the free-ion Sternheimer parameter realistic models are developed.

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[17] However, as we move from Ce^{3+} to Lu^{3+}, the $4f$ shell is gradually being filled up. The shielding-antishielding of the unfilled $4f$ shell should therefore be considered and included for each case presented here. One prescription would be to calculate the $4f$-shell effect by first considering it to be complete and then include only that fraction of it which is filled. The downward trend $-\lambda_0$ and λ_{4f} with increasing Z would then be reduced.

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Bethe–Salpeter Equation: Numerical Experience with a Hydrogenlike Atom*

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As a test of the accuracy of numerical techniques used in solving the Bethe–Salpeter equation, we compute the binding energy of a hydrogenlike atom including one-photon exchange only. A 5% deviation from the result predicted from the Dirac equation with a Coulomb potential is in agreement with a result which we derive analytically, $E_b = (1/4)m\alpha^2[1-(4\alpha/\pi)\ln(2/\alpha)+\cdots]$. E_b cannot be expanded in a power series in α^2 similar to the series expansion of the Sommerfeld expression for E_b resulting from the Dirac theory. This apparently startling result is not due to a failure of quantum electrodynamics, of course, but to the fact that we have used the relativistic interaction $\gamma_\mu^{(1)}(1/k^2)\gamma_\mu^{(2)}$ rather than working in the Coulomb gauge as is usually done. Salpeter remarked in 1952 that doing the calculation as we have done it would result in a slowly convergent series for E_b; nevertheless the precise magnitudes involved are surprising.

I. INTRODUCTION

We began this work as a check on the numerical accuracy of techniques[1,2] for solving the Bethe–Salpeter equation appropriate to the scattering problem for two fermions. We assumed that the binding energy of the ground state of a hydrogenlike atom[3] composed of two fermions with opposite charges $\pm e$ ($-e$ is the electron charge; $e^2/4\pi = 1/137.03802$) and equal mass m (m is the electron mass; $m = 0.51100410$ MeV) is well known and that a calculation of this quantity would provide such a check.

The Bethe–Salpeter equation for the scattering problem is, symbolically,

$$\varphi = G + (1/\pi^2)GS\varphi\ , \tag{1}$$

where G includes all irreducible graphs (graphs without two-particle cuts) and S is the product of the fermion propagators. (For notation and more details consult our earlier paper, Ref. 2.) The bound-state problem is obtained by dropping the inhomogeneous term; then the Bethe–Salpeter equation becomes

$$\varphi = (1/\pi^2)GS\varphi\ . \tag{2}$$

Much of the formalism of Ref. 2 is simplified for the bound-state problem: because the total energy