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Quadrupole antishielding factors for some $3d^5$, $4d^5$, and $5d^5$ ions

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With the use of restricted numerical Hartree-Fock-Slater wave functions and the perturbation-numerical approach of Sternheimer, the ionic antishielding factor γ_∞ has been calculated for the following three isoelectronic series of ions: Cr^+, Mn^{2+}, Fe^{3+}, Co^{4+}, Ni^{5+}, Cu^{6+}; Mo^+, Tc^{2+}, Ru^{3+}, Rh^{4+}, Pd^{5+}, Ag^{6+}; and W^+, Re^{2+}, Os^{3+}, Ir^{4+}, Pt^{5+}, Au^{6+}. For the ions of the first two series, γ_∞ values have been correlated to their distance of outermost maximum in the total radial electron density distribution function. Also, it has been observed that within an isoelectronic series, γ_∞ values can be satisfactorily represented in terms of a polynomial in Z^{-1}, the reciprocal of atomic number.

I. INTRODUCTION

The knowledge of the Sternheimer antishielding factor,[1] γ_∞, is essential in interpreting the nuclear quadrupole coupling measurements in solids. The transition-metal ions of group VIII in the periodic table of elements with d^5 electronic configuration are important in Mössbauer-effect studies. In this region, γ_∞ values for Mn^{2+} and Fe^{3+} have been reported earlier by Burns and Wikner[2] and by Sternheimer,[3] while Gupta *et al.*[4] have calculated γ_∞ for the W^+ ion. Very recently, Ray *et al.*[5] have calculated γ_∞ for the Fe^{3+} ion using differential-equation[1] (DE) and linked-cluster many-body perturbation theory (LCMBPT) methods in order to include higher-order terms due to consistency and correlation effects, respectively.

In this paper we report the results of our calculations of γ_∞ to zeroth order using the DE method for the following three isoelectronic series of ions in the d^5 electronic configuration: Cr^+, Mn^{2+}, Fe^{3+}, Co^{4+}, Ni^{5+}, Cu^{6+}; Mo^+, Tc^{2+}, Ru^{3+}, Rh^{4+}, Pd^{5+}, Ag^{6+}; and W^+, Re^{2+}, Os^{3+}, Ir^{4+}, Pt^{5+}, Au^{6+}. We have used restricted numerical Hartree-Fock-Slater[6] (HFS) wave functions to describe the unperturbed ^6S state of all of the ions considered above. γ_∞ values for $3d^5$ and $4d^5$ series of ions have been correlated to their distance of the outermost maximum, ρ_m, in the total radial electron density distribution function. Owing to a rather flat distribution observed in this function at larger radii, in the case of the $5d^5$ series of ions a similar correlation could not be obtained. Lahiri and Mukherji[7] had earlier obtained such correlations for the ions isoelectronic with the He, Be, Ne, and Ar configurations, respectively. We have observed that a satisfactory polynomial fit between γ_∞ and the reciprocal of atomic number, Z^{-1}, can be given for each of the three isoelectronic series considered here.

In Sec. II we describe in brief the perturbation-numerical approach (DE) of Sternheimer adopted in this work, along with other computational details. In Sec. III we present the results of our calculations and compare them with other data available in the literature. Finally, in Sec. IV we give the main conclusions arrived at in the present work.

II. DETAILS OF CALCULATION

In Sternheimer's method, the quadrupole-moment perturbed radial perturbation $u_1'(nl\to l')$ of the core orbital $u_0'(nl)$ is obtained by direct solution of the first-order perturbed radial equation given by

$$\left(-\frac{d^2}{dr^2}+\frac{l'(l'+1)}{r^2}+V_0(r)-E_0\right)u_1'(nl\to l') = u_0'(nl)\left(\frac{1}{r^3}-\left\langle\frac{1}{r^3}\right\rangle\delta_{ll'}\right), \quad (1)$$

where $u_0'(nl)$ is normalized as

$$\int_0^\infty u_0'^2(nl)\,dr = 1, \quad (2)$$

and where $u_1'(nl\to l)$ obeys the following orthogonality condition:

$$\int_0^\infty u_0'(nl)u_1'(nl\to l)\,dr = 0. \quad (3)$$

In actual calculations $V_0(r)-E$ was approximated[3] as

$$V_0(r)-E=\frac{1}{u_0'}\frac{d^2u_0'}{dr^2}-\frac{l(l+1)}{r^2}. \quad (4)$$

γ_∞ is then given by

$$\gamma_\infty=\sum_{nl}c(nl\to l')\int_0^\infty u_0'(nl)u_1'(nl\to l')r^2\,dr, \quad (5)$$

where $c(nl\to l')$ give the results of integration over angular variables, and where their values for various $nl\to l'$ excitations have been tabulated by Sternheimer.[8] For the outermost d orbital, the $c(nl \rightarrow l')$ were divided by 2 in all cases.

Our numerical procedure for obtaining the well-behaved solutions $u_1'(nl \rightarrow l')$ from the difference equation corresponding to Eq. (1) has been described earlier.[9] Thus we first generated the HFS wave functions for the ion being considered over a 441-point mesh using a modified Herman-Skillman program adopted for the IBM 7044/1401 system at the Indian Institute of Technology, Kanpur. The radius of maximum charge density ρ_m was defined as

$$\rho_m = \int \sum_i \psi_k^*(i)\psi_k(i) r_i^2 \, d\Omega_i \, , \tag{6}$$

where i varies over all occupied core orbitals, including the outermost d orbitals, and $\psi_k(i)$ gives the wave function of the ith electron in the kth orbital. The radial perturbations ($l = l'$) were obtained by carrying out inward and outward integrations up to some suitable matching point in the intermediate region, and the corresponding multiplicative constants were adjusted in an iterative manner to give a solution which is continuous and is orthogonal to u_0'. For angular perturbations ($l \neq l'$) the criterion of continuity in slope was demanded in place of orthogonality. All integrals were evaluated using the method of finite differences,[10] employing the formula for integration through adjacent intervals, including differences up to fourth order.

The polynomial fittings of $|\gamma_\infty|$ in terms of

$$|\gamma_\infty| = \sum_{i=0}^{3} a_i \rho_m^i \tag{7}$$

and

$$|\gamma_\infty| = \sum_{i=1}^{4} b_i Z^{-i} \tag{8}$$

were performed in double precision by minimizing the average percentage error using normal equations.[11]

III. RESULTS AND DISCUSSION

In Table I we present the results of our calculations of γ_∞. In order to be consistent with the notation adopted in recent works,[5,12] our γ_∞ values will be hereafter denoted by $(\gamma_\infty)_0$, meaning that the present calculations do not include consistency and correlation effects. In column 2 of Table I we have also given other $(\gamma_\infty)_0$ results previously reported in the literature. The slight differences between our result and those of Sternheimer[3] and Ray *et al.*[5] probably arises as a result of a different choice of zero-order wave functions made by us. The variation-perturbation method[13] adopted by Burns and Wikner seems to give less reliable results. We note here that γ_∞ for the W^+ ion, as calculated by Gupta *et al.*,[4] is -56.848; this does not include the contribution from the $5d$ orbital. These terms amount to -23.04, according to our present calculations. The previously calculated $(\gamma_\infty)_0$ for W^+ can therefore be quoted as -79.89. A slightly larger value obtained in this way can be attributed to the fact that the neutral-atom Hartree-Fock wave functions were used in the previous calculation for the W^+ ion.

TABLE I. Zeroth-order ionic antishielding factor $(\gamma_\infty)_0$ for various ions. ρ_m gives the distance of the farthest peak in the total electron density distribution [Eq. (6)].

Ion	$-(\gamma_\infty)_0$	ρ_m (a.u.)
Cr^+	16.67	0.767
Mn^{2+}	11.96 (6.81 [a], 11.37 [b])	0.721
Fe^{3+}	9.64 (6.17 [a], 9.47 [c])	0.675
Co^{4+}	8.13	0.643
Ni^{5+}	7.04	0.600
Cu^{6+}	6.21	0.571
Mo^+	39.36	1.014
Tc^{2+}	30.62	0.986
Ru^{3+}	25.71	0.938
Rh^{4+}	22.27	0.891
Pd^{5+}	19.70	0.865
Ag^{6+}	17.68	0.819
W^+	77.31	
Re^{2+}	61.67	
Os^{3+}	52.66	
Ir^{4+}	46.10	
Pt^{5+}	41.35	
Au^{6+}	37.49	

[a] See Ref. 2.
[b] See Ref. 3.
[c] See Ref. 5.

The downward trend in $(\gamma_\infty)_0$ values as Z increases within an isolectronic series is due to the progressively increasing binding energy obtained for the outer orbitals. In Table II we have given the individual radial and total angular contributions to $(\gamma_\infty)_0$ for the Os^{3+} ion. The most significant antishielding contribution arises from the radial excitation of the outermost p orbitals; this is true in general for all of the ions considered in this work.

Recent LCMBPT calculations of Ray *et al.*[12] have shown that in the case of the Fe^{3+} ion the correlation effects contribute $<0.5\%$ of the total $(\gamma_\infty)_0$ value. Very recently, Ray[5,12] and co-workers have performed DE and LCMBPT calculations to include the consistency effects $(\gamma_\infty)_1$ for Rb^+, Cs^+, Mn^{2+}, Fe^{3+}, F^-, Cl^-, and Br^- ions. These authors

TABLE II. Individual radial and total angular contributions to $(\gamma_\infty)_0$ for the Os^{3+} ion. $\langle r^{-3}\rangle_{nl}$ gives the expectation value of r^{-3} over the unperturbed wave function.

Perturbation ($nl \to l'$)	$-(\gamma_\infty)_0$	$\langle r^{-3}\rangle_{nl}$
$2p \to p$	0.176	15 566.16
$3p \to p$	0.978	3368.87
$4p \to p$	5.164	782.69
$5p \to p$	35.300	128.17
$3d \to d$	0.200	599.12
$4d \to d$	1.488	121.92
$5d \to d$	9.547	12.36
$4f \to f$	1.345	25.35
Total radial	54.109	
Total angular	−1.452	
Total	52.657	

conclude that in general the consistency effects are within 15% of the total $(\gamma_\infty)_0$ values. In particular, $(\gamma_\infty)_1$ for Fe^{3+} is calculated to be ~ 8% of the total $(\gamma_\infty)_0$. Our antishielding-factor calculations are therefore, from this point of view, reliable to within 15% in most cases.

In most of the experimental conditions for studying nuclear quadrupole interactions the ion of interest is situated in a crystalline lattice. Because of changes in the electron distribution in going from the free ion to the crystalline state the antishielding factors are likely to be modified considerably. In the absence of good wave functions for ions in the solid state we thought it worthwhile to correlate $(\gamma_\infty)_0$ values to the position of the outermost maximum ρ_m in the total radial distribution function defined by Eq. (6) for the ions in each isoelectronic series. Similar correlations have been earlier reported by Lahiri and Mukherji[7] in the case of the isoelectronic series corresponding to He, Be, Ne, and Ar configurations, respectively. In Table III, column 3 gives the coefficients a_i defining a four-parameter polynomial fit given by Eq. (7). The average percentage error for the fit is, respectively, 2% and 3% for the $3d^5$ and $4d^5$ series of ions. In the cases where accurate electronic distribution is available, from the single-crystal x-ray data, for example, it is hoped that the present interpolation relations would provide an improvement over the free-ion $(\gamma_\infty)_0$ values. In solids one expects the cations to expand, and for a typical increase in the ρ_m value by ~ 10% the antishielding factor is expected to increase by ~ 40% for the Fe^{3+} ion and ~ 60% for the Ru^{3+} ion. We note here that the recent cluster calculations[14] indicate that for octahedral FeF_6^{3-} the d component in the t_{2g} orbital has a maximum of the radial distribution function only at ~ 1% above the value for the free Fe^{3+} ion.

TABLE III. Values of coefficients a_i in $|(\gamma_\infty)_0| = \sum_{i=0}^{3} a_i \rho_m^i$ for the $3d^5$ and $4d^5$ isoelectronic series.

Series	i	a_i
$3d^5$	0	+ 9.943 319
	1	+ 56.518 661
	2	−247.487 450
	3	+241.137 866
$4d^5$	0	+ 25.889 976
	1	+254.745 834
	2	−671.611 792
	3	+426.218 040

TABLE IV. The coefficients b_i in $|(\gamma_\infty)_0| = \sum_{i=1}^{4} b_i Z^{-i}$; the value of C is 10^5, 10^6, and 10^7, respectively, for the $3d^5$, $4d^5$, and $5d^5$ series.

Series	i	b_i/C
$3d^5$	1	− 0.304 128
	2	+ 25.190 173
	3	− 694.757 557
	4	+ 6 424.128 560
$4d^5$	1	− 0.441 065
	2	+ 60.668 197
	3	− 2 783.708 012
	4	+ 42 697.050 192
$5d^5$	1	− 0.759 240
	2	+ 177.639 258
	3	− 13 861.434 764
	4	+ 360 887.472 128

Within an isoelectronic series, using Z-perturbation theory, Dalgarno *et al.*[15] and Cohen *et al.*[16] have obtained the quadrupole shielding factor γ_∞ in terms of a power series in Z^{-1} for two- and four-electron atoms and ions in their ground states. We have observed that an excellent fit can be obtained for $(\gamma_\infty)_0$ as a four-parameter polynomial in Z^{-1}, as defined in Eq. (8) for all of the ions discussed here. The corresponding b_i are given in Table IV. The average percentage error for the fit is 0.6%, 0.4%, and 0.36%, respectively, for the $3d^5$, $4d^5$, and $5d^5$ series of ions. These polynomials can be used to obtain $(\gamma_\infty)_0$ values for other positive ions in the given isoelectronic series.

IV. CONCLUSIONS

The main purpose of the present work has been to make available the theoretical values of the Sternheimer antishielding factor γ_∞ for the ions with d^5 configuration in group VIII of the periodic table. In light of the recent LCMBPT calculations,[5,12] the present DE results are reliable to within 15% of the total γ_∞ value. For the ions of the $3d^5$ and $4d^5$ series, our $(\gamma_\infty)_0$ values have been correlated, using Eq. (7), to the position of the farthest peak in the total radial charge distribution function, as defined in Eq. (6). In the cases where ρ_m can be obtained from solid-state data, Eq. (7) should provide improvement over the free-ion $(\gamma_\infty)_0$ values. More reliable calculations using good crystalline wave functions seem to be highly desirable at this point. Finally, $(\gamma_\infty)_0$ values have been expressed in terms of a four-parameter polynomial in Z^{-1} to enable us to make an estimate of the antishielding factor for the other positive ions in each isoelectronic series considered in this work.

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