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Sternheimer valence shielding and antishielding factors for some ions of interest in Mössbauer spectroscopy

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Using nonrelativistic Hartree-Fock-Slater wave functions and Sternheimer's uncoupled perturbation-numerical method the valence shielding-antishielding factor R including exchange has been calculated for Cr, Mn^+, Fe^{2+}, Co^{3+}, Ni^{4+} (all in $3d^6$ isoelectronic configuration), Ru^{2+} ($4d^6$), Os^{2+} ($5d^6$), Pr^{3+} ($4f^2$), Tm^{3+} ($4f^{12}$), and Np^{6+} ($5f^1$) to be 0.26, 0.15, 0.12, 0.10, 0.08, −0.06, −0.12, 0.12, 0.18, and 0.01, respectively. The quadrupole splitting data on Fe_2O_3, Al_2O_3:Fe^{3+}, yttrium iron garnet (T_d and O_h Fe^{3+} sites), and $FeSiF_6 \cdot 6H_2O$ have been reinterpreted using more reliable values of Sternheimer shielding-antishielding factors to obtain $Q(^{57}Fe^m)$ as 0.154, 0.179, 0.146, 0.139, and 0.156 b, respectively. The repercussions of the changes in the charge spread of the $3d^6$ ions in the crystalline lattice on R have also been discussed.

I. INTRODUCTION

In the absence of the first-principles calculations of the electric field gradient q on the transition-metal compounds the quadrupole splitting (QS) data on these systems obtained by means of Mössbauer spectroscopy have been generally interpreted as

$$q=(1-\gamma_\infty)q_{\text{lat}}+(1-R)q_{\text{val}}\,, \qquad (1)$$

where q_{lat} and q_{val} give the field gradient contributions due to lattice charges and the valence electrons, respectively. γ_∞ and R are known as Sternheimer shielding-antishielding factors[1] which take into account the polarization of the core electrons due to q_{lat} and q_{val}, respectively.

Along with the accurate knowledge of q_{lat} and q_{val}, the interpretation of the experimental data obtained in the crystalline compounds require also the knowledge of reliable values of the change in γ_∞ and R as the ion goes from free state into the crystalline state. Recently we have studied[2] the influence of such effects on γ_∞ by correlating the latter to the position of the outermost maximum in the total radial electron density distribution, ρ_m, where it has been shown that an increase in ρ_m by ~10% increases γ_∞ by ~40%. The purpose of this paper is to report the results of a similar analysis of the Sternheimer valence shielding factor R including exchange for the isoelectronic series consisting of Cr, Mn^+, Fe^{2+}, Co^{3+}, and Ni^{4+} in $3d^6$ isoelectronic configuration. We also report here the results of our calculations of R including exchange for $Ru^{2+}(4d^6)$, $Os^{2+}(5d^6)$, $Pr^{3+}(4f^2)$, $Tm^{3+}(4f^{12})$, and $Np^{6+}(5f^1)$ ions. We have used the nonrelativistic Hartree-Fock-Slater (HFS) wave functions[3] to describe the unperturbed state and the first-order perturbations of the core orbitals were obtained by means of Sternheimer's perturbation-numerical method.

The calculations of R for Fe^{2+} ion have been reported earlier by several workers[4-6] using methods which differ in accuracy. Ingalls[4] has used the analytic perturbation-variation method of Das and Bersohn[7] and obtained R as +0.22 for Fe^{2+} ions. One of the limitations of this method is that of the arbitrariness in the choice of the perturbed wave functions. Freeman and Watson[5] employed the orbitally polarized unrestricted-Hartree-Fock method to obtain the radial contribution to $(1-R)\langle r^{-3}\rangle$ as 4.93 a.u., where $\langle r^{-3}\rangle$ gives the expectation value of r^{-3} over the wave functions corresponding to $3d$ orbitals. This method is superior to the analytic perturbation-variation method in its proper handling of orthogonality, self-consistency, and exchange. Unfortunately due to the computational difficulties arising out of the inclusion of angular distortions and in view of the uncertainties related to the breakdown of symmetry, the unrestricted-Hartree-Fock results are available only corresponding to the radial distortions. Ingalls[8] has combined Freeman and Watson's results with his own calculations of the angular contributions and obtained $R=+0.32$ for Fe^{2+}. A more reliable value of $R=0.12$ has been recently reported by Sternheimer[6] using Hartree-Fock wave functions. A comparison of the present calculation of R for Fe^{2+} with those of Sternheimer shows excellent quantitative agreement and serves as a check on the reliability of our calculations on the other open shell systems.

Using the most recent values of γ_∞ and R we have recalculated the value of the nuclear quadrupole moment for $^{57}Fe^m$ nucleus, $Q(^{57}Fe^m)$, from Sharma's analysis[9] of the QS data on some ferric compounds such as Fe_2O_3, Al_2O_3:Fe^{3+}, and yttrium iron garnet (YIG). The effect of the change in $\langle r^{-3}\rangle_{3d}$ value for Fe^{2+} ion in ferrous compounds on γ_∞ and R has been estimated from the polynomial relationship obtained in this paper for γ_∞ and R in terms of $\langle r^{-3}\rangle_{3d}$, respectively, within the $3d^6$ isoelectronic series. Using the appropriate values of γ_∞ and R factors so obtained we have recalculated $Q(^{57}\mathrm{Fe}^m)$ from Ingalls's analysis[10] of the QS data on $\mathrm{FeSiF_6\cdot 6H_2O}$. The $Q(^{57}\mathrm{Fe}^m)$ obtained in the cases of $\mathrm{FeSiF_6\cdot 6H_2O}$, $\mathrm{Fe_2O_3}$, $\mathrm{Al_2O_3:Fe^{3+}}$, YIG ($T_d\,\mathrm{Fe^{3+}}$ site), and YIG ($O_h\,\mathrm{Fe^{3+}}$ site) are given by 0.156, 0.154, 0.179, 0.146, and 0.139 b. It has been possible to express $(1-R)\langle r^{-3}\rangle_{3d}$ in terms of a polynomial in ρ_m within the $3d^6$ isoelectronic series. Such a correlation shows that an increase of ~10% in ρ_m decreases $(1-R)\langle r^{-3}\rangle_{3d}$ by ~47% with respect to the free-ion value.

The results of the calculations of R for $\mathrm{Ru}^{2+}(4d^6)$ and $\mathrm{Os}^{2+}(5d^6)$ yield a net antishielding ($R<0$) effect of -0.0612 and -0.1174, respectively. In the cases of Pr^{3+} and Tm^{3+} the earlier calculations[11] of R did not include the contributions due to the exchange terms. The presently calculated values of the net exchange contribution in these cases are 0.008 and -0.008, respectively, which leaves the agreement obtained with the experimental results in the earlier calculations[11] essentially unchanged.

II. CALCULATIONS

The following equations [Eqs. (2)–(11)] and the notation, which were used in the present work, are essentially identical to those of Sternheimer.[12] The major computational step involves the calculation of the first-order moment-perturbed radial distortion $v(nl\to l')$ of the core orbital $u(nl)$ characterized by the quantum numbers nl. The pertinent inhomogeneous differential equation is given by

$$\left(-\frac{d^2}{dr^2}+\frac{l'(l'+1)}{r^2}+V_0-E_0\right)v(nl\to l') = u(nl)\left(r^{-3}-\langle r^{-3}\rangle_{nl}\,\delta_{ll'}\right), \qquad (2)$$

where $u(nl)$ is normalized as

$$\int_0^\infty u(nl)\,dr=1 \qquad (3)$$

and $v(nl\to l')$ satisfies the orthogonality condition

$$\int_0^\infty u(nl)v(nl\to l')\,dr=0. \qquad (4)$$

Denoting the valency electron wave function by $\omega(n_e l_e)$, the direct contribution to R due to the excitation $(nl\to l')$ of the core orbital is given by

$$R_D(nl\to l';n_e l_e) = \int_0^\infty \gamma(nl\to l';r)[\omega(n_e l_e)]^2 r^{-3}\,dr\Big/\langle r^{-3}\rangle_{n_e l_e}, \qquad (5)$$

where

$$\gamma(nl\to l';r)=\frac{1}{Q}\left(\int_0^r Q_i(nl\to l')\,dr' + r^5\int_r^\infty Q_i(nl\to l')r'^{-5}\,dr'\right), \qquad (6)$$

with

$$Q_i(nl\to l')=c(nl\to l')Q\,u(nl)v(nl\to l')r^2. \qquad (7)$$

$Q_i(nl\to l')$ gives the direct contribution to the density of the induced moment corresponding to $nl\to l'$ excitation.

The contribution to R due to the exchange term arising from $nl\to l'$ is given by

$$R_E(nl\to l';n_e l_e;L)=-C(nl\to l';n_e l_e;L)\int_0^\infty u(n)\,\omega(n_e l_e)g_L\,dr\Big/\langle r^{-3}\rangle_{n_e l_e}, \qquad (8)$$

where

$$g_L(nl\to l';n_e l_e)=\frac{1}{r^{L+1}}\int_0^r v(nl\to l')\omega(n_e l_e)r'^L\,dr' + r^L\int_r^\infty v(nl\to l')\omega(n_e l_e)r'^{-L-1}\,dr'. \qquad (9)$$

The net R is given by

$$R=\sum_{nl}\left[R_D(nl\to l';n_e l_e)+\sum_L R_E(nl\to l';n_e l_e;L)\right]. \qquad (10)$$

The constants c and C in Eqs. (6) and (7) have been tabulated by Sternheimer.[12]

The functions $u(nl)$ were generated over the 441-point mesh using a modified version of the Herman-Skillman program[13] adopted for IBM 7044/1401 computer system at Indian Institute of Technology, Kanpur. The effective potential V_0-E_0 was calculated according to the local approximation[1]

$$V_0-E_0=\frac{1}{u}\frac{d^2u}{dr^2}-\frac{l(l+1)}{r^2}. \qquad (11)$$

TABLE I. Individual direct and exchange contributions R_D and R_E to the Sternheimer valence shielding factor R for Cr, Mn^+, Fe^{2+}, Co^{3+}, and Ni^{4+} in $3d^6$ configuration. R_E values have been given in parentheses in each case below R_D values. ρ_m and $\langle r^{-3}\rangle_{3d}$ values are in Bohr units and the $3d$ orbital eigenvalues are given in Rydberg units.

Perturbation	Cr	Mn^+	Fe^{2+}	Co^{3+}	Ni^{4+}
$1s \rightarrow d$	0.0279	0.0268	0.0257	0.0247	0.0237
	(−0.0008)	(−0.0008)	(−0.0008)	(−0.0008)	(−0.0008)
$2s \rightarrow d$	0.0476	0.0444	0.0416	0.0389	0.0367
	(−0.0127)	(−0.0122)	(−0.0118)	(−0.0113)	(−0.0109)
$3s \rightarrow d$	0.0236	0.0207	0.0184	0.0161	0.0145
	(−0.0091)	(−0.0079)	(−0.0070)	(−0.0060)	(−0.0053)
$2p \rightarrow f$	0.0703	0.0661	0.0624	0.0590	0.0560
	(−0.0146)	(−0.0141)	(−0.0137)	(−0.0132)	(−0.0128)
$3p \rightarrow f$	0.0376	0.0335	0.0300	0.0271	0.0248
	(−0.0137)	(−0.0122)	(−0.0108)	(−0.0097)	(−0.0087)
$3d \rightarrow s$	−0.0090	−0.0085	−0.0084	−0.0081	−0.0078
$3d \rightarrow g$	0.0167	0.0171	0.0169	0.0164	0.0158
R_D (ang):	0.2147	0.2001	0.1866	0.1741	0.1637
R_E (ang):	(−0.0509)	(−0.0472)	(−0.0441)	(−0.0410)	(−0.0385)
Total (ang)	0.1638	0.1529	0.1425	0.1331	0.1252
$2p \rightarrow p$	−0.3626	−0.3308	−0.3027	−0.2782	−0.2569
	(0.2698)	(0.2535)	(0.2387)	(0.2251)	(0.2127)
$3p \rightarrow p$	0.1587	0.1750	0.1790	0.1748	0.1667
	(−0.1275)	(−0.1581)	(−0.1773)	(−0.1848)	(−0.1848)
$3d \rightarrow d$	0.1558	0.0625	0.0389	0.0283	0.0223
R_D (rad):	−0.0481	−0.0933	−0.0848	−0.0751	−0.0679
R_E (rad):	(0.1423)	(0.0954)	(0.0614)	(0.0403)	(0.0279)
Total (rad)	0.0942	−0.0021	−0.0234	−0.0348	−0.0400
Net R	0.2580	0.1550	0.1191	0.0983	0.0852
γ_∞	−16.67	−11.96	−9.64	−8.13	−7.04
ρ_m	0.767 33	0.732 73	0.687 35	0.643 35	0.612 27
$\langle r^{-3}\rangle_{3d}$	2.967 471	4.264 828	5.773 645	7.499 87	9.458 906
$-\epsilon_{3d}$	0.292 534	1.161 839	2.418 018	3.984 175	5.825 47

The method of solution of the difference equation corresponding to Eq. (2) has been described in our earlier work.[14] All the integrals were calculated using the finite difference method[15] including differences up to fourth order.

The position of the outermost maximum in the total radial charge density distribution function was obtained from

$$\rho_m = \int \sum_i \psi_k^*(i)\psi_k(i) r_i^2 \, d\Omega_i , \tag{12}$$

where i varies over all occupied orbitals given by ψ_k. The polynomial fitting of R and γ_∞, respectively, in terms of $\langle r^{-3}\rangle_{3d}$ and of $(1-R)\langle r^{-3}\rangle_{3d}$ in terms of ρ_m were performed according to

$$R = \sum_{N=1}^{3,4,\text{ or } 5} a_N (\langle r^{-3}\rangle_{3d})^{-N}, \tag{13}$$

$$\gamma_\infty = \sum_{N=1}^{3,4,\text{ or } 5} a_N (\langle r^{-3}\rangle_{3d})^{-N}, \tag{14}$$

$$(1-R)\langle r^{-3}\rangle_{3d} = \sum_{N=1}^{4 \text{ or } 5} a_N \rho_m^{-N} , \tag{15}$$

by minimizing the average percentage error via normal equations.[16]

III. RESULTS AND DISCUSSION

In Table I we have presented the results of various individual direct and exchange contributions (given in parentheses in the table) to R due to all angular and radial excitations, net R, γ_∞,

ρ_m, $\langle r^{-3}\rangle_{3d}$, and the one-electron orbital eigenvalue ϵ_{3d} corresponding to Cr, Mn^+, Fe^{2+}, Co^{3+}, and Ni^{4+}. We note here that the γ_∞ values correspond to Cr^+, Mn^{2+}, Fe^{3+}, Co^{4+}, and Ni^{5+} ions using the HFS wave functions and have been reported earlier.[2]

The most significant contributions to R come from the radial excitations of $np\rightarrow p$ type. The exchange contribution R_E corresponding to these excitations is always > 70% of the direct contribution R_D and is opposite in sign. In the case of $2p\rightarrow p$ excitations the direct contribution predominates over the exchange term and the net effect is antishielding. As Z increases within the isoelectronic series the valence electrons experience greater binding and a stronger overlap effect is obtained between $3d$ and the p orbitals in the core. This is reflected in the increasing percentage of the exchange term with respect to the direct term corresponding to $2p\rightarrow p$ contributions to R presented in Table I. Thus $R_E(2p\rightarrow p, 3d)$ is, respectively, 74.4%, 76.6%, 78.8%, 80.9% and, 82.8% of $R_D(2p\rightarrow p, 3d)$ for Cr, Mn^+, Fe^{2+}, Co^{3+}, and Ni^{4+}. Interestingly, an even larger effect corresponding to $3p\rightarrow p$ excitations can be noticed in Table I. For Cr, $R_E(3p\rightarrow p, 3d)$ is 80% of the direct term and the net effect is shielding. Beyond the case of Fe^{2+} ion in the series where the two contributions almost cancel each other, the exchange term predominates and the net $3p\rightarrow p$ contribution becomes antishielding. In the case of $3d^6$ electronic configuration which is of interest to us here, the exchange term corresponding to $3d\rightarrow d$ excitation is zero and the direct term gives rise to shielding which decreases with increasing Z in the series. As a result, except in the case of Cr atom, where due to a large $3d\rightarrow d$ direct contribution to R one obtains a net shielding effect, the total radial contribution to R is antishielding and increases in magnitude with increase in Z. The total angular contribution to R is always shielding, and predominates over the total radial contributions to R. With increasing Z the total angular contribution decreases and in overall the net R is shielding and decreases with increasing Z.

Very recently Das *et al.*[17] have carried out linked-cluster many-body perturbation-theory (LCMBPT) calculations of R for Fe^{2+} ion and their results show that the zeroth-order contribution to R value amounts to 0.13 as compared to our calculated value of 0.12 using HFS wave functions. As noted earlier Sternheimer's calculations give $R(Fe^{2+})=0.12$. The sum of consistency and correlation contributions in the LCMBPT calculation amounts to -0.01 and thus the most reliable estimate of R gives a net shielding of 12% and the corresponding $\langle r^{-3}\rangle_{3d}=5.086$ a.u. for Fe^{2+} free ion. The calculations of the relativistic effects on R have not been performed so far, but they are expected to be smaller than the correlation effects.

Using γ_∞ and $1-R$ as 10.47 and 0.88, respectively, and the various local, nonlocal, and distant contributions to the field gradient as calculated by Sharma[9] for Fe_2O_3, $Al_2O_3:Fe^{3+}$, and the tetrahedral and octahedral Fe^{3+} sites in YIG we obtain $Q(^{57}Fe^m)$ as 0.154, 0.179, 0.146, and 0.139b, respectively. These values are to be compared with Sharma's values of 0.180 b for Fe_2O_3 and 0.204 b for $Al_2O_3:Fe^{3+}$. It will be seen that the present values are in better agreement with $Q(^{57}Fe^m)$ value derived from $FeSiF_6\cdot 6H_2O$ data corresponding to the Fe^{2+} ion.

It has been possible to express γ_∞ values obtained in Ref. 2 and the presently calculated values of R in terms of a polynomial in the inverse of $\langle r^{-3}\rangle_{3d}$, respectively. The various coefficients corresponding to Eq. (13)–(15) have been presented in Table II. It is gratifying to note that the interpolated value of R corresponding to $\langle r^{-3}\rangle_{3d}=5.086$ is 0.132 which is in good agreement with the zeroth-order contribution obtained from the LCMBPT calculation[17] for the Fe^{2+} case. From these polynomials we shall obtain the scaling factors for γ_∞ and R corresponding to the changes in the Fe^{2+} ion appropriate to the situation in $FeSiF_6\cdot 6H_2O$. Ingalls[10] has used a covalency factor of 10% to reduce the free ionic $\langle r^{-3}\rangle_{3d}$ in $FeSiF_6\cdot 6H_2O$. The appropriate values of γ_∞ and $1-R$ corresponding to the $\langle r^{-3}\rangle_{3d}$ value of 4.622 a.u. are obtained from Table II as 12.07 and 0.855, respectively, to give $Q(^{57}Fe^m)$ as 0.156 b which is in closer agreement with $Q(^{57}Fe^m)$ obtained from ferric compound data. We note here that in the interpretation of the latter no account has been taken of the covalency effects although there is a good deal of evidence in the literature[18] of such effects in the ferric systems. The present estimates of $Q(^{57}Fe^m)$ may be compared with a theoretical estimate of $Q(^{57}Fe^m)$ based on the nuclear model calculation[19] which gives a value of 0.16 ± 0.02 b.

The average electronic charge distribution of the ion in actual solids is expected to be different from the free-ion value. The position ρ_m of the outermost peak in the total radial electronic charge distribution can be regarded as a sensitive measure of the expansion or contraction of the ionic charge spread inside the actual solid and a correlation of $(1-R)\langle r^{-3}\rangle_{3d}$ with ρ_m within an isoelectronic series would be useful in estimating the influence of such changes on the electric field gradient due to valence electrons. In Table II,

TABLE II. Values of various coefficients, a_N, defining R, γ_∞, and $(1-R)\langle r^{-3}\rangle_{3d}$ in terms of polynomials[a] in $\langle r^{-3}\rangle_{3d}$, $\langle r^{-3}\rangle_{3d}$ and ρ_m, respectively. APE denotes the average percentage error in each fit.

		R			γ_∞		$(1-R)\langle r^{-3}\rangle_{3d}$	
Coefficients	$N=3$	$N=4$	$N=5$	$N=3$	$N=4$	$N=5$	$N=4$	$N=5$
a_1	1.149 68	1.246 24	1.736 06	90.950 05	102.795 19	118.328 34	−365.052 60	−1027.308 95
a_2	−4.284 26	−5.867 94	−17.053 43	−285.638 62	−479.901 53	−834.619 81	730.951 60	2548.880 01
a_3	9.331 27	17.220 54	107.639 16	483.226 57	1450.967 39	4318.356 06	−488.038 59	−2354.997 49
a_4		−12.012 83	−318.371 10		−1473.557 79	−11 188.905 40	109.801 78	959.936 66
a_5			367.204 65			11 644.930 49		−144.828 62
APE	0.4	0.3	Exact	0.6	0.1	Exact	0.3	Exact

[a] See Eqs. (13)–(15) of text.

column 4 gives the coefficients of the interpolation polynomials representing $(1-R)\langle r^{-3}\rangle_{3d}$ in terms of ρ_m as defined in Eq. (15). Such a correlation shows that an increase of ~10% in ρ_m decreases $(1-R)\langle r^{-3}\rangle_{3d}$ by ~47% which is a significant effect. We recall here that a similar increase in ρ_m increases γ_∞ by ~40% in case of the $3d^5$ isoelectronic series. When more accurate crystalline wave functions become available the present correlation would be directly relevant.

In Table III we have presented the results of various contributions to R for $Ru^{2+}(4d^6)$, $Os^{2+}(5d^6)$, $Pr^{3+}(4f^2)$, $Tm^{3+}(4f^{12})$, and $Np^{6+}(5f^1)$ ions. The small net antishielding effect of − 0.0612 and − 0.1174 is obtained in the cases of $Ru^{2+}(4d^6)$ and $Os^{2+}(5d^6)$, respectively, and these results should be quoted within an accuracy of 20%.

The earlier calculations of R for the rare-earth ions did not include the contributions due to the exchange terms. It is evident from Table III that the exchange contributions (given in parentheses in the table) due to the $(np \rightarrow p)$ excitations are significant as compared to the direct contribution. The net exchange term however adds up to a small fraction of the net direct term giving the total R for $Pr^{3+}(4f^2)$ and $Tm^{3+}(4f^{12})$ as +0.1183 and 0.1794, respectively, which is in good agreement with the experimental estimates of R obtained for the rare-earth ions.

In the case of $Np^{6+}(5f^1)$ the present calculations using nonrelativistic HFS wave functions give a net shielding of $R=+0.0066$. The only literature value available in this case is the estimate of +0.32 obtained by Dunlap *et al.*[20] from the Mössbauer experiments on $(UO_2)^{2+}$ and $(NpO_2)^{2+}$ coordination compounds. These authors however assumed that the difference in field gradient in the two cases is directly related to the valence-electron contribution due to $5f$ shell in Np^{6+}. The relativistic effects have been shown[21] to be quite significant (~60%) in the case of γ_∞ calculations and we expect an effect of similar magnitude for R factor as well.

IV. SUMMARY

Calculations of the Sternheimer valency shielding antishielding factor R have been reported for Cr, Mn^+, Fe^{2+}, Co^{3+}, Ni^{4+} (all in $3d^6$ isoelectric configuration); $Re^{2+}(4d^6)$; $Os^{2+}(5d^6)$; $Pr^{3+}(4f^2)$; $Tm^{3+}(4f^{12})$; and $Np^{6+}(5f^1)$ using nonrelativistic HFS wave functions and Sternheimer's perturbation-numerical approach. The most reliable free-ionic values of γ_∞ and R have been utilized in recalculating $Q(^{57}Fe^m)$ from the Mössbauer effect QS data on Fe_2O_3, $Al_2O_3:Fe^{3+}$, YIG (T_d and O_h Fe^{3+} sites) and $FeSiF_6 \cdot 6H_2O$, respectively, as 0.154, 0.179, 0.146, 0.139, and

TABLE III. Separate direct and exchange contributions R_D and R_E to R for $\mathrm{Ru}^{2+}(4d^6)$, $\mathrm{Os}^{2+}(5d^6)$, $\mathrm{Pr}^{3+}(4f^2)$, $\mathrm{Tm}^{3+}(4f^{12})$, and $\mathrm{Np}^{6+}(5f^1)$ ions. R_E values appear in the parentheses below the R_D values.

Perturbation	Ru^{2+}	Os^{2+}	Pr^{3+}	Tm^{3+}	Np^{6+}
$1s \to d$	0.0148	0.0083	0.0114	0.0097	0.0072
	(−0.0008)	(−0.0005)	(0.0000)	(0.0000)	(−0.0000)
$2s \to d$	0.0180	0.0082	0.0252	0.0208	0.0145
	(−0.0059)	(−0.0027)	(−0.0008)	(−0.0008)	(−0.0009)
$3s \to d$	0.0096	0.0044	0.0328	0.0249	0.0139
	(−0.0005)	(−0.0005)	(−0.0054)	(−0.0044)	(−0.0026)
$4s \to d$	0.0082	0.0038	0.0177	0.0117	0.0091
	(−0.0037)	(−0.0002)	(−0.0038)	(−0.0023)	(−0.0003)
$5s \to d$		0.0042	0.0036	0.0028	0.0187
		(−0.0019)	(−0.0004)	(−0.0003)	(−0.0046)
$6s \to d$					0.0037
					(−0.0006)
$2p \to f$	0.0299	0.0149	0.0351	0.0294	0.0209
	(−0.0077)	(−0.0041)	(−0.0008)	(−0.0008)	(−0.0009)
$3p \to f$	0.0164	0.0077	0.0537	0.0411	0.0235
	(−0.0011)	(−0.0006)	(−0.0078)	(−0.0065)	(−0.0041)
$4p \to f$	0.0123	0.0065	0.0323	0.0224	0.0151
	(−0.0051)	(−0.0005)	(−0.0068)	(−0.0046)	(−0.0006)
$5p \to f$		0.0055	0.0072	0.0043	0.0171
		(−0.0023)	(−0.0009)	(−0.0005)	(−0.0041)
$6p \to f$					0.1202
					(−0.0315)
$3d \to s$	−0.0084	−0.0037	−0.0165	−0.0124	0.0073
	(0.0026)	(0.0012)	(0.0011)	(0.0008)	(0.0007)
$4d \to s$	0.0021	−0.0014	−0.0116	−0.0087	−0.0024
		(0.0006)	(0.0029)	(0.0022)	(0.0004)
$5d \to s$		−0.0001			0.0005
					(−0.0004)
$3d \to g$	0.0225	0.0110	0.0667	0.0526	0.0324
	(−0.0028)	(−0.0012)	(−0.0077)	(−0.0065)	(−0.0046)
$4d \to g$	(0.0059)	0.0085	0.0401	0.0287	0.0203
		(−0.0007)	(−0.0081)	(−0.0056)	(−0.0005)
$5d \to g$		0.0028			0.0160
		δ			(−0.0036)
$4f \to p$		−0.0045		−0.0163	−0.0146
		(0.0003)		(0.0043)	(0.0021)
$4f \to h$		0.0096		0.0236	0.0256
		(−0.0006)		(−0.0039)	(−0.0020)
R_D (ang):	0.1233	0.0857	0.2977	0.2347	0.3344
R_E (ang):	(−0.0222)	(−0.0137)	(−0.0385)	(−0.0289)	(−0.0581)
Total (ang)	0.1011	0.0720	0.2592	0.2057	0.2763
$2p \to p$	−0.1076	−0.0430	−0.2222	−0.1795	−0.1183
	(0.0847)	(0.0299)	(0.0190)	(0.0188)	(0.0175)
$3p \to p$	−0.1386	−0.0579	−0.5876	−0.3961	−0.1576
	(−0.0161)	(0.0221)	(0.2399)	(0.1741)	(0.0524)

TABLE III. (*Continued*)

Perturbation	Ru^{2+}	Os^{2+}	Pr^{3+}	Tm^{3+}	Np^{6+}
$4p \to p$	0.0183 (0.0613)	−0.1299 (−0.0482)	0.1903 (−0.0769)	0.1974 (−0.0930)	−0.2367 (0.0028)
$5p \to p$		−0.0275 (0.1618)	0.5130 (−0.1684)	0.3279 (−0.0941)	−0.1093 (0.1432)
$6p \to p$					0.4390 (−0.1943)
$3d \to d$	−0.0336 (−0.0598)	−0.0110 (−0.0189)	−0.1462 (0.0736)	−0.1015 0.0542	−0.0470 (0.0348)
$4d \to d$	0.0291	−0.0374 (−0.0438)	0.0648 (−0.0402)	0.0573 (−0.0372)	−0.0580 (−0.0036)
$5d \to d$		0.0281			−0.0010 (0.0330)
$4f \to f$		(0.0146)		0.0470 (−0.0016)	−0.0278 (−0.0392)
R_D (rad)	−0.2324	−0.3069	−0.1879	−0.0475	−0.3167
R_E (rad)	(0.0701)	(0.1175)	(0.0470)	(0.0212)	(0.0466)
Total (rad)	−0.1623	−0.1894	−0.1409	−0.0263	−0.2697
Net R	−0.0612	−0.1174	+0.1183	+0.1794	+0.0066

0.156 b, which is close to the predicted theoretical value[19] of 0.16 ± 0.02 b. The repercussions of the changes in the charge spread of the ion as it goes from free state into a crystalline lattice on R factor have been estimated by correlating $(1-R)\langle r^{-3}\rangle_{3d}$ to the position of the outermost maximum in the total radial electron density distribution, ρ_m, within the $3d^6$ isoelectronic series. Such a correlation shows that an increase in ρ_m by ~10% brings down the value of $(1-R)\langle r^{-3}\rangle_{3d}$ by ~47% which is quite significant compared to the consistency, correlation, and relativistic effects. The results of the calculation of R for $Ru^{2+}(4d^6)$, $Os^{2+}(5d^6)$, $Pr^{3+}(4f^2)$, $Tm^{3+}(4f^{12})$, and $Np^{6+}(5f^1)$ are, respectively, given by -0.06, -0.12, 0.12, 0.18, and 0.01.

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