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Quadrupole antishielding factors and polarizabilities in ionic crystals

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Using nonrelativistic Hartree-Fock-Slater wave functions and Sternheimer's perturbation-numerical method, the quadrupole antishielding factor γ_∞ and quadrupole polarizability α_q have been calculated for 35 free ions isoelectronic with He, Ne, Ar, Kr, Xe, and Rn configurations. Assuming an additional potential due to a charged hollow sphere of Watson type around the ion in crystals, the self-consistent wave functions for 10 additional negative ions O^{2-}, S^{2-}, Se^{2-}, Te^{2-}, P^{3-}, As^{3-}, Sb^{3-}, Si^{4-}, Ge^{4-}, and Sn^{4-} have been generated in order to calculate γ_∞ and α_q for a total of 45 closed-shell ions in crystals. In the presence of the spherical potential, the negative-ion γ_∞ and α_q values decrease while the positive-ion values increase as compared to the corresponding free-ion values, respectively. The effect of contraction of wave functions on γ_∞ and α_q for singly and doubly negative ions has been studied as a function of the radius of the hollow sphere over a range of values around the Pauling ionic radius and in each case a satisfactory polynomial relationship has been assigned.

I. INTRODUCTION

The quantitative treatment of electric quadrupole interactions in ionic solids attempted[1] so far has met with only limited success. In calculating the field gradient at an ionic site due to distant charges, which can be treated as point multipoles, an accurate knowledge of the quadrupole antishielding factor[2] γ_∞ for the ion becomes essential. These calculations[1] suggest that the γ_∞ values for the negative ions in solids are substantially smaller than the corresponding free-ion values. In the case of positive ions, however, the γ_∞ values are expected to be larger than the free-ion values. To our knowledge, there have been only two calculations[3,4] so far which estimate the effect of the changes in the ionic wave functions on γ_∞ as the ion goes from the free state into the crystalline lattice, and both of them have utilized the variation-perturbation method.[5] Thus Burns and Wikner[3] have calculated γ_∞ and the quadrupole polarizability α_q for O^{2-}, F^-, and Cl^- using contracted wave functions and found that for F^- and Cl^-, γ_∞ decreases from its free-ion value by ~20% and ~45%, respectively. Paschalis and Weiss[4] have calculated the electron density distribution, diamagnetic susceptibility, dipole polarizability, and quadrupole antishielding factors for Li^+, Be^{2+}, O^{2-}, F^-, Na^+, Mg^{2+}, Al^{3+}, S^{2-}, Cl^-, K^+, Ca^{2+}, Sc^{3+}, and Ti^{4+} in crystals and observed that while for positive ions such as Al^{3+} the crystal-ion γ_∞ value is ~40% more than the free-ion value, the contractions in γ_∞ for the negative ions are still larger. We thought it worthwhile to make an estimate of such effects by considering a large number of ions and making calculations under similar approximations. Using Hartree-Fock-Slater[6] wave functions and Sternheimer's perturbation-numerical method[2] we first calculated γ_∞ and α_q for the following free ions: $Li^+, Be^{2+}, B^{3+}, C^{4+}, N^{5+}, O^{6+}$; $F^-, Na^+, Mg^{2+}, Al^{3+}, Si^{4+}, P^{5+}, S^{6+}$; $Cl^-, K^+, Ca^{2+}, Sc^{3+}, Ti^{4+}, V^{5+}, Cr^{6+}$; $Br^-, Rb^+, Sr^{2+}, Y^{3+}, Zr^{4+}, Nb^{5+}, Mo^{6+}$; $I^-, Cs^+, Ba^{2+}, La^{3+}$; and $At^-, Fr^+, Ra^{2+}, Ac^{3+}$. The crystal-ion wave functions for all these ions as well as another 10 negative ions, namely, O^{2-}; S^{2-}, P^{3-}, Si^{4-}; $Se^{2-}, As^{3-}, Ge^{4-}$; and $Te^{2-}, Sb^{3-}, Sn^{4-}$ were generated by superimposing around each ion a charged hollow sphere of the type first proposed by Watson.[7] γ_∞ and α_q corresponding to the crystal-ion wave functions were then calculated by using the perturbation-numerical method. For the negative ions of $F^-, Cl^-, Br^-, I^-, O^{2-}, S^{2-}, Se^{2-}$, and Te^{2-}, γ_∞ and α_q values were also calculated in each case as a function of radius of the superimposed sphere in the vicinity of the corresponding ionic radius due to Pauling[8] and the results have been satisfactorily expressed in terms of a three- or four-parameter polynomial in r_{ion}^{-1}, where r_{ion} is the ionic radius.

In Sec. II we describe in short the perturbation-numerical method of Sternheimer[2] adopted in this work along with the other major computational steps. In Sec. III our results of γ_∞ and α_q are presented and discussed vis-à-vis the earlier available results. Finally, in Sec. IV a summary of the present work has been given.

II. CALCULATIONS

The free-ion wave functions were generated using the Hamiltonian

$$\mathcal{H}^{\text{free ion}} = -\sum_{i=1}^{N}\left(\nabla_i^2 + \frac{2Z}{r_i}\right) + \sum_{i,j=1}^{N}{}' \frac{1}{r_{ij}}, \tag{1}$$

where the exchange part was handled according to Slater's[6] prescription

$$V_{\text{exch}} = -6[(3/8\pi)\rho]^{1/3}. \tag{2}$$

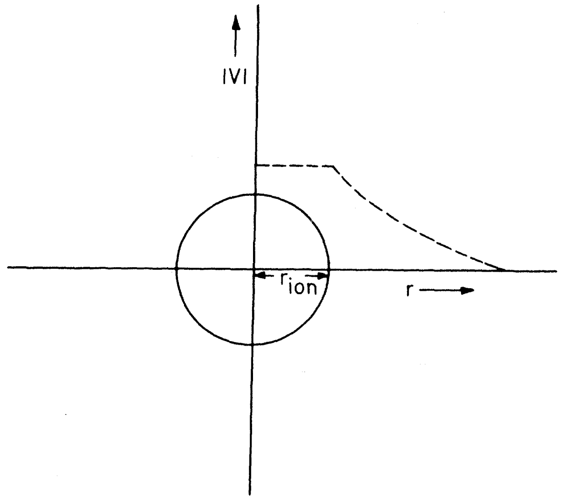

FIG. 1. Potential due to the superimposed charged hollow sphere with radius r_{ion} as a function of radial distance r.

The additional potential V in the Watson model for the ion in a solid has been shown in Fig. 1. The ion with an electric charge n_{ion} is surrounded by a hollow sphere of radius r_{ion} and carries a uniformly distributed charge of $-n_{ion}$ units. Equation (1) for the ion in a solid can be written

$$\mathcal{H}^{\text{crystal ion}} = -\sum_{i=1}^{N}\left(\nabla_i^2 + \frac{2Z}{r_i} - \frac{2n}{r_{ion}}\right) + {\sum_{i,j=1}^{N}}' \frac{1}{r_{ij}} \tag{3}$$

for $r_i \le r_{ion}$ and

$$\mathcal{H}^{\text{crystal ion}} = -\sum_{i=1}^{N}\left(\nabla_i^2 + \frac{2Z}{r_i} - \frac{2n}{r_i}\right) + {\sum_{i,j=1}^{N}}' \frac{1}{r_{ij}} \tag{4}$$

for $r_i \ge r_{ion}$. Throughout this work r_{ion} has been taken from Pauling's table[8] of ionic radii, except in the case of Fr^+, Ra^{2+}, Ac^{3+}, and At^- where Zachariasen's[9] values have been used. All the wave functions were generated over a 441-point mesh using a modified Herman-Skillman[10] program adopted for an IBM 7044/1401 system at IIT Kanpur.

The unperturbed radial functions $u_1^0(nl)$ were used to obtain the external charge-perturbed radial wave functions $u_1'(nl \to l')$ for various $nl \to l'$ excitations by direct solution of the following inhomogeneous differential equation:

$$\left(-\frac{d^2}{dr^2} + \frac{l'(l'+1)}{r^2} + V(r) - E\right) u_1'(nl \to l') = u_0(nl)\left(r^2 - \langle r^2\rangle_{nl}\delta_{ll'}\right), \tag{5}$$

where $u_0'(nl)$ is normalized as

$$\int_0^\infty u_0'(nl)^2\, dr = 1 \tag{6}$$

and $u_0'(nl \to l)$ follows the orthogonality criterion

$$\int_0^\infty u_0'(nl) u_1'(nl \to l')\, dr = 0\,. \tag{7}$$

The local approximation[11]

$$V(r) - E = \frac{1}{u_0}\frac{d^2 u_0}{dr^2} - \frac{l(l+1)}{r^2} \tag{8}$$

was used in Eq. (5). Finally, γ_∞ and α_q are, respectively, given by

$$\gamma_\infty = \sum_{nl} c(nl \to l') \int_0^\infty u_0'(nl) u_1'(nl \to l') r^{-3}\, dr\,, \tag{9}$$

$$\alpha_q = 0.0415 \sum_{nl} c(nl \to l') \int_0^\infty u_0'(nl) u_1'(nl \to l') r^2\, dr \text{ Å}^5\,. \tag{10}$$

The coefficients $c(nl \to l')$ which arise from the integration over the angular variables have been tabulated by Sternheimer.[12]

Both outward and inward solutions of Eq. (5) were performed for each excitation $nl \to l'$ of the core electrons and the solutions were matched in the suitable intermediate region in an iterative manner. All the relevant integrals were evaluated by using the formula[13] for integration through adjacent intervals including fourth-order differences.

The polynomial fittings of γ_∞ and α_q in terms of

$$|\gamma_\infty| \quad (\text{or } \alpha_q) = \sum_{i=0}^{2 \text{ or } 3} a_i (r_{ion})^{-i} \tag{11}$$

were performed by minimizing the average percentage error using the method of normal equations.[14]

III. RESULTS AND DISCUSSION

Our results for γ_∞ and α_q for all the ions have been given in Table I and II, respectively. For the purpose of comparison we have included the other available results in the literature. In what follows, only γ_∞ results will be discussed in detail. The general trends observed in the case of γ_∞ results are also applicable to α_q values.

Using an uncoupled method similar to ours, Feiock and Johnson[15] have calculated the free-ion multipole polarizabilities and shielding factors for the majority of closed-shell ions considered here using relativistic Hartree-Fock-Slater (HFS) wave functions. These values have been presented in column three of Table I. Since the accuracy in obtaining the perturbed wave functions is comparable for the Feiock and Johnson and the present method, a comparison of these two results should give an estimate of the relativistic effects on the total γ_∞. Using the negative halogen-ion γ_∞ values in two

TABLE I. Total γ_∞ values for the free ions and ions in crystals. The crystal-ion values correspond to Pauling's ionic radius.

	Free ion			Crystal ion		
Ion	Present	Feiock and Johnson	Others	Present	Others	Experimental[a]
Li^{+}	0.261	0.257	0.256[b]; 0.248[c]; 0.247[d]; 0.248[f]; 0.257[g]	0.282	0.271[e]	+4.4
Be^{2+}	0.187	0.185	0.185[b]; 0.189[h]; 0.181[c]; 0.180[d]; 0.186[g]	0.208	0.190[e]	
B^{3+}	0.146	0.145	0.145[b]; 0.142[c]; 0.142[d]; 0.147[i]; 0.145[g]	0.162		
C^{4+}	0.119	0.119	0.117[d]	0.131		
N^{5+}	0.101		0.099[d]	0.110		
O^{6+}	0.088			0.094		
O^{2-}			−429.4, −950.5[g]	−24.19	−28.22, −25.30, −33.90[j]; −9.056[e]	
F^{-}	−41.109	−42.190	−66.86, −23.22, −25.71, −21.11[j]; −22.53[k]; −23.03, −22.15, −22.12, −22.0[g]; −29.88[l]; −37.61[m]	−14.583	−10.62[e]	
Na^{+}	−5.029	−5.072	−4.532[b]; −4.514, −4.505, −4.497[g]; −5.178[l]; −4.56[h,n]; −5.961[m]	−7.686	−4.747[e]	−9
Mg^{2+}	−3.320	−3.350	−3.038[g]; −3.485[l]; −3.898[m]			
Al^{3+}	−2.434	−2.462	−2.59[b]; −2.4[i]; −2.236[g]; −2.57[l]; −2.749[m]	−5.715	−3.217[e]	−4.9
Si^{4+}	−1.902	−1.927	−1.32[m]	−4.508		
P^{5+}	−1.550			−3.449		
S^{6+}	−1.302	−1.323		−2.594		
Si^{4-}				−131.99		
P^{3-}				−80.15		
S^{2-}			−197.1[e]	−54.99	−37.64[e]	
Cl^{-}	−82.047	−83.50	−53.91[g]; −101.116[m]; −56.6[o]; −49.28[p]; −78.3[q]; −63.21[r]	−38.915	−27.04[j]; −37.90[e]	−10
K^{+}	−18.768	−19.16	−12.17[g]; −17.32[h,n]; −27.21[m]; −12.84[p]; −18.27[r]	−28.701	−22.83[e]	
Ca^{2+}	−13.625	−13.95	−12.12[g]; −19.66[m]; −13.32[r]	−25.71	−20.58[e]	
Sc^{3+}	−10.677		−9.461[j]	−20.04	−20.34[e]	−19
Ti^{4+}	−8.761	−9.006	−7.721[g]; −12.50[e]	−14.616	−25.51[e]	
V^{5+}	−7.417			−10.744		
Cr^{6+}	−6.423	−6.636		−8.368		
Ge^{4-}				−323.47		
As^{3-}				−201.53		
Se^{2-}				−137.36		
Br^{-}	−195.014	−210.0	123.0[k]; −244.3[m]; −99.0[p]; −100[s]	−97.424		−35
Rb^{+}	−51.196	−54.97	−47.9[f]; −113.776[h]; −49.29[p]; −50[s]	−77.063		
Sr^{2+}	−38.423	−41.35		−70.063		
Y^{3+}	−30.889		−33.6[t]	−53.326		
Zr^{4+}	−25.867	−28.09		−38.398		
Nb^{5+}	−22.204			−28.991		
Mo^{6+}	−19.215	−21.43		−23.861		
Sn^{4-}				−546.85		
Sb^{3-}				−344.18		
Te^{2-}				−241.33		
I^{-}	−331.633	−396.10	−178.75[p]; −175[s]; −138.4[u]	−177.732		−45
Cs^{+}	−102.755	−121.3	−103.05[f]; −110.44[p]; −110[s]	−156.896		
Ba^{2+}	−79.397	−94.23		−141.187		
La^{3+}	−65.278	−77.88	−65.82[v]			

TABLE I *(Continued)*

Ion	Free ion Present	Feiock and Johnson	Others	Crystal ion Present	Others	Experimental[a]
Fr^+	−192.035		-193.01^{w}	−295.958		
Ra^{2+}	−150.746		-151.60^{w}	−261.234		
Ac^{3+}	−125.049		-126.06^{w}	−196.517		
Al^-	−578.637			−317.655		

[a] Experimental values have been discussed in Sec. III of the text.
[b] See Ref. 5 of text.
[c] J. Lahiri and A. Mukherji, Phys. Rev. 141, 428 (1966).
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[r] J. Lahiri and A. Mukherji, Phys. Rev. 155, 24 (1967).
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[u] R. M. Sternheimer, Phys. Rev. 146, 140 (1966).
[v] R. P. Gupta and S. K. Sen, Phys. Rev. A 7, 850 (1973).
[w] R. P. Gupta and S. K. Sen, Phys. Rev. A 8, 1169 (1973).

TABLE II. Free- and crystal-ion total quadrupole polarizability values, α_q, in Å^5 units.

Ion	Free ion Present	Feiock and Johnson	Others	Crystal ion Present
Li^+	0.005 214	0.004 712	$0.004\,71^{a}; 0.004\,648^{b}; 0.004\,66^{c}; 0.004\,699^{d}; 0.004\,73^{e}$	0.007 992
Be^{2+}	0.000 683	0.000 637	$0.000\,633^{a}; 0.000\,630^{b}; 0.000\,638^{c}; 0.000\,642^{d}$	0.001 217
B^{3+}	0.000 150	0.000 143	$0.000\,142^{a}; 0.000\,141^{b}; 0.000\,143^{c}; 0.000\,144^{d}$	0.000 262
C^{4+}	0.000 045	0.000 043	$0.000\,043^{c}$	0.000 074
N^{5+}	0.000 016		$0.000\,016^{c}$	0.000 026
O^{6+}	0.000 007			0.000 010
O^{2-}				4.391 510 $(6.238, 7.738, 3.227^{f})$
F^-	6.898 07	7.843	$3.457^{d}; 2.937^{g}; 4.409^{h}; 21.76, 2.877, 2.382^{f}$	1.028 660 (1.802^{f})
Na^+	0.063 013	0.063 250	$0.067^{a}; 0.064\,17, 0.0641, 0.063\,87^{d}; 0.0632^{g}; 0.088\,48^{h}; 0.0634; 0.0649^{i}$	0.115 088
Mg^{2+}	0.020 956	0.021 000	$0.021\,88^{d}; 0.0215^{g}; 0.030^{h}$	0.059 505
Al^{3+}	0.008 668	0.008 671	$0.001\,01^{a}; 0.009\,104^{d}; 0.008\,95^{g}; 0.011\,85^{h}$	0.032 727
Si^{4+}	0.004 158		$0.005\,97^{h}$	0.018 167
P^{5+}	0.002 139			0.014 177
S^{6+}	0.001 197	0.001 192		0.005 960

TABLE II. *(Continued)*

Ion	Free ion Present	Feiock and Johnson	Others	Crystal ion Present
Si^{4-}				276.158 78
P^{3-}				50.888 31
S^{2-}				14.163 75
Cl^-	19.178 35	19.46	13.1[f]; 11.79, 19.44[d]; 19.759[h]; 11.92[j]; 13.77[e]; 13.05[k]	4.770 722
K^+	0.638 469	0.637 500	0.7194[d]; 1.047[h]; 0.674[j]; 0.735[e]; 0.717[k]; 0.721[i]	1.199 525
Ca^{2+}	0.273 318	0.272 00	0.3008[d]; 0.4381[h]; 0.290[j]	0.778 462
Sc^{3+}	0.137 123		0.1524[d]	0.479 939
Ti^{4+}	0.076 042	0.075 32		0.289 070
V^{5+}	0.045 287			0.169 139
Cr^{6+}	0.028 438	0.027 99		0.099 532
Ge^{4-}				280.104 62
As^{3-}				62.260 01
Se^{2-}				19.806 73
Br^-	27.865 03	28.99	31.442[h]	7.541 961
Rb^+	1.407 357	1.376	3.117[h]; 1.592[l]	2.705 311
Sr^{2+}	0.691 121	0.6692		2.029 917
Y^{3+}	0.391 197			1.406 932
Zr^{4+}	0.241 542	0.2310		0.909 730
Nb^{5+}	0.158 216			0.573 686
Mo^{6+}	0.108 594	0.1027		0.367 894
Sn^{4-}				377.029 49
Sb^{3-}				93.983 83
Te^{2-}				33.729 70
I^-	44.872 40	49.84		14.559 47
Cs^+	3.660 668	3.443	4.907[l]	6.893 71
Ba^{2+}	2.052 602	1.892		5.603 819
La^{3+}	1.383 249	1.214	1.390[m]	4.112 645
Fr^+	5.759 481			10.973 830
Ra^{2+}	3.438 726			8.892 337
Ac^{3+}	2.363 332			7.665 737
At^-	57.036 99			19.786 38

[a] Table I, footnote b.

[b] Table I, footnote c.

[c] Table I, footnote d.

[d] Table I, footnote g.

[e] R. M. Sternheimer, Phys. Rev. 107, 1565 (1957).

[f] Table I, footnote j.

[g] Table I, footnote l.

[h] Table I, footnote m.

[i] G. Burns, Phys. Rev. 115, 357 (1959).

[j] Table I, footnote r.

[k] P. G. Khubchandani, R. R. Sharma, and T. P. Das, Phys. Rev. 126, 594 (1962).

[l] R. M. Sternheimer, Phys. Rev. A 1, 321 (1970).

[m] Table I, footnote v.

cases to give the upper limit of the effect in each isoelectronic series, it is found that up to the ions in the Kr isoelectronic series the relativistic effects contribute to within ~7% of the nonrelativistic values of γ_∞. For the Xe isoelectronic series the upper limit becomes ~19%.

The present γ_∞ values of F^-, Cl^-, Br^- obtained by using HFS wave functions are −41, −82, and −195, respectively, as against Sternheimer's earlier values of −22, −55, and −134, respectively. The latter calculations employed Hartree-Fock (HF) wave functions for the ions. This trend has been also noticed by Feiock and Johnson and it appears that for the negative ions the HFS wave functions are more external than the HF wave functions at least for the outer orbitals. For the positive ions our results are in good agreement with the other perturbation-numerical calculations (see references under Tables I and II).

The present uncoupled calculations are less accurate than the coupled calculations performed earlier[16] since the latter include the intra- and intershell coupling effects or the so-called consistency effects. Recently linked-cluster many-body perturbation-theory and differential-equation calculations have been performed[17] to include consistency effects in γ_∞ for Na^+, F^-, Cl^-, Br^-, Mn^{2+}, and Fe^{3+}. These results show that in most of the cases, including ions in solids, the higher-order effects should be ~15% of the zeroth-order contribution. We note here that the present γ_∞ values refer in this context to the zeroth-order contribution.

In column five of Table I, we have given the present values for the ions in crystal obtained by using the wave functions derived in presence of the potential due to Watson's sphere corresponding to the Pauling ionic radii. As compared to the free-ion values, γ_∞ in a crystal is ~50% smaller for the negative ions. For the positive ions, on the other hand, almost a similar increase is obtained in a large number of cases. This effect is estimated to be ~3 times the relativistic or consistency effects.

Experimental estimates of γ_∞ are available for a large number of ions in ionic solids. Kawamura[18] and Fukai[1] have independently obtained the effective $\gamma_\infty = -9$ for Na^+ in sodium-halide solid solutions using nuclear magnetic-resonance (NMR) data. The present crystal-ion value of -7.7 is in good agreement with the experimental results. Raymond[19] has estimated the best fit value of γ_∞ for Al^{3+} in the polymorphs of Al_2SiO_5 as -4.9, which is in satisfactory agreement with our crystal-ion value of -5.7. Bhide and Hegde[20] have combined the electric-field-gradient data on ^{44}Sc and ^{57}Fe nuclei to estimate $\gamma_\infty = -19$ for Sc^{3+}, which is to be compared with the present crystal-ion value of -20. Recently, Anderson and Karra[21] have estimated $\gamma_\infty = +4.4$ for Li^+ in a LiF single crystal from acoustic NMR data. The interpolated result of $+0.34$ due to Lahiri and Mukherji[16] and the present value of $+0.28$ are significantly lower than the experimental results. For the tripositive rare-earth ions the crystal-ion calculations[22] give a value of ~-100 which is in reasonable agreement with the experimental values obtained using the Mössbauer effect,[23] and optical and electron paramagnetic resonance[24] experiments. In overall, the theoretical results of γ_∞ seem to be satisfactory for the positive ions.

The experimental estimates[3] of γ_∞ for Cl^-, Br^-, and I^- center around -10, -35, and -45, respectively. Our values using contracted wave functions for the ions are -39, -97, and -178, respectively. In view of the discrepancy between the HFS and HF values of γ_∞ for the free ions it would be interesting to perform the perturbation-numerical calculations for these ions with a superimposed sphere under the HF treatment of the exchange. Assuming the contraction in the HFS and HF wave functions to be similar and including the consistency corrections due to Beri *et al.*,[17] the antishielding factors for F^-, Cl^-, and Br^- are estimated to be -5, -28, and -74, respectively, in the HF case. The Cl^- and Br^- theoretical estimates are still twice as large as the experimental estimates mentioned above. We recall here that in these calculations our choice of the radius r_{ion} of the sphere was fixed at the values tabulated by Pauling. For the negative ions in solids a range of ionic radii is quite natural due to their easy deformability. It was therefore of in-

TABLE III. Variation of γ_∞ and α_q as a function of radius of the charged sphere around the mono- and dinegative ions. Pauling's ionic radii r_{ion} and α_q are given, respectively, in Å and Å^5 units.

Ion (r_{ion})	Radius	$r_{\text{ion}}-0.3$	$r_{\text{ion}}-0.2$	$r_{\text{ion}}-0.1$	r_{ion}	$r_{\text{ion}}+0.1$	$r_{\text{ion}}+0.2$	$r_{\text{ion}}+0.3$
F^-	$-\gamma_\infty$	11.76	12.73	13.65	14.583	15.35	16.12	16.81
(1.36)	α_q	0.731 12	0.825 00	0.921 86	1.028 66	1.119 37	1.217 53	1.313 72
Cl^-	$-\gamma_\infty$	34.27	35.852	37.367	38.91	40.12	41.31	42.40
(1.81)	α_q	3.916 86	4.201 256	4.476 530	4.770 72	4.999 56	5.248 30	5.485 22
Br^-	$-\gamma_\infty$	87.12	90.62	93.98	97.42	100.06	102.75	105.20
(1.95)	α_q	6.322 63	6.720 65	7.112 44	7.541 961	7.860 92	8.211 85	8.545 06
I^-	$-\gamma_\infty$	161.83	167.19	172.34	177.73	181.71	185.88	189.70
(2.16)	α_q	12.633 54	13.265 93	13.882 20	14.559 47	15.047 11	15.587 97	16.099 56
O^{2-}	$-\gamma_\infty$		17.61	20.69	24.19	28.18		
(1.40)	α_q		2.738 87	3.476 23	4.391 51	5.529 79		
S^{2-}	$-\gamma_\infty$	41.19	45.43	50.03	54.99	60.28	65.98	72.06
(1.84)	α_q	9.158 33	10.618 11	12.278 50	14.163 75	16.283 88	18.705 92	21.448 42
Se^{2-}	$-\gamma_\infty$	106.38	115.93	126.26	137.36	149.15	161.64	174.78
(1.98)	α_q	13.316 41	15.238 05	17.396 08	19.806 73	22.507 76	25.519 39	28.847 86
Te^{2-}	$-\gamma_\infty$	195.73	210.02	225.23	241.33	258.27	276.01	294.54
(2.21)	α_q	24.453 48	27.275 90	30.360 75	33.729 70	37.402 21	41.400 90	45.754 37

TABLE IV. Parameters a_i in the equation $|\gamma_\infty|$ (or α_q) $=\sum_{i=0}^{2\text{ or }3} a_i (r_{\text{ion}})^{-i}$. The average percentage error APE in each fit has been given in the last column.

Ion	a_i	a_0	a_1	a_2	a_3	APE
F^-	$\|\gamma_\infty\|$	41.109	−70.142	63.751	−23.777	0.2
	α_q	6.898	−18.631	20.344	−7.984	0.7
Cl^-	$\|\gamma_\infty\|$	82.047	−138.379	154.426	−82.365	0.1
	α_q	19.178	−56.394	77.357	−40.820	0.2
Br^-	$\|\gamma_\infty\|$	195.014	−311.460	315.728	−156.969	0.1
	α_q	27.865	−81.764	113.142	−60.741	0.3
I^-	$\|\gamma_\infty\|$	331.633	−545.901	658.673	−430.379	0.05
	α_q	44.872	−130.374	195.036	−119.285	0.1
O^{2-}	$\|\gamma_\infty\|$	158.062	−300.195	158.005		0.2
	α_q	46.932	−98.498	54.567		0.4
S^{2-}	$\|\gamma_\infty\|$	319.261	−787.365	553.842		0.5
	α_q	142.118	−395.202	293.815		1.5
Se^{2-}	$\|\gamma_\infty\|$	755.323	−1976.609	1490.665		0.3
	α_q	189.063	−561.066	447.203		1
Te^{2-}	$\|\gamma_\infty\|$	1208.988	−3441.039	2878.0738		0.2
	α_q	278.854	900.622	792.930		0.6

terest to us to calculate the dependence of γ_∞ and α_q, for the negative ions, in particular, by varying the radius of the superimposed charged sphere around Pauling's ionic radii. The results of such calculations on F^-, Cl^-, Br^-, I^-, O^{2-}, S^{2-}, Se^{2-}, and Te^{2-} have been given in Table III. On the basis of these calculations it is observed that for a typical reduction in the value of the radius by ~20% the γ_∞ values decrease by ~(15–20)% for the singly charged negative ions and by (25–30)% for the doubly charged negative ions. It has been possible to express both γ_∞ and α_q values for each of these ions in terms of a polynomial in $(r_{\text{ion}})^{-1}$ defined in Eq. (11) (see Sec. II). In the case of halogen negative ions we have actually fitted the positive difference between the free-ion and the crystal-ion γ_∞ and α_q values at every r_{ion}. Due to lack of free-ion γ_∞ values for the doubly negative ions such a correlation could not be attempted and the fit has been obtained over the range of r_{ion} values given in Table IV using the corresponding γ_∞ and α_q values. These polynomials can be used to interpolate γ_∞ and α_q values at any value of r_{ion} within a given crystal.

This simple model for ions in solids, namely, a superimposed charged hollow sphere carrying an equivalent but opposite charge to that of the ion at its centre, preserves the symmetry of the free ion and the electroneutrality of the crystal. It can be generalized by incorporating the proper symmetry of the ion within the crystalline lattice. A semiempirical procedure for the choice of radius and a better approximation for the potential outside the hollow sphere would be interesting modifications. The neglect of overlap and the use of similar potential for both positive and negative ions, however, remain the major drawbacks of the model.

IV. SUMMARY

The Sternheimer antishielding factor γ_∞ and quadrupole polarizability α_q have been calculated for a large number of closed-shell ions under similar approximations. In order to estimate the effects of the modification of ionic wave functions in solids, the calculations were performed using two types of wave functions: (a) 441-point mesh nonrelativistic Hartree-Fock-Slater wave functions and (b) functions generated according to the Watson model for ions in crystals. Comparing the present free-ion γ_∞ values with Feiock and Johnson's γ_∞ calculations obtained by using relativistic HFS wave functions, it has been estimated that the relativistic effects are within + 7% of the nonrelativistic γ_∞ up to the ions isoelectronic with Kr configuration. For the ions isoelectronic with Xe configuration the upper limit has been estimated to be as much as + 19%. Through the procedure of type (b) mentioned above the difficulty in obtaining reasonably good wave functions for O^{2-}, S^{2-}, Se^{2-}, Te^{2-}, P^{3-}, As^{3-}, Sb^{3-}, Si^{4-}, Ge^{4-}, and Sn^{4-} has been overcome and the corresponding γ_∞ and α_q values have been obtained. Use of such wave functions reproduces the well-established experimental trend in γ_∞ for ions in solids, namely, an increase for the positive ions and decrease for the negative ions as compared to the free-ion value. In a large number of cases the free-ion γ_∞ values change by as much as 50% in going from the free to the solid state. For the positive ions good agreement exists between theory and experiment whereas for the negative ions the theoretical estimates of the contracted HF γ_∞ values are still twice as large.

Note added in proof. Gupta and Sen [Phys. Ref. A 8, 1169 (1973)] have also reported values for Fr^+, Ra^{2+}, and Ac^{3+} as − 193, − 152, and − 126, respectively. These values are in excellent agreement with the presently calculated values of − 192, − 151, and − 125, respectively, as given in Table I. In their paper Gupta and Sen have noted that γ_∞ value of + 4.46 obtained for Li atom in $1s^2 2p^1$ configuration is the same as the experimental estimate of 4.4 (± 13%) obtained by Anderson and Karra[21] from nuclear-acoustic-resonance studies on ^7Li in LiF single crystal. The $1s^2 2p^1$ configuration is difficult to envisage for Li^+ in LiF and therefore this theoretical result of γ_∞ for $Li(1s^2 2p^1)$ cannot be compared with the experimental value. It is interesting to note that in a similar nuclear-acoustic-resonance study on LiF crystal, Antokol'skii, Sarnatskii, and Shutilov [Sov. Phys.-Acoustics 17, 114 (1971)] have estimated $\gamma_\infty(Li^+) = 0.5 \pm 0.3$ which is quite close to the presently calculated theoretical result of 0.28 for Li^+ ion in solids as given in Table I.

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