Sternheimer Shielding-Antishielding. II

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The Sternheimer shielding-antishielding parameters are reported for 77 ions in $3d$, $4d$, $5d$, and $5f$ groups, as well as for gold and lithium atoms. The parameters λ and R, which take into account, respectively, the effect of the core electrons on the quadrupole perturbing potential outside the ion and within the ion (owing to unfilled valence-shell electrons), have been calculated for varying ionic charge and varying atomic number in each group. The electronic wave functions used throughout the work are of the nonrelativistic Hartree-Fock-Slater type. Interesting differences of the results in each group are seen to be the values of Sternheimer parameters and α_q for ions with and without the closed-shell configurations. Also, for the lithium atom with $1s^2 2p^1$ configuration we obtained $1 - \lambda_0 = 3.46$, assuming $2p^1$-shell perturbation to be one-sixth that of the closed p shell. This value, incidentally, is the same as that measured recently by Anderson and Karra for the lithium ion (Li^+) in LiF. For gold atoms the configurations $5d^{10}6p^1$ and $5d^{10}6s^1$ were considered and we obtained the ratios of atomic core $5p_{3/2}$ to $4p_{3/2}$ energy-level splittings as 1.6 and 1.7, respectively, against approximately 2 determined experimentally by Novakov and Hollander for Au in gold-cyanide compounds. The significance of these calculations is emphasized by the possibility of experimentally determining the quadrupole splittings of the atomic core by high-resolution electron spectroscopy.

I. INTRODUCTION

In a previous paper[1] (I) we reported the Sternheimer shielding-antishielding parameters for some rare-earth ions in $4f$ group and described the theory and the numerical procedure used to obtain the parameters accurately within the limitation of the electronic wave function of the ions used. Present work is an extension of I to some ions in the $3d$, $4d$, $5d$, and $5f$ groups, and to lithium and gold. For most of the ions the results are believed to be new. The comparison is made with the known results wherever possible but no attempt is made to be comprehensive in this regard. The nonrelativistic Hartree-Fock-Slater electronic wave functions[2] have been used throughout the work.

II. DEFINITIONS

The definitions are given with reference to Fig. 1 and Paper I. The perturbing potential at the site of an electron $v(3)$ due to unfilled valence-shell electrons represented by wave function $w(1)$ is written as

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

where the term with P_{13} accounts for the exchange interaction. We limit ourselves to the consideration of the quadrupole parts of Eq. (1) without exchange. The core-electron wave functions $u_0(2)$ are perturbed by $H_1(2)$ to $u_0 + u_1$, which in turn perturb $v(3)$ through a potential given by

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

The Sternheimer parameter R for an electron with wave function v is then defined as

$$R_v = -\sum \langle v | H_1' | v \rangle / \langle v | H_1 | v \rangle , \tag{3}$$

where the summation is over all the electrons in the filled shells of an ion. The radial part of the denominator,

$$\langle v' | \langle w' | r_<^2 / r_>^3 | w' \rangle | v' \rangle ,$$

is written as $\langle F^2 \rangle$.

The Sternheimer parameter λ is defined similarly as

$$\lambda_v = -\sum \langle v | H_1' | v \rangle / \langle v | H_1 | v \rangle , \tag{4}$$

where the perturbing potential originating from outside the ion is given by

$$H_1 = A r^2 Y_2^0 . \tag{5}$$

The Sternheimer parameters at the nuclear site are written as R_0 and λ_0 and obtained from Eqs. (3) and (4), respectively, replacing the wave function v by a δ function.

III. RESULTS

A. $3d$ Group

The configuration considered is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{(Z - N_q - 18)}$, where N_q is the number of positive charges of the ion. The results are reported for thirty-three ions of the $3d$-transition

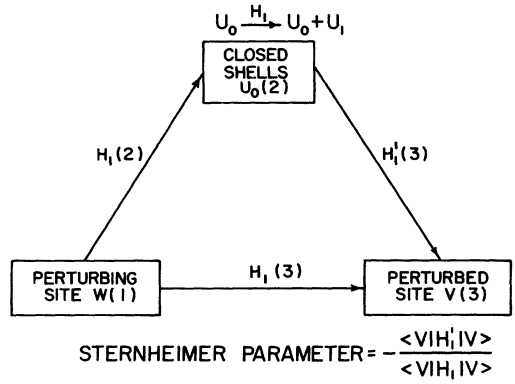

FIG. 1. Schematic diagram showing Sternheimer effect.

group in Table I.[3] The perturbation of the core electrons possible and considered are $1s \rightarrow d$, $2s \rightarrow d$, $2p \rightarrow f$, $2p \rightarrow p$, $3s \rightarrow d$, $3p \rightarrow f$, and $3p \rightarrow p$. For Cu^+ the configuration is $3d^{10}$, i.e., the $3d$ shell is full and therefore $3d \rightarrow g$, $3d \rightarrow d$, and $3d \rightarrow s$ perturbation are also calculated and included in the result. This is why Sternheimer parameters for Cu^+ are not as near to Ni^+ as one would otherwise expect.

B. 4d Group

The configuration considered is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$, $4s^2$, $4p^6$, $4d^{(Z-N_c-36)}$. The calculation of Sternheimer parameters is reported for twenty-six $4d$-group transition ions in Table I.[3] The λ parameter for Kr atom is also included in the table to show that the presence of $4d$ electrons outside $4p$ closed shell makes a major difference in the value of λ_0. The closed-shell perturbations considered are $1s \rightarrow d$, $2s \rightarrow d$, $2p \rightarrow f$, $2p \rightarrow p$, $3s \rightarrow d$, $3p \rightarrow f$, $3p \rightarrow p$, $3d \rightarrow g$, $3d \rightarrow d$, $3d \rightarrow s$, $4s \rightarrow d$, $4p \rightarrow f$, and $4p \rightarrow p$.

C. 5d Group

The configuration considered is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$, $4s^2$, $4p^6$, $4d^{10}$, $4f^n$, $5s^2$, $5p^6$, $5d^{(Z-N_c-n-54)}$, where $n=0$ for La^{2+} and $n=14$ for all other ions. The Sternheimer parameters for six $5d$-group transition ions La^{2+}, Ir^{3+}, Pt^{3+}, Re^{4+}, Ir^{4+}, and Pt^{4+} are given in Table I.[3] The La^{2+} has the $5d^1$ configuration but with $4f$ shell empty in contrast to all other ions which have $4f$ shell full. This is why Sternheimer parameters for La^{2+} are so different from those of other ions in its group. The closed-shell perturbations considered are $1s \rightarrow d$, $2s \rightarrow d$, $2p \rightarrow f$, $2p \rightarrow p$, $3s \rightarrow d$, $3p \rightarrow f$, $3p \rightarrow p$, $3d \rightarrow g$, $3d \rightarrow d$, $3d \rightarrow s$, $4s \rightarrow d$, $4p \rightarrow f$, $4p \rightarrow p$, $4d \rightarrow g$, $4d \rightarrow d$, $4d \rightarrow s$, $4f \rightarrow h$, $4f \rightarrow f$, $4f \rightarrow p$, $5s \rightarrow d$, $5p \rightarrow f$, and $5p \rightarrow p$. The $4f$-shell perturbations were considered absent in La^{2+}.

TABLE I. The Sternheimer parameters R_0, λ_0, and λ_{val} calculated in this work with the available values of other workers. λ_{val} is the Sternheimer parameter at the valence-electron site arising from the perturbing potential outside the ion.

Ion	R_0	λ_0	λ_{val}
Li^+		0.261	
		0.257 [a]	
		0.263 [b]	
		0.248 [c]	
		0.249 [d]	
$Li(1s^2, 2p^1)$	0.172	0.250 [e]	0.000
	0.182 [f,g]	−2.46 [h]	
Sc	−0.085 [g,i]	−11.52 [i]	
Sc^+	−0.078	−13.58	0.034
Sc^{2+}	−0.018	−12.26	0.060
Sc^{3+}		−11.2 [i]	
		−9.46 [a]	
Ti^+	−0.028	−12.32	0.038
Ti^{2+}	0.010	−11.21	0.061
Ti^{3+}	0.032	−9.96	0.081
Ti^{4+}		−7.72 [a]	
V^+	0.002	−11.35	0.041
V^{2+}	0.027	−10.41	0.061
V^{3+}	0.043	−9.33	0.079
V^{4+}	0.052	−8.33	0.095
V^{5+}		−6.50 [a]	
Cr^+	0.021	−10.57	0.042
Cr^{2+}	0.039	−9.75	0.060
Cr^{3+}	0.051	−8.81	0.077
Cr^{4+}	0.057	−7.92	0.091
Mn^+	0.034	−9.92	0.043
Mn^{2+}	0.048	−9.19	0.059
		−11.37 [b]	
Mn^{3+}	0.056	−8.36	0.074
Mn^{4+}	0.060	−7.57	0.087
Fe^+	0.043	−9.36	0.043
Fe^{2+}	0.053	−8.71	0.058
	0.094 [g,i]	−10.97 [i]	
	0.22 [j]		
Fe^{3+}	0.059	−7.97	0.072
		−9.14 [b]	
		−6.17 [k]	
Fe^{4+}	0.063	−7.25	0.084
Co^+	0.050	−8.88	0.043
Co^{2+}	0.057	−8.29	0.057
Co^{3+}	0.062	−7.63	0.069
Co^{4+}	0.064	−6.97	0.080
Ni^+	0.054	−8.45	0.042
Ni^{2+}	0.060	−7.92	0.055
Ni^{3+}	0.064	−7.32	0.067
Ni^{4+}	0.065	−6.72	0.077
Cu^+		−17.29	0.581
		−15.0 [b]	
		−17.0 [l]	
Cu^{2+}	0.062	−7.59	0.054

TABLE I *(Continued)*

Ion	R_0	λ_0	λ_{val}
Cu^{3+}	0.065	−7.04	0.065
Cu^{4+}	0.066	−6.49	0.074
Kr		−78.74	
Y^{2+}	−0.344	−33.75	0.055
Y^{3+}		−31.06	
Zr^{2+}	−0.275	−30.41	0.060
Zr^{3+}	−0.230	−28.16	0.073
Nb^{2+}	−0.227	−27.89	0.063
Nb^{3+}	−0.194	−25.94	0.076
Nb^{4+}	−0.168	−24.08	0.086
Mo^{+}	−0.222	−27.53	0.052
Mo^{2+}	−0.191	−25.88	0.066
Mo^{3+}	−0.166	−24.16	0.077
Mo^{4+}	−0.145	−22.50	0.087
Mo^{5+}	−0.129	−21.02	0.095
Tc^{2+}	−0.164	−24.21	0.067
Tc^{3+}	−0.144	−22.67	0.078
Tc^{4+}	−0.127	−21.19	0.087
Ru^{2+}	−0.142	−22.79	0.069
Ru^{3+}	−0.126	−21.40	0.079
Ru^{4+}	−0.112	−20.06	0.087
Rh	−0.155		
Rh^{+}	−0.139	−22.78	0.059
Rh^{2+}	−0.124	−21.57	0.070
Rh^{3+}	−0.111	−20.30	0.079
Rh^{4+}	−0.100	−19.08	0.087
Pd^{2+}	−0.109	−20.49	0.070
Pd^{3+}	−0.098	−19.34	0.079
Ag^{2+}	−0.096	−19.54	0.070
Ag^{3+}	−0.087	−18.48	0.079
La^{2+}	−0.430	−70.99	0.119
Re^{4+}	−0.242	−43.84	0.073
Ir^{3+}	−0.221	−41.87	0.069
Ir^{4+}	−0.206	−39.78	0.076
Pt^{3+}	−0.204	−39.98	0.070
Pt^{4+}	−0.191	−38.07	0.076
$Au(6s^1)$	−0.005	−71.97	
$Au(6p^1)$	−0.222	−68.35	0.010
Rn		−275.84	
Fr^{+}		−193.01	
Ra^{2+}		−151.60	
Ac^{3+}		−126.06	
Th^{3+}	−0.208	−122.72	0.773
Th^{4+}		−108.46	
Pa^{4+}	−0.177	−106.08	1.014
Pa^{5+}		−95.44	
U^{3+}	−0.147	−117.52	0.877
U^{4+}	−0.152	−103.98	1.115

TABLE I *(Continued)*

Ion	R_0	λ_0	λ_{val}
Np^{4+}	−0.131	−102.11	1.249 0.881 [m]
Np^{6+}	−0.139		
Pu^{4+}	−0.112	−100.43	1.440

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[g] Only the direct part of Sternheimer's calculation is compared.

[h] Including one-sixth of the $2p$-closed-shell perturbation.

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D. $5f$ Group

The configuration considered is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$, $4s^2$, $4p^6$, $4d^{10}$, $4f^{14}$, $5s^2$, $5p^6$, $5d^{10}$, $6s^2$, $6p^6$, $5f^{(Z-N_q-86)}$. The Sternheimer parameters for twelve $5f$-group ions are given in Table I.[3] The perturbations considered are $1s \rightarrow d$, $2s \rightarrow d$, $2p \rightarrow f$, $2p \rightarrow p$, $3s \rightarrow d$, $3p \rightarrow f$, $3p \rightarrow p$, $3d \rightarrow g$, $3d \rightarrow d$, $3d \rightarrow s$, $4s \rightarrow d$, $4p \rightarrow f$, $4p \rightarrow p$, $4d \rightarrow g$, $4d \rightarrow d$, $4d \rightarrow s$, $4f \rightarrow h$, $4f \rightarrow f$, $4f \rightarrow p$, $5s \rightarrow d$, $5p \rightarrow f$, $5p \rightarrow p$, $5d \rightarrow g$, $5d \rightarrow d$, $5d \rightarrow s$, $6s \rightarrow d$, $6p \rightarrow f$, and $6p \rightarrow p$. For the U^{6+} and Np^{6+} ions the values of λ_0 obtained are −88.26 and −84.37, respectively, while the other Sternheimer parameters have too high a value because of the $6p \rightarrow f$ perturbation. However, since the contribution to λ_0 due to $6p \rightarrow f$ perturbation was quite small, λ_0 values could be considered reliable. It is believed that for high-Z ions with high ionic charge the free-ion HFS potential $V_0(r)$ and the electronic wave function are not good enough to give reliable values of Sternheimer parameter. The best procedure, therefore, would be to try the relativistic Hartree-Fock free-ion wave functions to calculate λ's and compare them with the present results. This will also give some indication of how reliable the free-ion Sternheimer parameters are to use for the ions in complexes.

E. Li and Au

Lithium was considered in $1s^2$ configuration (Li^+) and $1s^22p^1$ configuration (Li atom). Gold was considered in $5d^{10}6p^1$ and in $5d^{10}6s^1$ configurations. The results are presented in Table I.[3] The perturbations considered are $1s \rightarrow d$ for Li^+, $1s \rightarrow d$, $\frac{1}{6}(2p \rightarrow f)$, and $\frac{1}{6}(2p \rightarrow p)$ for Li, and $1s \rightarrow d$, $2s \rightarrow d$, $2p \rightarrow f$, $2p \rightarrow p$, $3s \rightarrow d$, $3p \rightarrow f$, $3p \rightarrow p$, $3d \rightarrow g$, $3d \rightarrow d$, $3d \rightarrow s$, $4s \rightarrow d$, $4p \rightarrow f$, $4p \rightarrow p$, $4d \rightarrow g$, $4d \rightarrow d$, $4d \rightarrow s$, $4f \rightarrow h$, $4f \rightarrow f$, $4f \rightarrow p$, $5s \rightarrow d$, $5p \rightarrow f$, $5p \rightarrow p$, $5d \rightarrow g$, $5d \rightarrow d$, and $5d \rightarrow s$ for Au. The value, $1-\lambda_0 = 3.46$, obtained for Li atom after considering the contribution of $2p^1$ electron perturbation to be one-sixth of that of the full $2p^6$ shell, is incidentally the same as $|1-\lambda_0| = 3.4 \pm 13\%$ measured by Anderson and Karra[4] for Li^+ ion in LiF by means of acoustic nuclear magnetic resonance.

The other interesting feature is observed when the present calculations are compared with the experimentally measured splittings of atomic core $5p_{3/2}$ and $4p_{3/2}$ levels of Au in gold cyanides by Novakov and Hollander.[5] If we ignore the contribution of the direct crystal potential to the atomic core $p_{3/2}$ level splittings, the ratio of the $5p_{3/2}$ to $4p_{3/2}$ splittings could be written[6,7] as

$$\frac{\Delta E 5p_{3/2}}{\Delta E 4p_{3/2}} = \frac{(1-R_{5p})\langle F^2\rangle_{5p}}{(1-R_{4p})\langle F^2\rangle_{4p}}. \quad (6)$$

This ratio is 1.7 for $Au(5d^{10}6s^1)$ and 1.6 for $Au(5d^{10}6p^1)$, as against approximately 2 measured by Novakov and Hollander.[5] The present calculations do not give any information on the magnitude of the splitting but they do show the significance of Sternheimer effect also for the core electrons. The s-p hybridized type of orbitals, believed to be present in physical situation, i.e., Au in gold cyanides, are not expected to alter the inference made here.

We also compare, in Table I, the results obtained in the present work with those already known.

The total time taken by the computations, presented here, including the computation of HFS wave function of the ions, was about 2 h on IBM 360(65) installation at the University of Manitoba.

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[3]Tables of λ, R, $\langle r^2\rangle$, $\langle F^2\rangle$ parameters at all the sites of the ion and the quadrupole polarizability α_q of the ion are given in a supplementary paper (unpublished). For this supplementary paper order NAPS Document No. 02148 for 20 pages of nine tables. Order from ASIS/NAPS, c/o Microfiche Publications, 305 East 46th Street, New York, N. Y. 10017. Remit with order $1.50 for microfiche or $5.00 for photocopies. Make checks payable to Microfiche Publications.

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