Sternheimer Antishielding Functions $\beta(r)$ and $\gamma(r)$ for Rare Earth Atoms*

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The Sternheimer shielding-antishielding functions $\beta(r)$ and $\gamma(r)$ are reported for all the fourteen lanthanide atoms at the uncoupled Hartree-Fock level of theory. Each atom is considered in two valence state configurations, $4f^n 5d^0$ and $4f^{n-1} 5d^1$, and the nonrelativistic HF wave functions have been used. The $5d^1$ configuration leads to a smaller net antishielding than the $4f^n$ configuration by $\sim 6-12\%$ in the series. The electron-electron self consistency effects are found to be less than 5% in the series. The importance of the calculated antishielding functions in the antishielding theory of electric field gradients in noncubic metals is discussed.

I. Introduction

The conventional theoretical analysis of the electric field gradient (EFG) data in noncubic metals as the sum of two terms, namely the lattice and conduction electron contributions, is now known to be oversimplified [1]. It has been argued [2] that the quadrupolar polarization of the core electrons represented in the conventional model by the Sternheimer shielding-antishielding factors [3] γ_∞ and R should be generalised in terms of the Sternheimer shielding-antishielding functions $\beta(r)$ and $\gamma(r)$, respectively, so as to appropriately include the quadrupolar polarization of the conduction electron density. Lodge [4] has derived an energy-based antishielding theory for noncubic metals correct to first order which leads to the following expression for the total EFG at a given quadrupolar nucleus:

$$Q V_{zz} = Q V_{zz}^{\text{latt}} - \gamma_\infty Q V_{zz}^{\text{latt}} + Q V_{zz}^{\text{cond}} - Q \int_0^\infty \gamma(r)\, V_{zz}^{\text{cond}}(r)\, \mathrm{d}r - V_{zz}^{\text{latt}} \int_0^\infty \beta(r)\, Q_i^{\text{cond}}(r)\, \mathrm{d}r - \int_0^\infty Q_i^{\text{cond}}(r)\, r^{-5} \cdot \left\{ \int_0^r [\beta(r') + \gamma(r) - \gamma_\infty]\, r'^5\, V_{zz}^{\text{cond}}(r')\, \mathrm{d}r' \right\} \mathrm{d}r - \int_0^\infty Q_i^{\text{cond}}(r) \left\{ \int_r^\infty [\beta(r) + \gamma(r') - \gamma_\infty]\, V_{zz}^{\text{cond}}(r')\, \mathrm{d}r' \right\} \mathrm{d}r \quad (1)$$

In (1) the seven contributions arise respectively from 1) the usual lattice EFG interacting with the nuclear electric quadrupole moment, Q, 2) the antishielded lattice EFG interacting with Q, 3) the usual conduction electron EFG interacting with Q, 4) the antishielded conduction electron EFG interacting with Q, 5) the lattice EFG interacting with the antishielded induced moment in the conduction electrons, 6) the induced EFG in the conduction electrons outside r interacting with the usual conduction electron moment inside r, and 7) the usual conduction electron EFG outside r interacting with the induced moment in the conduction electrons inside r. In the contributions 6)–7) the moment is antishielded by $\beta(r)$ and the EFG is antishielded by $\gamma(r)$, and a correction is to be made for counting the interaction twice on integration over r. In a recent calculation [5] such additional EFG arising from the quadrupolar polarization of the conduction electrons has been estimated for Be and Mg metals to be of the order of -1.5% and 12.8%, respectively, relative to the conventional conduction electron contribu-

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tion. It is therefore necessary to know the $\beta(r)$ and $\gamma(r)$ functions particularly for atoms with large core size in order to interpret the available EFG data on noncubic metals.

Whereas several previous calculations [6] exist in the literature for $\gamma(r)$ of atoms, the dual antishielding function $\beta(r)$ has so far been calculated only in the cases of Be^{2+}, Mg^{2+}, Zn^{2+} and Ga^{3+} ions [7]. Such calculations have been performed within the nonorthogonal Hartree-Fock (HF) perturbation method [8].

In this paper we report calculations of $\beta(r)$ for the core electrons corresponding to the fourteen rare earth atoms Ce-Lu within the uncoupled numerical HF method due to Sternheimer [3]. In order to estimate the effect of the changes in the valence electron configuration we have considered two different valence orbital occupations $4f^n 5d^m$ and $4f^{n-1} 5d^{m+1}$ for all atoms except Lu, in which case only the $4f^{14} 5d^1$ configuration has been included. We also report here the calculations of $\gamma(r)$ in all these cases. We note here that $\gamma(r)$ for Pr has been reported earlier [6c], and that the calculations of γ_∞ and R have been carried out by several workers for the rare earth atoms [3, 11–12]. We further report the results of our calculations of the consistency effects for a few representative elements in the series in order to obtain a coupled HF estimate of γ_∞ in this region of the periodic table. Such estimates enable us to provide the error bar over the reported $\beta(r)$ and $\gamma(r)$ functions.

In Sect. II we present a brief outline of the method of calculation. The results are presented and discussed in Sect. III. Finally, the main conclusions arrived at in the present work are listed in Section IV.

II. Method of Calculation

a) Unperturbed Wave Functions

The core electron configuration of the atoms has been defined as the one isoelectronic with Xe. The triple zeta outer shell non-relativistic Roothaan HF wave functions reported recently for the neutral atoms in the configurations $4f^n 5d^m$ and $4f^{n-1} 5d^{m+1}$ [9] have been used in this work to describe the unperturbed atoms. The radial wave functions have been generated over a 441-mesh.

b) Calculation of $\gamma(r)$

The nuclear moment perturbed uncoupled differential equation (DE)

$$\left[-\frac{d^2}{dr^2}+\frac{l'(l'+1)}{r^2}+V_0^{HF}(nl)-\varepsilon_0^{nl}\right]u_1(nl\to l') = u_0(nl)\,(r^{-3}-\langle r^{-3}\rangle_{nl}\,\delta_{ll'}) \quad (2)$$

has been solved numerically for all the quadrupolar perturbations of the core electrons $u_1(nl\to l')$ using an iterative computer code described earlier [6b]. The Sternheimer antishielding function $\gamma(r)$ is calculated according to

$$\gamma(r)=\sum_n\sum_{ll'}\frac{C_{ll'}}{Q}\left(\int_0^r u_0(nl)\,u_1(nl\to l')\,r'^2\,dr' + r^5\int_r^\infty r'^{-3}\,u_0(nl)\,u_1(nl\to l)\,dr'\right). \quad (3)$$

$\gamma(r)$ as defined in (3) measures the total radial quadrupole moment density at r induced in the core by the nuclear quadrupole moment Q. At $r=\infty$, $\gamma(\infty)$ equals the Sternheimer ionic antishielding factor γ_∞.

c) Calculation of $\beta(r)$

An equivalent external charge perturbed DE approach of calculating γ_∞ can be derived from the result that the ratio of the total induced EFG to the external EFG is the same as the ratio of the total induced quadrupole moment to the nuclear quadrupole moment Q. The resulting DE

$$\left[-\frac{d^2}{dr^2}+\frac{l'(l'+1)}{r^2}+V_0^{HF}(nl)-\varepsilon_0^{nl}\right]u_1'(nl\to l') = u_0(nl)\,(r^2-\langle r^2\rangle_{nl}\,\delta_{ll'}) \quad (4)$$

has been solved numerically in a manner similar to that employed for (2) to obtain the charge perturbed wave functions $u_1'(nl\to l')$ for the various radial ($l=l'$) and the angular $|l-l'|=2$ polarizations of all the core electrons. The Sternheimer antishielding function $\beta(r)$ is calculated according to

$$\beta(r)=\sum_r\sum_{ll'}\frac{C_{ll'}}{V_{zz}^{latt}}\left(r^{-5}\int_0^r r'^2\,u_0(nl)\,u_1'(nl\to l')\,dr' + \int_r^\infty u_0(n\,l)\,u_1'(nl\to l')\,r'^{-3}\,dr'\right). \quad (5)$$

The function $\beta(r)$ as defined in (5) measures the total induced EFG density in the core at r which originates from the perturbing effect of an external source charge. At $r = 0$, the function $\beta(r)$ equals γ_∞. At other values of r there is no direct relationship between the two antishielding functions $\beta(r)$ and $\gamma(r)$ except that $\beta(r)$ approaches zero as $r \to \infty$ and $\gamma(r)$ approaches zero as $r \to 0$.

The uncoupled DE approaches adopted in this work and described in subsections b) and c) above were originally developed and applied by Sternheimer [3].

d) Calculation of the Consistency Effect

We have employed the perturbed wave functions u_1 and u_1' to calculate the electron consistency effects using a theoretical model [10] which uses the essence of the many body perturbation theory. Such calculations reported here for Ce, Pr, Eu and Tm in the two valency configurations provide values of γ_∞ for rare earth atoms at the coupled HF level of accuracy.

III. Results and Discussion

The results of our calculations on $\beta(r)$ for the rare earth atoms Ce-Lu in $4f^n\,5d^m$ (denoted as f) and $4f^{n-1}\,5d^{m+1}$ (denoted as d) configurations are given in Table 1. In f configuration n varies from 1 – 14 for Ce-Lu and $m = 0$. In d configuration one of the electrons from the 4f orbital is placed in 5d. In the representative case of Eu we have plotted the function $\beta(r)$ corresponding to the two configurations in Figure 1. As noted in Sect. II, the value of $\beta(r)$ at $r = 0$ gives the charge perturbed ionic antishielding factor γ_∞. Calculations of γ_∞ for the Xe-like core in the rare earth atoms Pr and Tm have been reported earlier by several workers [3, 11, 6c]. Gupta and Sen [12] have also carried out such calculations of γ_∞ for all the rare earth tripositive ions using Hartree-Fock-Slater wave functions. The present calculations of $\beta(0)$ are in excellent agreement with the earlier calculations of Gupta et al. [11], who also employed HF wave functions.

We shall first discuss the general trends observed in Table 1. For the d configuration, $\beta(r)$ at $r = 0$ decreases in the series from -76 to -67. An extremely rapid decrease to almost 1% of the maximum value of $\beta(r)$ is attained at $\sim 0.2\,a_0$. This is

Table 1. Sternheimer $\beta(r)$ function for the core electrons in the rare earth atoms (La-Lu). The core configuration is defined as $(4d^{10}\ 5s^2\ 5p^6)$. The term d represents the valence configuration $(5d^1\ 4f^{n-1})$ and the term f denotes the valence electron configuration $(5d^0\ 4f^n)$. All r values are given in multiples of $a_0 = 0.5292$ Å. At $r = 0$, $\beta(0) = \gamma_\infty$ as derived using the uncoupled numerical charge perturbed Hartree-Fock method.

r	Ce		Pr	
	d	f	d	f
0.0	−75.71	−79.59	−73.70	−78.43
0.01	−69.51	−72.94	−67.58	−72.04
0.02	−58.28	−60.75	−56.59	−60.41
0.03	−45.51	−46.82	−44.08	−47.13
0.04	−35.38	−35.61	−34.11	−36.52
0.05	−26.08	−25.11	−24.89	−26.68
0.06	−19.69	−17.68	−18.47	−19.82
0.07	−14.32	−11.21	−12.97	−13.96
0.08	−10.86	− 6.85	− 9.34	−10.10
0.09	− 7.81	− 2.84	− 6.08	− 6.63
0.10	− 6.12	− 0.53	− 4.22	− 4.67
0.11	− 4.90	1.17	− 2.87	− 3.24
0.12	− 4.00	2.38	− 1.89	− 2.20
0.13	− 3.33	3.20	− 1.06	− 1.30
0.14	− 2.71	3.80	− 0.62	− 0.81
0.14	− 2.32	4.02	− 0.32	− 0.46
0.16	− 1.98	4.05	− 0.12	− 0.21
0.17	− 1.69	3.94	0.04	0.04
0.17	− 1.29	3.54	0.09	0.14
0.18	− 1.04	3.17	0.10	0.21
0.19	− 0.81	2.74	0.09	0.25
0.21	− 0.59	2.26	0.06	0.27
0.22	− 0.38	1.75	0.02	0.28
0.23	− 0.18	1.23	− 0.03	2.27
0.23	0.00	0.69	− 0.09	0.26
0.24	0.17	0.16	− 0.19	0.22
0.25	0.33	− 0.36	− 0.26	0.19
0.26	0.54	− 1.09	− 0.33	0.16
0.27	0.66	− 1.55	− 0.40	0.13
0.28	0.77	− 1.98	− 0.47	0.09
0.29	0.87	− 2.37	− 0.53	0.06
0.39	1.30	− 4.24	− 0.79	− 0.09
0.48	1.25	− 3.15	− 0.35	− 0.16
0.58	1.16	− 1.49	0.33	0.54
0.68	1.08	0.01	0.84	0.82
0.79	1.01	0.95	1.18	0.99
0.88	0.97	1.40	1.33	1.06
0.97	0.92	1.61	1.35	1.06
1.06	0.84	1.56	1.24	0.99
1.17	0.84	1.56	1.24	0.99
1.27	0.80	1.46	1.13	0.92
1.36	0.75	1.32	1.04	0.86
1.45	0.69	1.18	0.92	0.79
1.56	0.65	1.09	0.82	0.72
1.67	0.59	0.96	0.75	0.67
1.74	0.54	0.84	0.66	0.61
1.85	0.50	0.77	0.57	0.54
1.96	0.44	0.67	0.52	0.50
2.04	0.39	0.58	0.45	0.44
2.15	0.36	0.53	0.39	0.39

Table 1. Continued

r	Nd		Pm		Sm	
	d	f	d	f	d	f
0.0	−70.57	−73.47	−66.72	−76.98	−73.40	−79.96
0.01	−64.46	−66.28	−60.43	−69.66	−66.30	−72.32
0.02	−54.19	−54.34	−50.08	−57.51	−54.68	−59.68
0.03	−43.07	−41.98	−39.20	−44.79	−42.50	−46.47
0.04	−32.40	−30.69	−29.06	−33.01	−31.20	−34.22
0.05	−24.46	−22.71	−21.75	−24.56	−22.18	−24.47
0.06	−17.34	−15.96	−15.41	−17.27	−16.02	−17.84
0.07	−12.47	−11.61	−10.34	−11.45	−10.38	−11.80
0.08	− 7.95	− 7.83	− 7.45	− 8.15	− 7.16	− 8.37
0.09	− 5.33	− 5.77	− 5.33	− 5.75	− 4.80	− 5.88
0.10	− 3.39	− 4.31	− 3.79	− 4.01	− 2.74	− 3.71
0.11	− 1.96	− 3.28	− 2.45	− 2.51	− 1.62	− 2.52
0.12	− 0.72	− 2.39	− 1.70	− 1.69	− 0.82	− 1.67
0.13	− 0.05	− 1.90	− 1.16	− 1.10	− 0.16	− 0.95
0.14	0.41	− 1.52	− 0.69	− 0.61	0.17	− 0.56
0.14	0.78	− 1.17	− 0.43	− 0.35	0.37	− 0.29
0.16	0.95	− 0.94	− 0.23	− 0.17	0.51	− 0.07
0.17	1.05	− 0.71	− 0.05	− 0.03	0.54	0.05
0.17	1.07	− 0.55	0.06	0.04	0.53	0.12
0.18	1-05	− 0.41	0.14	0.07	0.45	0.18
0.19	1.01	− 0.29	0.20	0.08	0.36	0.19
0.21	0.94	− 0.19	0.26	0.06	0.27	0.19
0.22	0.86	− 0.10	0.29	0.03	0.16	0.17
0.23	0.72	0.00	0.31	− 0.01	0.04	0.15
0.23	0.63	0.06	0.32	− 0.05	− 0.07	0.12
0.24	0.53	0.10	0.32	− 0.11	− 0.19	0.09
0.25	0.44	0.14	0.31	− 0.16	− 0.36	0.03
0.26	0.35	0.16	0.31	− 0.22	− 0.46	− 0.00
0.27	0.27	0.18	0.29	− 0.30	− 0.56	− 0.04
0.28	0.19	0.19	0.28	− 0.35	− 0.65	− 0.07
0.29	0.08	0.20	0.27	− 0.40	− 0.73	− 0.10
0.39	− 0.19	0.23	0.24	− 0.52	− 0.90	− 0.16
0.48	0.07	0.41	0.46	− 0.06	− 0.28	0.20
0.58	0.48	0.65	0.70	0.43	0.43	0.61
0.68	0.78	0.83	0.87	0.83	0.90	0.87
0.79	0.93	0.91	0.94	1.04	1.14	0.99
0.88	1.01	0.93	0.95	1.11	1.21	1.03
0.97	1.01	0.92	0.93	1.10	1.19	1.00
1.06	0.98	0.89	0.89	1.06	1.14	0.96
1.17	0.92	0.85	0.84	1.00	1.04	0.90
1.27	0.87	0.81	0.78	0.92	0.96	0.84
1.36	0.79	0.75	0.73	0.85	0.87	0.78
1.45	0.73	0.71	0.67	0.78	0.76	0.70
1.56	0.66	0.65	0.61	0.71	0.70	0.65
1.67	0.59	0.59	0.54	0.63	0.61	0.58
1.74	0.54	0.55	0.50	0.58	0.53	0.52
1.85	0.48	0.49	0.44	0.52	0.48	0.48
1.96	0.42	0.44	0.39	0.45	0.42	0.42
2.04	0.39	0.40	0.34	0.40	0.36	0.37
2.15	0.34	0.36	0.31	0.36	0.31	0.32

Table 1. Continued

r	Eu		Gd		Tb	
	d	f	d	f	d	f
0.0	−70.09	−76.09	−76.38	−76.75	−69.68	−75.44
0.01	−63.00	−68.44	−68.56	−69.03	−62.06	−67.60
0.02	−51.52	−55.98	−56.00	−56.48	−49.29	−54.22
0.03	−38.36	−41.72	−41.70	−42.09	−36.57	−40.71
0.04	−28.84	−31.43	−31.46	−31.68	−26.03	−29.36
0.05	−20.35	−22.29	−22.44	−22.40	−18.81	−21.50
0.06	−14.05	−15.54	−15.86	−15.51	−12.83	−14.93
0.07	− 9.54	−10.74	−11.24	−10.57	− 8.66	−10.31
0.08	− 6.68	− 7.71	− 8.37	− 7.44	− 5.55	− 6.84
0.09	− 4.20	− 5.10	− 5.93	− 4.73	− 3.87	− 4.95
0.10	− 2.84	− 3.68	− 4.61	− 3.25	− 2.69	− 3.62
0.11	− 1.88	− 2.66	− 3.46	− 1.98	− 1.70	− 2.48
0.12	− 1.06	− 1.79	− 2.81	− 1.30	− 1.16	− 1.86
0.13	− 0.62	− 1.31	− 2.31	− 0.82	− 0.71	− 1.31
0.14	− 0.32	− 0.96	− 1.81	− 0.42	− 0.48	− 1.00
0.14	− 0.07	− 0.64	− 1.47	− 0.21	− 0.32	− 0.77
0.16	0.05	− 0.45	− 1.16	− 0.07	− 0.17	− 0.51
0.17	0.12	− 0.31	− 0.74	0.06	− 0.13	− 0.38
0.17	0.17	− 0.15	− 0.48	0.10	− 0.11	− 0.27
0.18	0.17	− 0.07	− 0.23	0.11	− 0.11	− 0.19
0.19	0.15	− 0.02	0.00	0.11	− 0.14	− 0.12
0.21	0.11	0.03	0.22	0.09	− 0.20	− 0.05
0.22	0.06	0.06	0.51	0.04	− 0.26	− 0.02
0.23	0.01	0.07	0.69	− 0.00	− 0.32	0.01
0.23	− 0.08	0.08	0.84	− 0.05	− 0.38	0.02
0.24	− 0.15	0.08	0.98	− 0.10	− 0.45	0.03
0.25	− 0.21	0.08	1.11	− 0.14	− 0.55	0.03
0.26	− 0.27	0.07	1.22	− 0.19	− 0.61	0.03
0.27	− 0.33	0.05	1.35	− 0.25	− 0.66	0.02
0.28	− 0.38	0.04	1.42	− 0.29	− 0.71	0.02
0.29	− 0.45	0.02	1.48	− 0.32	− 0.75	0.01
0.39	− 0.49	0.04	0.58	− 0.29	− 0.64	0.10
0.48	0.02	0.35	1.29	0.18	0.02	0.43
0.58	0.55	0.66	1.01	0.59	0.61	0.72
0.68	0.88	0.85	0.76	0.86	0.95	0.88
0.79	1.04	0.93	0.61	0.99	1.09	0.93
0.88	1.08	0.93	0.53	1.01	1.11	0.92
0.97	1.05	0.91	0.51	0.98	1.06	0.88
1.06	1.00	0.87	0.49	0.92	0.99	0.84
1.17	0.92	0.82	0.49	0.86	0.90	0.78
1.27	0.85	0.77	0.48	0.79	0.82	0.72
1.36	0.76	0.71	0.46	0.73	0.73	0.66
1.45	0.68	0.64	0.44	0.66	0.66	0.61
1.56	0.60	0.58	0.41	0.59	0.58	0.54
1.67	0.55	0.54	0.37	0.52	0.50	0.49
1.74	0.48	0.48	0.35	0.48	0.46	0.45
1.85	0.42	0.43	0.31	0.43	0.40	0.40
1.96	0.38	0.39	0.28	0.37	0.34	0.35
2.04	0.33	0.35	0.26	0.34	0.29	0.30
2.15	0.29	0.30	0.22	0.30	0.27	0.28

noted throughout the series. In f configuration an increase in the $\beta(0)$ value is noted for all the atoms. The $\beta(0) = \gamma_\infty$ values now decrease from -81 to -69 down the rare earth series. We consider this increase of 6–12% in going from the d to the f configuration to be significant. As seen from Fig. 1, the entire $\beta(r)$ function is significantly contracted in the f configuration. In the rare earths one frequently encounters changes in the valence states and parallel changes in the antishielding function $\beta(r)$, which should have important consequences via the terms 5)–7) in (1).

In Table 2 we have presented the analogous results for $\gamma(r)$. The shape of this function in the

Table 1. Continued

r	Dy		Ho		Er	
	d	f	d	f	d	f
0.0	−69.72	−78.36	−69.31	−75.07	−68.20	−69.79
0.01	−62.46	−70.13	−60.81	−66.55	−60.82	−62.30
0.02	−50.24	−56.22	−46.91	−52.36	−48.59	−49.78
0.03	−37.90	−42.34	−33.51	−38.40	−36.30	−37.24
0.04	−27.54	−30.89	−22.76	−26.90	−25.96	−26.76
0.05	−19.60	−22.31	−14.86	−18.39	−17.98	−18.74
0.06	−14.38	−16.82	− 9.33	−12.29	−12.12	−12.91
0.07	−10.17	−12.53	− 5.24	− 7.71	− 7.56	− 8.44
0.08	− 7.01	− 9.44	− 3.08	− 5.25	− 5.02	− 5.97
0.09	− 5.29	− 7.81	− 1.58	− 3.52	− 2.83	− 3.86
0.10	− 3.82	− 6.43	− 0.37	− 2.09	− 1.64	− 2.71
0.11	− 3.00	− 5.63	0.24	− 1.33	− 0.80	− 1.89
0.12	− 2.39	− 4.99	− 0.69	− 0.71	− 0.12	− 1.18
0.13	− 1.83	− 4.30	0.86	− 0.39	0.22	− 0.78
0.14	− 1.48	− 3.79	0.91	− 0.15	0.46	− 0.43
0.14	− 1.12	− 3.15	0.84	− 0.04	0.55	− 0.23
0.16	− 0.82	− 2.51	0.66	0.02	0.58	− 0.04
0.17	− 0.60	− 1.99	0.46	0.03	0.55	0.07
0.17	− 0.40	− 1.48	0.21	− 0.00	0.45	0.19
0.18	− 0.22	− 0.97	− 0.21	− 0.09	0.37	0.25
0.19	0.03	− 0.24	− 0.51	− 0.16	0.26	0.29
0.21	0.17	0.22	− 0.81	− 0.25	0.15	0.33
0.22	0.30	0.65	− 1.12	− 0.35	0.04	0.35
0.23	0.42	1.05	− 1.42	− 0.45	− 0.12	0.36
0.23	0.52	1.41	− 1.84	− 0.59	− 0.22	0.37
0.24	0.64	1.88	− 2.10	− 0.69	− 0.32	0.37
0.25	0.71	2.16	− 2.33	− 0.77	− 0.41	0.36
0.26	0.77	2.39	− 2.53	− 0.85	− 0.52	0.36
0.27	0.82	2.59	− 2.78	− 0.95	− 0.58	0.35
0.28	0.86	2.76	− 2.92	− 1.00	− 0.63	0.34
0.29	0.91	2.95	− 3.02	− 1.04	− 0.66	0.34
0.39	0.96	2.92	− 2.59	− 0.82	− 0.42	0.43
0.48	0.92	2.00	− 0.96	− 0.06	− 0.22	0.62
0.58	0.89	1.19	0.37	0.56	0.68	0.74
0.68	0.86	0.69	1.18	0.92	0.92	0.78
0.79	0.82	0.41	1.41	1.02	0.98	0.77
0.88	0.78	0.33	1.44	1.02	0.96	0.74
0.97	0.74	0.31	1.37	0.98	0.91	0.71
1.06	0.70	0.32	1.23	0.90	0.84	0.67
1.17	0.65	0.34	1.11	0.84	0.76	0.63
1.27	0.61	0.35	0.96	0.75	0.69	0.59
1.36	0.56	0.36	0.85	0.69	0.61	0.54
1.45	0.51	0.36	0.71	0.60	0.54	0.49
1.56	0.46	0.35	0.64	0.55	0.47	0.44
1.67	0.41	0.33	0.55	0.49	0.43	0.41
1.74	0.36	0.30	0.47	0.43	0.37	0.36
1.85	0.33	0.28	0.40	0.37	0.32	0.32
1.96	0.29	0.26	0.34	0.32	0.28	0.28
2.04	0.25	0.23	0.31	0.29	0.24	0.25
2.15	0.22	0.21	0.26	0.25	0.22	0.22

Table 1. Continued

r	Tm		Yb		Lu
	d	f	d	f	d
0.0	−68.98	−74.94	−67.74	−69.30	−67.45
0.01	−61.01	−66.38	−60.16	−61.63	−59.02
0.02	−48.00	−52.28	−47.79	−49.00	−46.05
0.03	−35.20	−38.43	−35.48	−36.45	−32.24
0.04	−24.67	−27.09	−25.23	−26.04	−20.97
0.05	−16.69	−18.53	−17.40	−18.14	−11.84
0.06	−10.90	−12.37	−11.70	−12.44	− 4.71
0.07	− 6.45	− 7.68	− 7.31	− 8.09	0.68
0.08	− 4.00	− 5.12	− 4.90	− 5.71	4.98
0.09	− 1.92	− 2.95	− 2.83	− 3.68	7.32
0.10	− 0.81	− 1.80	− 1.71	− 2.58	9.13
0.11	0.10	− 0.83	− 0.78	− 1.63	9.82
0.12	0.54	− 0.33	− 0.30	− 1.11	9.91
0.13	0.85	0.06	0.08	− 0.66	9.46
0.14	0.94	0.25	0.26	− 0.40	8.43
0.14	0.93	0.36	0.37	− 0.17	7.30
0.16	0.84	0.39	0.40	− 0.02	5.30
0.17	0.62	0.35	0.38	0.13	0.84
0.17	0.44	0.29	0.34	0.21	2.33
0.18	0.24	0.21	0.28	0.27	0.84
0.19	0.03	0.12	0.21	0.32	− 1.33
0.21	− 0.19	0.01	0.09	0.36	− 2.68
0.22	− 0.50	− 0.14	0.02	0.39	− 3.93
0.23	− 0.70	− 0.25	− 0.06	0.40	− 5.07
0.23	− 0.88	− 0.34	− 0.13	0.41	− 6.55
0.24	− 1.05	− 0.44	− 0.23	0.41	− 7.37
0.25	− 1.26	− 0.56	− 0.29	0.41	− 8.07
0.26	− 1.38	− 0.62	− 0.34	0.41	− 8.88
0.27	− 1.48	− 0.68	− 0.38	0.41	− 9.27
0.28	− 1.55	− 0.73	− 0.42	0.40	− 9.55
0.29	− 1.63	− 0.77	− 0.44	0.40	− 9.73
0.39	− 1.15	− 0.47	− 0.16	0.49	− 7.15
0.48	− 0.12	0.18	0.36	0.64	− 2.68
0.58	0.63	0.63	0.72	0.73	0.53
0.68	1.02	0.86	0.89	0.74	1.89
0.79	1.12	0.92	0.91	0.72	2.34
0.88	1.11	0.90	0.88	0.70	2.28
0.97	1.03	0.85	0.82	0.66	2.07
1.06	0.94	0.79	0.75	0.63	1.78
1.17	0.84	0.73	0.69	0.59	1.49
1.27	0.75	0.67	0.62	0.55	1.28
1.36	0.66	0.60	0.56	0.51	1.02
1.45	0.57	0.54	0.49	0.46	0.90
1.56	0.50	0.47	0.43	0.41	0.75
1.67	0.43	0.42	0.38	0.37	0.62
1.74	0.39	0.38	0.33	0.33	0.51
1.85	0.33	0.33	0.28	0.29	0.43
1.96	0.28	0.29	0.25	0.26	0.35
2.04	0.24	0.25	0.22	0.23	0.31
2.15	0.21	0.22	0.19	0.20	0.26

representative case of Eu has been plotted in Fig. 2 for the d and f configuration, respectively. The general trends observed for $\beta(r)$ near the nucleus ($r = 0$) are also valid for $\gamma(r)$ as r approaches ∞. At $r = \infty$ $\gamma(r)$ corresponds to the moment perturbed uncoupled HF estimate of γ_∞.

The moment-perturbed γ_∞ values are always found to be slightly smaller ($\sim 1\%$) than the charge-perturbed analogues, which is a consequence of the local approximation [3] used in solving the DE in the two cases. We wish to point out here that in the molecular orbital calculations [13] of the EFG in the

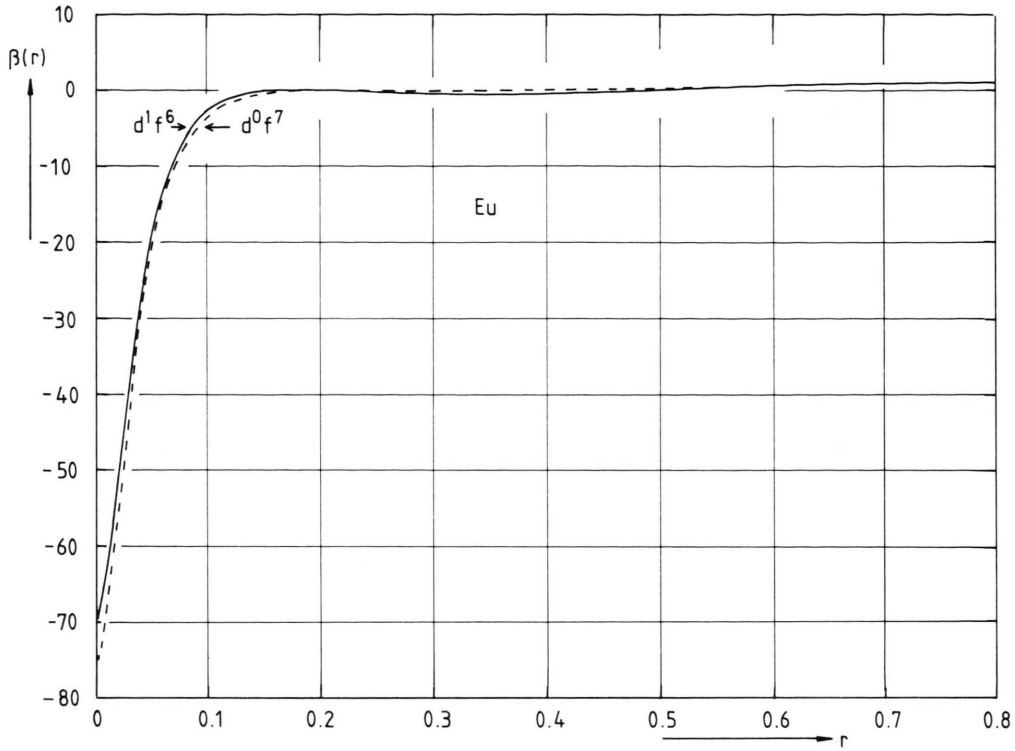

Fig. 1. The Sternheimer function $\beta(r)$ for Eu in the $4f^6\,5d^1$ and in the $4f^7\,5d^0$ configurations. The r values are in multiples of $a_0 = 0.5292$ Å.

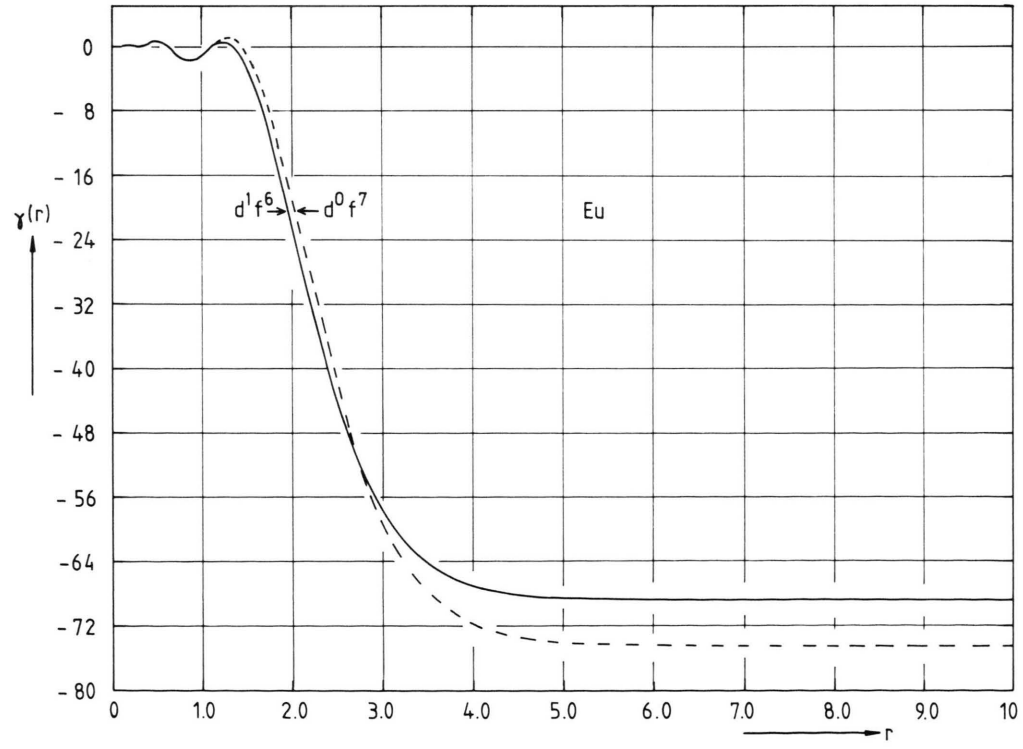

Fig. 2. The Sternheimer function $\gamma(r)$ for Eu in the $4f^6\,5d^1$ and in the $4f^6\,5d^0$ configurations. The r values are in multiples of $a_0 = 0.5292$ Å.

Table 2. Sternheimer $\gamma(r)$ function for the rare earth atoms (La-Lu). The core configuration is defined as ($4d^{10}\ 5s^2\ 5p^6$). The term d denotes the valence electron configuration ($5d^1\ 4f^{n-1}$) and the term f denotes the valence electron configuration ($5d^0\ 4f^n$). All r values are given in multiples of $a_0 = 0.5292$ Å. At $r = \infty$, $\gamma(\infty) = \gamma_\infty$ as calculated using the uncoupled Hartree-Fock method.

r	Co		Pr	
	d	f	d	f
0.0	0.0	0.0	0.0	0.0
0.10	0.05	0.05	0.05	0.05
0.19	0.22	0.17	0.21	0.21
0.29	0.13	− 0.02	0.09	0.08
0.39	0.13	− 0.10	0.12	0.11
0.48	0.65	0.38	0.63	0.62
0.58	0.81	0.54	0.69	0.69
0.68	0.15	− 0.10	− 0.01	0.02
0.79	− 0.97	− 1.20	− 1.11	1.08
0.88	− 1.81	− 2.02	− 1.93	− 1.92
0.97	− 2.13	− 2.29	− 2.01	− 2.00
1.06	− 1.85	− 1.91	− 1.61	− 1.55
1.17	− 1.31	− 1.17	− 1.00	− 0.80
1.27	− 0.84	− 0.39	− 0.44	0.05
1.36	− 0.75	0.19	− 0.44	0.38
1.45	− 1.54	0.01	− 1.30	0.01
1.56	− 2.63	− 0.66	− 3.20	− 1.39
1.67	− 5.15	− 2.54	− 5.04	− 2.91
1.74	− 8.62	− 5.43	− 8.56	− 6.00
1.85	−11.38	− 7.86	−12.81	− 9.94
1.96	−16.01	−12.12	−15.94	−12.94
2.04	−21.04	−16.92	−20.91	−17.83
2.15	−24.50	−20.32	−26.02	−23.00
2.22	−29.71	−25.57	−29.41	−26.51
2.33	−33.12	−29.09	−34.37	−31.75
2.44	−38.07	−34.29	−39.07	−36.83
2.52	−42.71	−39.30	−42.03	−40.08
2.63	−45.60	−42.49	−46.14	−44.69
2.74	−49.62	−46.98	−48.66	−47.57
2.81	−53.22	−51.11	−52.11	−51.57
2.92	−55.40	−53.64	−56.09	−56.29
3.14	−62.41	−62.06	−60.84	−62.09
3.44	−66.13	−66.72	−64.35	−66.52
3.66	−68.82	−70.20	−67.55	−70.69
3.88	−71.23	−73.42	−69.16	−72.82
4.17	−72.41	−75.05	−70.30	−74.34
4.39	−73.23	−76.19	−71.31	−75.68
4.61	−73.93	−77.19	−71.81	−76.33
4.84	−74.26	−77.68	−72.17	−76.78
5.13	−74.49	−78.00	−72.48	−77.16
5.35	−74.64	−78.22	−72.63	−77.33
5.57	−74.76	−78.40	−72.74	−77.44
5.87	−74.82	−78.48	−72.82	−77.52
6.16	−74.87	−78.55	−72.88	−77.58
6.31	−74.89	−78.59	−72.92	−77.61
6.60	−74.90	−78.60	−72.93	−77.62
6.90	−74.91	−78.61	−72.95	−77.64
7.04	−74.91	−78.62	−72.96	−77.64
7.34	−74.92	−78.62	−72.96	−77.64
7.64	−74.92	−78.62	−72.96	−77.65

Table 2. Continued

r	Nd		Pm		Sm	
	d	f	d	f	d	f
0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.10	0.05	0.05	0.05	0.05	0.05	0.05
0.19	0.21	0.20	0.20	0.21	0.21	0.21
0.29	0.09	0.00	0.04	0.06	0.06	0.06
0.39	0.24	0.17	0.17	0.24	0.27	0.26
0.48	0.75	0.62	0.59	0.75	0.73	0.73
0.58	0.78	0.62	0.42	0.66	0.47	0.48
0.68	− 0.01	− 0.17	− 0.45	− 0.21	− 0.50	− 0.49
0.79	− 0.93	− 1.09	− 1.47	− 1.33	− 1.45	− 1.48
0.88	− 1.57	− 1.73	− 1.82	− 1.81	− 1.79	− 1.87
0.97	− 1.47	− 1.60	− 1.55	− 1.68	− 1.44	− 1.54
1.06	− 0.92	− 0.94	− 0.65	− 0.94	− 0.77	− 0.81
1.17	− 0.07	0.17	0.20	− 0.16	− 0.01	0.13
1.27	0.42	0.99	0.85	0.47	0.21	0.59
1.36	0.32	1.42	0.78	0.44	− 0.20	0.49
1.45	− 0.51	1.09	0.00	− 0.27	− 2.01	− 0.85
1.56	− 2.48	− 0.26	− 1.92	− 2.11	− 3.71	− 2.27
1.67	− 5.47	− 2.66	− 4.85	− 5.00	− 7.06	− 5.28
1.74	− 7.96	− 4.79	− 7.28	− 7.44	−11.21	− 9.16
1.85	−12-25	− 8.66	−11.48	−11.73	−14.29	−12.14
1.96	−17.01	−13.15	−16.13	−16.58	−19.22	−17.02
2.04	−20.34	−16.37	−21.00	−21.77	−24.32	−22.21
2.15	−25.40	−21.41	−24.28	−25.31	−29.39	−27.49
2.22	−30.39	−26.51	−29.12	−30.61	−32.68	−30.99
2.33	−33.62	−29.88	−33.75	−35.78	−37.38	−36.08
2.44	−38.22	−34.78	−36.67	−39.09	−41.75	−40.90
2.52	−42.47	−39.41	−40.77	−43.79	−44.45	−43.93
2.63	−45.10	−42.32	−44.48	−48.13	−48.16	−48.17
2.74	−48.70	−46.39	−46.74	−50.81	−51.45	−52.00
2.81	−52.09	−50.26	−49.99	−54.68	−53.61	−54.53
2.92	−54.71	−53.38	−52.49	−57.76	−56.05	−57.51
3.14	−59.25	−58.88	−56.84	−63.17	−61.37	−64.16
3.44	−63.46	−64.19	−60.88	−68.35	−64.07	−67.69
3.66	−65.58	−66.97	−62.93	−71.04	−65.94	−70.25
3.88	−67.05	−68.96	−64.77	−73.46	−67.54	−72.55
4.17	−68.33	−70.74	−65.70	−74.66	−68.29	−73.69
4.39	−68.94	−71.60	−66.35	−75.50	−68.91	−74.67
4.61	−69.36	−72.20	−66.94	−76.22	−69.19	−75.14
4.84	−69.71	−72.70	−67.24	−76.56	−69.37	−75.46
5.13	−69.87	−72.94	−67.44	−76.79	−69.53	−75.73
5.35	−69.98	−73.09	−67.62	−76.98	−69.59	−75.85
5.57	−70.08	−73.22	−67.70	−77.06	−69.64	−75.93
5.87	−70.13	−73.29	−67.78	−77.13	−69.67	−75.99
6.16	−70.15	−73.31	−67.82	−77.17	−69.69	−76.02
6.31	−70.17	−73.34	−67.83	−77.18	−69.71	−76.04
6.60	−70.18	−73.35	−67.85	−77.20	−69.71	−76.05
6.90	−70.18	−73.35	−67.86	−77.21	−69.71	−76.06
7.04	−70.19	−73.36	−67.87	−77.21	−69.72	−76.06
7.34	−70.19	−73.36	−67.87	−77.21	−69.72	−76.06
7.63	−70.19	−73.36	−67.87	−77.21	−69.72	−76.06

Table 2. Continued

r	Eu		Gd		Tb	
	d	f	d	f	d	f
0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.10	0.05	0.05	0.05	0.05	0.05	0.05
0.19	0.21	0.21	0.22	0.21	0.21	0.21
0.29	0.05	0.05	0.09	0.05	0.06	0.06
0.39	0.29	0.27	0.51	0.37	0.41	0.41
0.48	0.71	0.69	0.99	0.73	0.71	0.73
0.58	0.37	0.35	0.63	0.33	0.14	0.18
0.68	− 0.61	− 0.64	− 0.42	− 0.70	− 0.89	− 0.86
0.79	− 1.49	− 1.55	− 1.34	− 1.57	− 1.61	− 1.63
0.88	− 1.69	− 1.79	− 1.61	− 1.73	− 1.54	− 1.58
0.97	− 1.23	− 1.32	− 1.31	− 1.23	− 0.80	− 0.82
1.06	− 0.49	− 0.49	− 0.71	− 0.25	− 0.03	0.06
1.17	0.30	0.52	− 0.45	0.47	0.55	0.87
1.27	0.49	0.98	− 0.84	0.76	0.41	1.02
1.36	− 0.16	0.76	− 1.96	0.28	− 0.67	0.32
1.45	− 1.89	− 0.53	− 4.34	− 1.30	− 2.54	− 1.21
1.56	− 4.69	− 2.91	− 7.78	− 3.97	− 5.66	− 3.98
1.67	− 7.08	− 5.05	−12.08	− 7.61	− 9.64	− 7.69
1.74	−11.27	− 8.97	−15.30	−10.46	−12.65	−10.58
1.85	−15.99	−13.54	−20.49	−15.23	−17.51	−15.38
1.96	−19.30	−16.83	−25.89	−20.37	−22.58	−20.51
2.04	−24.37	−21.98	−29.50	−23.90	−27.64	−25.77
2.15	−29.38	−27.21	−34.79	−29.20	−30.94	−29.26
2.22	−34.20	−32.34	−39.82	−39.82	−35.67	−34.36
2.33	−37.25	−35.65	−44.50	−39.28	−40.05	−39.19
2.44	−41.53	−40.38	−47.39	−42.38	−44.05	−43.68
2.52	−45.41	−44.76	−51.37	−46.72	−46.48	−46.46
2.63	−47.77	−47.47	−54.90	−50.65	−49.78	−50.29
2.74	−50.97	−51.20	−58.00	−54.17	−52.67	−53.71
2.81	−53.76	−54.53	−59.83	−56.29	−55.93	−57.66
2.92	−56.92	−58.37	−63.00	−60.01	−57.32	−59.38
3.14	−60.56	−62.95	−66.63	−64.42	−60.68	−63.64
3.44	−63.16	−66.34	−69.87	−68.50	−63.67	−67.59
3.66	−65.43	−69.43	−71.44	−70.55	−65.11	−69.58
3.88	−66.52	−70.98	−72.51	−71.98	−66.33	−71.34
4.17	−67.26	−72.07	−73.41	−73.22	−66.90	−72.20
4.39	−67.88	−73.01	−73.83	−73.80	−67.37	−72.93
4.61	−68.16	−73.47	−74.17	−74.30	−67.59	−73.28
4.84	−68.40	−73.85	−74.33	−74.53	−67.74	−73.51
5.13	−68.51	−74.03	−74.44	−74.68	−67.86	−73.70
5.35	−68.58	−74.16	−74.53	−74.81	−67.92	−73.79
5.57	−68.65	−74.27	−74.67	−74.88	−67.96	−73.86
5.87	−68.66	−74.30	−74.60	−74.92	−67.99	−73.90
6.16	−68.68	−74.34	−74.61	−74.93	−68.00	−73.92
6.31	−68.69	−74.36	−74.62	−74.95	−68.00	−73.93
6.60	−68.70	−74.36	−74.63	−74.95	−68.01	−73.93
6.90	−68.70	−74.37	−74.63	−74.96	−68.01	−73.94
7.04	−68.70	−74.38	−74.63	−74.96	−68.02	−73.94
7.34	−68.71	−74.38	−74.63	−74.96	−68.02	−73.94
7.63	−68.71	−74.38	−74.63	−74.96	−68.02	−73.94

Table 2. Continued

r	Dy		Ho		Er	
	d	f	d	f	d	f
0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.10	0.05	0.05	0.05	0.05	0.05	0.05
0.19	0.20	0.20	0.20	0.20	0.19	0.18
0.29	0.05	0.07	0.07	0.07	0.05	0.01
0.39	0.40	0.47	0.47	0.48	0.49	0.37
0.48	0.62	0.78	0.68	0.70	0.55	0.35
0.58	− 0.02	0.18	0.01	0.04	− 0.25	− 0.45
0.68	− 1.05	− 0.88	− 1.13	− 1.13	− 1.29	− 1.46
0.79	− 1.71	− 1.63	− 1.53	− 1.57	− 1.61	− 1.73
0.88	− 1.58	− 1.58	− 1.17	− 1.24	− 1.15	− 1.14
0.97	− 0.81	− 0.87	− 0.43	− 0.45	− 0.36	− 0.12
1.06	− 0.07	− 0.12	0.46	0.58	0.54	1.18
1.17	0.41	0.45	0.77	1.11	0.81	2.01
1.27	0.16	0.33	0.28	0.94	0.27	2.02
1.36	− 1.09	− 0.73	− 0.94	0.03	− 1.43	1.01
1.45	− 3.09	− 2.58	− 4.08	− 2.71	− 4.23	− 1.12
1.56	− 6.37	− 5.72	− 6.44	− 4.89	− 7.97	− 4.28
1.67	−10.47	− 9.78	−10.64	− 8.89	−10.86	− 6.85
1.74	−15.14	−14.52	−15.38	−13.55	−15.60	−11.24
1.85	−18.45	−17.94	−20.40	−18.64	−20.60	−16.05
1.96	−23.54	−23.29	−25.50	−23.92	−25.65	−21.06
2.04	−28.59	−28.72	−28.84	−27.45	−30.56	−26.07
2.15	−33.45	−34.05	−33.67	−32.65	−33.69	−29.34
2.22	−38.02	−39.15	−38.18	−37.61	−38.12	−34.04
2.33	−40.86	−42.37	−42.31	−42.24	−42.15	−38.43
2.44	−44.78	−46.89	−44.84	−45.12	−45.77	−42.47
2.52	−48.29	−51.00	−48.28	−49.10	−48.97	−46.11
2.63	−51.37	−54.68	−51.31	−42.67	−50.88	−48.32
2.74	−53.20	−56.91	−54.12	−56.02	−53.59	−51.50
2.81	−56.37	−60.81	−56.20	−58.60	−55.59	−53.94
2.92	−57.72	−62.51	−57.53	−60.24	−58.00	−56.91
3.14	−61.84	−67.84	−61.57	−65.39	−60.72	−60.35
3.44	−63.87	−70.57	−63.57	−68.01	−63.11	−63.47
3.66	−65.26	−72.51	−65.29	−70.33	−64.24	−65.00
3.88	−66.44	−74.21	−66.10	−71.43	−65.00	−66.03
4.17	−67.00	−75.03	−66.77	−72.35	−65.62	−66.89
4.39	−67.45	−75.72	−67.07	−72.77	−65.90	−67.28
4.61	−67.66	−76.05	−67.32	−73.10	−66.13	−67.58
4.84	−67.84	−76.32	−67.42	−73.24	−66.23	−67.71
5.13	−67.91	−76.44	−67.51	−73.35	−66.30	−67.81
5.35	−67.98	−76.54	−67.54	−73.39	−66.33	−67.85
5.57	−68.01	−76.58	−67.56	−73.42	−66.36	−67.88
5.87	−68.03	−76.62	−67.58	−73.44	−66.37	−67.89
6.16	−68.04	−76.64	−67.59	−73.45	−66.37	−67.90
6.31	−68.04	−76.64	−67.59	−73.45	−66.38	−67.90
6.60	−68.05	−76.65	−67.59	−73.45	−66.38	−67.90
6.90	−68.05	−76.65	−67.59	−73.45	−66.38	−67.90
7.04	−68.05	−76.65	−67.60	−73.45	−66.38	−67.90
7.34	−68.05	−76.65	−67.60	−73.45	−66.38	−67.90
7.63	−66.05	−76.65	−67.60	−73.45	−66.38	−67.90

covalent systems, the first four terms in (1) are usually considered as the valence electron contributions. The perturbing charge can be considered as localised in the bonding regions. In that case the values given in Table 2 can be used to compute the overlap part of the EFG in molecules containing rare earth atoms.

We shall now discuss the electron-electron self consistency effect on γ_∞. Previous calculations at the coupled HF level of accuracy which include such effects have been reported only in the case of Pr^{3+} [14, 6c]. The two estimates significantly disagree with each other. It is therefore necessary to evaluate such effects preferably using an indepen-

Table 2. Continued

r	Tm		Yb		Lu
	d	f	d	f	d
0.0	0.0	0.0	0.0	0.0	0.0
0.10	0.05	0.05	0.05	0.05	0.05
0.19	0.18	0.18	0.17	0.16	0.16
0.29	0.05	0.04	0.07	0.02	0.08
0.39	0.47	0.44	0.51	0.37	0.54
0.48	0.44	0.40	0.45	0.23	0.44
0.58	− 0.43	− 0.50	− 0.43	− 0.64	− 0.55
0.68	− 1.46	− 1.57	− 1.39	− 1.57	− 1.34
0.79	− 1.69	− 1.85	− 1.51	− 1.61	− 1.35
0.88	− 1.21	− 1.36	− 0.94	− 0.90	− 0.54
0.97	− 0.26	− 0.31	0.08	0.45	0.34
1.06	0.40	0.51	0.83	1.68	1.04
1.17	0.53	0.93	0.84	2.21	0.87
1.27	− 0.16	0.54	− 0.14	1.92	− 0.14
1.36	− 2.05	− 0.98	− 1.85	0.80	− 2.92
1.45	− 5.04	− 3.64	− 4.90	− 1.58	− 5.15
1.56	− 8.94	− 7.30	− 8.83	− 4.95	− 9.19
1.67	−13.50	−11.73	−13.40	− 9.09	−13.84
1.74	−16.77	−14.99	−18.33	−13.75	−18.81
1.85	−21.85	−20.16	−23.38	−18.71	−23.88
1.96	−26.93	−25.46	−26.06	−22.06	−28.85
2.04	−31.85	−30.72	−31.57	−27.05	−32.03
2.15	−36.49	−35.77	−36.13	−31.85	−36.54
2.22	−39.38	−38.98	−40.31	−36.37	−40.66
2.33	−43.39	−43.50	−44.08	−40.54	−44.36
2.44	−46.96	−47.62	−46.35	−43.11	−47.64
2.52	−50.12	−51.32	−49.42	−46.63	−50.51
2.63	−52.86	−54.61	−52.08	−49.75	−52.21
2.74	−54.65	−56.76	−54,37	−52.50	−54.44
2.81	−56.61	−59.21	−56.91	−55.61	−56.92
2.92	−58.96	−62.17	−57.98	−56.94	−57.96
3.14	−61.60	−65.59	−60.52	−60.20	−61.08
3.44	−63.89	−68.67	−62.72	−63.12	−62.58
3.66	−64.98	−70.17	−64.02	−64.90	−63.83
3.88	−65.90	−71.44	−64.62	−65.74	−64.39
4.17	−66.32	−72.02	−65.11	−66.43	−64.84
4.39	−66.66	−72.49	−65.32	−66.74	−65.04
4.61	−66.81	−72.69	−65.49	−66.98	−65.19
4.84	−66.94	−72.85	−65.57	−67.08	−65.25
5.13	−66.99	−72.92	−65.62	−67.15	−65.29
5.35	−67.03	−72.96	−65.64	−67.18	−65.31
5.57	−67.05	−72.99	−65.66	−67.21	−65.32
5.87	−67.06	−73.00	−65.67	−67.22	−65.33
6.16	−67.07	−73.00	−65.67	−67.22	−65.33
6.31	−67.07	−73.00	−65.67	−67.22	−65.33
6.60	−67.07	−73.01	−65.67	−67.22	−65.33
6.90	−67.07	−73.01	−65.68	−67.23	−65.33
7.04	−67.07	−73.01	−65.68	−67.23	−65.33
7.34	−67.07	−73.01	−65.68	−67.23	−65.33
7.63	−67.08	−73.01	−65.68	−67.23	−65.33

dent equivalet method for some rare earth atoms as such calculations are extremely time-consuming. We have calculated the consistency correction term γ_∞^1 for the Xe-like core electrons in Ce, Pr, Eu and Tm atoms using a method based on the many-body perturbation theory, which has extensively been

Table 3. The electron-electron self consistency correction factor γ_∞^1 to the uncoupled HF estimates of γ_∞ for the Xe-like core electrons in some rare earth atoms.

Atom		γ_∞	γ_∞^1	γ_∞^{CHF}
Ce	d	−74.92	−1.81	−76.73
	f	−78.62	−2.90	−81.50
Pr	d	−72.96	−2.83	−75.79
	f	−77.65	−2.60	−80.25
		(−84.77)[c]		(−142.1[a], −65.9[b])
Eu	d	−68.71	−2.11	−70.82
	f	−74.38	−2.91	−77.29
Tm	d	−67.08	−2.52	−69.60
	f	−73.01	−3.24	−76.25
		(−72.86)[c]		

[a] Ref. [14], [b] Ref. [6c], [c] Ref. [11].

tested in its ability to reproduce the coupled HF values of γ_∞ [10] for the He, Ne, Ar, Kr, Xe, and Fe^{3+}-isoelectronic series. Our results are listed in Table 3. It is found that the consistency corrections in this region are much less significant and are generally less than 5%. A comparison of our results with the earlier results shows that the calculations of Lauer et al. [6c] provide estimates of γ_∞^1 closer to the present results. Using a conservative estimate of the electron correlation effects to be in the range of ~ 5% from the known values on other atoms [15], we set the reliability of the $\beta(r)$ and $\gamma(r)$ functions given in Tables 1 and 2 to ~ 10%.

IV. Conclusions

The following main conclusions have been obtained in this work.

a) The antishielding functions $\beta(r)$ and $\gamma(r)$ for the Xe-like core electrons in the rare earth atoms are found to vary significantly with the change in the valence electron configuration. The valence configuration $4f^n\,5d^0$ leads to a larger net antishielding effect relative to the $4f^{n-1}\,5d^1$ configuration by ~ 6−12%.

b) The consistency effects are less significant. Over the entire series the consistency correction is estimated to be less than 5%.

c) First calculations of the function $\beta(r)$ for all the rare earth atoms and those of $\gamma(r)$ for most of the rare earth atoms (except Pr) are reported at the uncoupled HF level of accuracy. These results are

believed to be reliable to within 10% from the most accurate calculations which would have included the electron-electron interaction to all orders. We therefore conclude that the $\beta(r)$ and $\gamma(r)$ functions made available here for the rare earths could be directly used in order to test the antishielding theory of the EFG in metals and molecular orbital theory of covalent systems containing the rare earth atoms.

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