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Theory of electron-electron interaction effects on antishielding factors of negative ions*

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The influence of electron-electron interaction effects on nuclear quadrupole antishielding factors γ_∞ is studied for the negative halide ions F^-, Cl^-, and Br^-. Using a procedure developed earlier which utilizes the nuclear-quadrupole-moment-perturbed and external-point-charge-perturbed wave functions for the ions, obtained by the differential equation procedure for the zero-order antishielding factor $(\gamma_\infty)_0$, we have computed the consistency contributions $(\gamma_\infty)_1$ to be +2.28, −1.50, and −7.16 in F^-, Cl^-, and Br^-, respectively. The resulting values of γ_∞ correct to first order in electron-electron interaction are then −19.29, −56.58, and −140.83. The appearance of negative signs for $(\gamma_\infty)_1$ in Cl^- and Br^- is seen to be due to large negative interactions between p electrons belonging to different shells. This intershell effect is not present in F^- $(1s^2 2s^2 2p^6)$. The contributions to $(\gamma_\infty)_1$ for all three ions are analyzed in detail, and a comparison is made of $(\gamma_\infty)_1$ for F^- and the isoelectronic positive ion Na^+. An explanation is proposed for the comparable values of the ratio $(\gamma_\infty)_1/(\gamma_\infty)_0$ found for these two ions, even though the F^- ion is substantially more deformable with a larger value of $(\gamma_\infty)_0$. From the results of the present investigations, as well as earlier ones in related positive ions, it is felt that the consistency contribution $(\gamma_\infty)_1$ should, in general, be less than 15% of $(\gamma_\infty)_0$ for most ions.

I. INTRODUCTION

A knowledge of the field gradients at nuclei in ions is important from an experimental point of view because of the availability of substantial data on nuclear quadrupole coupling constants in the solid state. For the negative halogen nuclei, with which we are concerned here, quadrupole coupling data on $^{35,37}Cl$, $^{79,81}Br$ and $^{127,129}I$ nuclei in the solid state (especially ionic crystals) are available in a variety of systems through nuclear magnetic and nuclear quadrupole resonance studies. Among such systems are noncubic crystals,[1] for example, $CdCl_2$ or $CdBr_2$ and crystals which are originally cubic but whose environment is rendered noncubic by the introduction of impurities, vacancies, or other imperfections, examples being solid solutions of alkali halides[2] and crystals made noncubic by the application of uniaxial stress.[3] The fluorine nucleus ^{19}F was not amenable to such studies because its ground state has spin $I=\frac{1}{2}$. However, recent experiments[4] on the excited $I=\frac{5}{2}$ state of ^{19}F by the time-dependent-perturbed-angular-correlation (TDPAC) technique have provided quadrupole coupling data in fluorine compounds and for fluorine ions implanted in metals.[5] A quantitative knowledge of the antishielding factors[6] (γ_∞) of these ions is important for interpretation of field-gradient data in these systems involving halogen nuclei.

Sternheimer[6] has studied the leading contribution $(\gamma_\infty)_0$ to antishielding (γ_∞) factors in the negative halogen ions using a differential equation procedure for solving the appropriate perturbation equations. Our aim in the present work is to study the next most important contribution to γ_∞, in these ions, namely that from the consistency effect,[7,8] which can be described as follows.[8] Thus, for $(\gamma_\infty)_0$, one considers the perturbation of an electron by an external point charge, with the perturbed electron producing a field gradient at the nucleus which either augments or opposes the field gradient due to the point charge. However, the perturbed electron could also perturb a second electron through its self-consistent potential, with the second electron then in turn producing a field gradient at the nucleus, which gives the consistency contribution $(\gamma_\infty)_1$ to the antishielding factor.

Several procedures are available for the study of such effects. Among these are the fully coupled Hartree-Fock procedure,[9] which includes the consistency effect, the differential equation (DE) procedure[8] which handles consistency as a perturbation, and the linked cluster many-body perturbation theory (LCMBPT) procedure[7] which provides both consistency and many-body correlation contributions. We have used the second method to study the consistency effect. In this procedure, one computes the Coulomb and exchange interaction energy between pairs of electrons, one member of the pair having been perturbed by the external charge and the other by the nuclear quadrupole moment.

Our aims in studying the consistency effects in these negative ions are twofold. First, we wanted to obtain quantitative results for γ_∞ which are essential for the interpretation of quadrupole coupling data. Also, intuitively, one expects the perturbation of negative ions by external charges to be much more substantial than for positive ions, because of the greater "looseness" and consequent deformability of the outer orbitals of the former. Thus consistency effects are expected in general to be larger for negative ions. Our second reason for studying the series of halide ions F^-, Cl^-, and Br^- was to test this point quantitatively.

The theory of the method used is presented briefly in Sec. II. In Sec. III our results are presented and discussed in detail both from the point of view of a shell-by-shell comparison for a single ion, and also the trends of contributions from corresponding shells in the three ions F^-, Cl^-, and Br^-. Also included is a discussion of the absolute and relative magnitudes of the various contributions to consistency effects in negative ions and a comparison with those in positive ions. Section IV summarizes our main conclusions with respect to the overall importance of consistency effects on γ_∞ in various ions.

II. THEORY

The theory of the consistency contribution to γ_∞ has been discussed in the literature.[8] For completeness and for the purpose of presenting the notations used in our calculation, we shall give only a brief resume of the procedure.

The perturbation Hamiltonian, $\Delta\mathcal{H}$, for the electrons of the ion in the presence of the nuclear quadrupole moment and the field gradient due to an external point charge is the sum of three terms, $\mathcal{H}'$, $\mathcal{H}''$, and $\mathcal{H}'''$ where

$$\mathcal{H}' = \sum_{i<j} \frac{e^2}{r_{ij}} - \sum_i V_i \,, \tag{1}$$

the difference between the instantaneous electron-electron interaction and the average one-electron approximation to it in the Hartree-Fock approximation;

$$\mathcal{H}'' = -\frac{e^2}{R^3} \sum_i r_i^2 P_2(\cos\theta_i), \tag{2}$$

the $l = 2$ component of the interaction of an external charge at a distance R from the nucleus with the electrons on the ion; and

$$\mathcal{H}''' = -e^2 \sum_i Q \frac{P_2(\cos\theta_i)}{2r_i^3}, \tag{3}$$

representing the interaction of the nuclear quadrupole moment eQ with the electrons.

The consistency contribution $(\gamma_\infty)_1$ to γ_∞ is obtained from the total perturbation energy[8]

$$\delta E = \sum_{n=0}^{\infty} \langle \Phi_0 | \Delta\mathcal{H} \left(\frac{\Delta\mathcal{H}}{E_0 - \mathcal{H}_0} \right)^n | \Phi_0 \rangle_L, \tag{4}$$

by picking out the sum $(\delta E)_1$ of all the terms in δE which contain one order each of $\mathcal{H}'$, $\mathcal{H}''$, and $\mathcal{H}'''$. In Eq. (4), Φ_0 is the determinantal eigenfunction with the energy E_0, corresponding to the ground state of $\mathcal{H}_0$. $(\delta E)_1$ is given by

$$(\delta E)_1 = A + B + C, \tag{5}$$

where

$$A = 4 \sum_{p,m,i,j} \frac{\langle p|\mathcal{H}'''|j\rangle \langle jm|1/r_{12}|pi\rangle \langle i|\mathcal{H}''|m\rangle}{(\epsilon_p - \epsilon_j)(\epsilon_m - \epsilon_i)}, \tag{6}$$

$$B = 2 \sum_{p,m,i,j} \frac{\langle p|\mathcal{H}'''|j\rangle \langle mj|1/r_{12}|pi\rangle \langle i|\mathcal{H}''|m\rangle}{(\epsilon_p - \epsilon_j)(\epsilon_m - \epsilon_i)}, \tag{7}$$

$$C = 2 \sum_{p,m,i,j} \left(\frac{\langle j|\mathcal{H}'''|p\rangle \langle mp|1/r_{12}|ji\rangle \langle i|\mathcal{H}''|m\rangle}{(\epsilon_p + \epsilon_m - \epsilon_i - \epsilon_j)(\epsilon_m - \epsilon_i)} + \frac{\langle j|\mathcal{H}'''|p\rangle \langle pm|1/r_{12}|ij\rangle \langle i|\mathcal{H}''|m\rangle}{(\epsilon_p + \epsilon_m - \epsilon_i - \epsilon_j)(\epsilon_p - \epsilon_j)} \right). \tag{8}$$

The term A in Eq. (6) corresponds to the sum of diagrams 2(a), 2(b) and 2(c) of Ref. 8, B in Eq. (7) to diagram 2(d), and C in Eq. (8) to the sum of diagrams 2(e) and 2(f) of Ref. 8. The summations over excited states in Eqs. (6), (7), and (8) can be absorbed[8] into the usual perturbed functions[6] of the differential equation procedure for $(\gamma_\infty)_0$, namely,

$$-\frac{Q}{2} \langle u_{1p}| = \sum_j \frac{\langle p|\mathcal{H}'''|j\rangle \langle j|}{\epsilon_p - \epsilon_j} \tag{9}$$

and

$$-\frac{1}{R^3} \langle \bar{u}_{1m}| = \sum_i \frac{\langle m|\mathcal{H}''|i\rangle \langle i|}{\epsilon_m - \epsilon_i} \tag{10}$$

referring to the perturbations of the one-electron states p and m due to the nuclear quadrupole moment and external field gradient, respectively. Hereafter, for the sake of brevity, we shall refer to the u_{1p} and the $\bar{u}_{1m}$ as the Q-perturbed and the Δ-perturbed functions, respectively, in keeping with the notation used in the diagrams of Ref. 8. Using

$$(\gamma_\infty)_1 = -\frac{(\delta E)_1}{e^2 Q / 2R^3} \tag{11}$$

together with Eqs. (6)–(10), one gets

$$(\gamma_\infty)_1 = (\gamma_\infty)_{1,A} + (\gamma_\infty)_{1,B} + (\gamma_\infty)_{1,C}, \tag{12}$$

where

$$(\gamma_\infty)_{1,A} = -4 \sum_{p,m} \langle u_{1p} m | 1/r_{12} | p \bar{u}_{1m} \rangle, \tag{13}$$

$$(\gamma_\infty)_{1,B} = 2 \sum_{p,m} \langle m u_{1p} | 1/r_{12} | p \bar{u}_{1m} \rangle, \tag{14}$$

$$(\gamma_\infty)_{1,C} = 2\sum_{p,m}\langle mp|1/r_{12}|u_{1p}\bar{u}_{1m}\rangle. \tag{15}$$

The perturbed functions u_{1p} and $\bar{u}_{1m}$ in Eqs. (13), (14), and (15) for the F^-, Cl^- and Br^- ions were calculated for the present work by numerical integration of the differential equations derived in Ref. 6, for all perturbations $nl \rightarrow l'$ (radial, $l' = l$, and angular, $l' \neq l$) for the three ions. In the summations in Eqs. (6), (7), and (8) and Eqs. (13), (14), and (15) one has to satisfy the Pauli exclusion principle.

The physical meanings of the expressions (13), (14), and (15) can be understood from the appropriate diagrams in Fig. 2 of Ref. 8. Thus, Eq. (13) represents the Coulomb interaction energy between the electrons in orbitals m and p, after they are perturbed by the external point charge and nuclear quadrupole moment, respectively. Equations (14) and (15) represent the exchange counterparts of this process.

III. RESULTS AND DISCUSSION

The net contributions from consistency effects for the three ions are listed in Table I, together with values of $(\gamma_\infty)_0$ from earlier work. In order to understand the nature and trends of the $(\gamma_\infty)_1$ in the three cases and because they provide physical insight into the various contributing mechanisms for negative ions, we have listed in Tables II, III, and IV the contributions from direct and exchange processes associated with various nl shells. In each of the integrals $[nl_i \rightarrow l_j, n'l_i' \rightarrow l_j']$ in Tables II, III, and IV, the first excitation within the brackets corresponds to the Q perturbation, while the second refers to the Δ perturbation. The trends in the $(\gamma_\infty)_1$ for the three ions can be understood best by partitioning the individual contributions into intrashell and intershell categories.

The intrashell effect involves interactions between Δ- and Q-perturbed electrons within a single shell, for example, the $n = 2$ shell in the case of F^-. The intershell effect, on the other hand, involves the interaction between electrons in (nl) states perturbed by Q and those in $(n'l')$ states (with $n \neq n'$) perturbed by Δ, an example being the interaction of Q- perturbed $3p$ electrons with Δ-perturbed $2p$ electrons in Cl^-. We shall first consider the F^- ion whose $(\gamma_\infty)_1$ is determined mainly by intrashell effects. The Cl^- and Br^- ions, on the other hand, involve interesting interplay between the intrashell and intershell effects, and will be considered separately.

A. F^-

The leading contributions to the consistency effect in F^- arise from the interaction of Δ-perturbed $2p$ electrons with Q-perturbed $2p$, $2s$ and $1s$ electrons. Of the latter three perturbations, the $2p$ state makes the largest contribution, mainly through the radial $2p \rightarrow p$ Q perturbation, which contributes about 70% of the net consistency effect. Among the contributions from the angular Q perturbations, it is interesting that the $1s \rightarrow d$ perturbation is the most important contributor. This result indicates that although the $1s$ shell interacts less strongly with the external charge than the $2s$, its proximity to the nucleus makes its perturbation relatively strong so as to reverse the order of its

TABLE I. Total intershell and intrashell contributions to $(\gamma_\infty)_1$ for F^-, Cl^-, Br^- and comparisons with corresponding $(\gamma_\infty)_0$.

Ion	Intershell $(\gamma_\infty)_1$	Intrashell $(\gamma_\infty)_1$	Total $(\gamma_\infty)_1$	$(\gamma_\infty)_0$	$\gamma_\infty^{(1)} = (\gamma_\infty)_0 + (\gamma_\infty)_1$	$\frac{(\gamma_\infty)_1}{(\gamma_\infty)_0}$
F^-	(A) 1.0157	(A) 3.3029	2.88	−22.2	−19.3	−11.8%
	(B) −0.3269	(B) −0.8258				
	(C) 0.0079	(C) −0.2970				
	Total 0.6967	Total 2.1801				
Cl^-	(A) 2.0470	(A) 5.2948	−1.50	−55.1	−56.6	2.8%
	(B) −3.7092	(B) −2.1005				
	(C) −3.4973	(C) 0.4626				
	Total −5.1595	Total 3.6569				
Br^-	(A) 3.4426	(A) 10.7492	−7.16	−133.7	−140.9	5.4%
	(B) −8.9866	(B) −6.7827				
	(C) −7.4042	(C) 1.8179				
	Total −12.9482	Total 5.7844				

importance with respect to the $2s$ shell.

It is also interesting to compare the consistency effect in F^- with the isoelectronic positive ion, Na^+. For both ions we have a shielding effect from consistency which opposes the zero-order antishielding factor $(\gamma_\infty)_0$ for the two ions. The absolute magnitude of the consistency effect in F^- is nearly three times that in Na^+. This is due to the larger perturbation expected for the $2p$ electrons in the negative ions, particularly the Δ perturbation. However, the values of the ratio $(\gamma_\infty)_1/(\gamma_\infty)_0$ for F^- and Na^+ are comparable, which is an interesting manifestation of the balance between two opposing effects. Thus, while the $2p \rightarrow p$ Q and Δ perturbations are both stronger for the more deformable F^- ion, their separation is smaller for the more tightly bound Na^+ ion allowing them to interact more strongly in the latter. The combination of these two effects makes the relative importance of the consistency contributions similar in the two cases.

B. Cl^-

From Table I, the net consistency effect in Cl^- is seen to be an antishielding effect which reinforces the zero-order $(\gamma_\infty)_0$. To understand this reversal in sign of the consistency effect in going from F^- to Cl^-, one has to examine the individual terms in Table III for Cl^-. The leading terms are again associated with the interaction of various Q-perturbed functions and the radial Δ perturbation of the outermost p state, namely $3p \rightarrow p$.

It is interesting to compare the relative magnitudes of similar terms in F^- and Cl^-. Thus, for example, in Cl^- the term involving $(3p \rightarrow p)_\Delta$ interacting with $(3p \rightarrow p)_Q$ is larger than the corresponding term in F^-, namely that involving the $(2p \rightarrow p)_\Delta$ and $(2p \rightarrow p)_Q$ perturbations. This is expected because Cl^-, being a larger negative ion, is more deformable. The most interesting feature of the results for Cl^-, however, is the opposing effect of corresponding intrashell and intershell terms. Leading examples of this type are respectively the interaction term involving the $3p \rightarrow p$ Δ perturbation and $3p \rightarrow p$ Q perturbation, and the one involving the $3p \rightarrow p$ Δ perturbation interacting with the $2p \rightarrow p$ Q perturbation. For the former, namely the intrashell case, the term A in Eq. (6) is the only contributor because B and C in Eqs. (7) and (8) related to the diagrams 2(d), 2(e), and 2(f) in Ref. 8 vanish because of the Pauli principle. For the intershell case, however, all three terms A, B, and C contribute with signs opposite to the intrashell case. Similar opposing signs are observed from Table III for other pairs of intershell and intrashell terms, such as the pair $(2p \rightarrow p)_Q$ interacting with $(3p \rightarrow f)_\Delta$ and $(3p \rightarrow p)_Q$ with $(3p \rightarrow f)_\Delta$ and the pair $(2p \rightarrow p)_Q$ interacting with $(3s \rightarrow d)_\Delta$ and $(3p \rightarrow p)_Q$ with $(3s \rightarrow d)_\Delta$.

The relative signs of the intershell and intrashell terms involving purely radial excitations can be

TABLE II. Details of intershell and intrashell contributions[a] to $(\gamma_\infty)_1$ for F^-.

Diagram type	Intershell $(\gamma_\infty)_1$ Radial	Intershell $(\gamma_\infty)_1$ Angular		Intrashell $(\gamma_\infty)_1$ Radial		Intrashell $(\gamma_\infty)_1$ Angular		Total contribution from diagram
A		$[1s \rightarrow d, 2p \rightarrow p]$	1.088	$[2p \rightarrow p, 2p \rightarrow p]$	1.982	$[2s \rightarrow d, 2p \rightarrow p]$	0.248	
						$[2p \rightarrow p, 2p \rightarrow f]$	0.806	
						$[2p \rightarrow f, 2p \rightarrow p]$	0.372	
		Other terms	−0.072	Other terms	−0.042	Other terms	−0.063	
		Total	1.016	Total	1.940	Total	1.363	4.319
B		$[1s \rightarrow d, 2p \rightarrow p]$	−0.326			$[2s \rightarrow d, 2s \rightarrow d]$	0.104	
		$[2s \rightarrow d, 2p \rightarrow p]$	−0.108			$[2p \rightarrow p, 2s \rightarrow d]$	−0.233	
						$[2p \rightarrow p, 2p \rightarrow f]$	−0.559	
						$[2p \rightarrow f, 2p \rightarrow p]$	−0.100	
		Other terms	0.022			Other terms	0.053	
		Total	−0.412			Total	−0.735	−1.147
C						$[2s \rightarrow d, 2p \rightarrow p]$	−0.109	
						$[2p \rightarrow p, 2p \rightarrow f]$	−0.201	
		Other terms	0.008			Other terms	0.023	
		Total	0.008			Total	−0.287	−0.279
								$(\gamma_\infty)_1^{F^-} = 2.873$

[a] Individual values are shown only for terms whose contribution to $(\gamma_\infty)_1$ is greater than 0.1 in absolute magnitude. The rest of the contributions are summed up for each class under "other terms."

TABLE III. Details of intershell and intrashell contributions[a] to $(\gamma_\infty)_1$ for Cl^-.

Diagram type	Intershell $(\gamma_\infty)_1$				Intrashell $(\gamma_\infty)_1$				Total contribution from diagram
	Radial		Angular		Radial		Angular		
A	$[2p\rightarrow p, 3p\rightarrow p]$	−2.044	$[1s\rightarrow d, 3p\rightarrow p]$	1.248	$[3p\rightarrow p, 3p\rightarrow p]$	4.304	$[3p\rightarrow p, 3s\rightarrow d]$	−1.186	
			$[2s\rightarrow d, 3p\rightarrow p]$	0.360			$[3p\rightarrow p, 3p\rightarrow f]$	2.145	
			$[2p\rightarrow p, 3s\rightarrow d]$	1.024			$[3p\rightarrow f, 3p\rightarrow p]$	0.216	
			$[2p\rightarrow p, 3p\rightarrow f]$	1.136					
			$[2p\rightarrow f, 3p\rightarrow p]$	0.770					
			Other terms	−0.447			Other terms	−0.184	
	Total	−2.044	Total	4.091	Total	4.304	Total	0.991	7.342
B	$[2p\rightarrow p, 3p\rightarrow p]$	−2.960	$[1s\rightarrow d, 3p\rightarrow p]$	−0.424			$[3s\rightarrow d, 3s\rightarrow d]$	0.190	
							$[3p\rightarrow p, 3p\rightarrow f]$	−2.186	
			Other terms	−0.325			Other terms	−0.105	
	Total	−2.960	Total	−0.749			Total	−2.101	−5.810
C	$[2p\rightarrow p, 3p\rightarrow p]$	−2.615	$[1s\rightarrow d, 3p\rightarrow p]$	−0.418			$[3p\rightarrow p, 3s\rightarrow d]$	1.147	
			$[2p\rightarrow p, 3s\rightarrow d]$	−0.327			$[3p\rightarrow p, 3p\rightarrow f]$	−0.536	
							$[3s\rightarrow d, 3p\rightarrow p]$	−0.111	
			Other terms	−0.137			Other terms	−0.037	
	Total	−2.615	Total	−0.882			Total	0.463	−3.034
									$(\gamma_\infty)_1^{Cl^-} = -1.502$

[a] Individual values are shown only for terms whose contribution to $(\gamma_\infty)_1$ is greater than 0.1 in absolute magnitude. The rest of the contributions are summed up for each class under "other terms."

TABLE IV. Details of intershell and intrashell contributions[a] to $(\gamma_\infty)_1$ for Br^-.

Diagram type	Intershell $(\gamma_\infty)_1$ Radial		Angular		Intrashell $(\gamma_\infty)_1$ Radial		Angular		Total contribution from diagram
A	$[2p\rightarrow p, 4p\rightarrow p]$	−1.701	$[3d\rightarrow d, 4s\rightarrow d]$	0.553	$[4p\rightarrow p, 4p\rightarrow p]$	9.922	$[4p\rightarrow p, 4s\rightarrow d]$	−2.599	
	$[3p\rightarrow p, 4p\rightarrow p]$	−5.145	$[3d\rightarrow d, 4p\rightarrow p]$	−1.728			$[4p\rightarrow p, 4p\rightarrow f]$	4.403	
			$[3d\rightarrow d, 4p\rightarrow f]$	1.302			$[4p\rightarrow f, 4s\rightarrow d]$	−1.048	
			$[3d\rightarrow g, 4p\rightarrow p]$	0.624					
			$[1s\rightarrow d, 4p\rightarrow p]$	1.444					
			$[2p\rightarrow f, 4p\rightarrow p]$	0.842					
			$[3p\rightarrow f, 4p\rightarrow p]$	0.516					
			$[3p\rightarrow p, 4p\rightarrow f]$	3.954					
			$[2p\rightarrow p, 4s\rightarrow d]$	0.922					
			$[3p\rightarrow p, 4s\rightarrow d]$	1.420					
			$[3d\rightarrow d, 4p\rightarrow f]$	0.564					
			Other terms	−0.124			Other terms	0.061	
	Total	−6.846	Total	10.289	Total	9.922	Total	0.827	14.192
B	$[2p\rightarrow p, 4p\rightarrow p]$	−2.472	$[1s\rightarrow d, 4p\rightarrow p]$	−1.353			$[4p\rightarrow p, 4s\rightarrow d]$	−1.145	
	$[3p\rightarrow p, 4p\rightarrow p]$	−5.304					$[4p\rightarrow p, 4p\rightarrow f]$	−5.595	
			Other terms	0.142			Other terms	−0.043	
	Total	−7.776	Total	−1.211			Total	−6.783	−15.770
C	$[2p\rightarrow p, 4p\rightarrow p]$	−2.053	$[3p\rightarrow p, 4s\rightarrow d]$	0.632			$[4p\rightarrow p, 4s\rightarrow d]$	3.083	
	$[3p\rightarrow p, 4p\rightarrow p]$	−4.880	$[1s\rightarrow d, 4p\rightarrow p]$	−0.528			$[4p\rightarrow p, 4p\rightarrow f]$	−1.101	
			Other terms	−0.575			Other terms	−0.164	
	Total	−6.933	Total	−0.471			Total	1.818	−5.586
									$(\gamma_\infty)_1^{\mathrm{Br}^-} = -7.164$

[a] Individual values are shown only for terms whose contribution to $(\gamma_\infty)_1$ is greater than 0.5 in absolute magnitude. The rest of the contributions are summed up for each class under "other terms."

understood from an examination of Eqs. (13), (14), and (15). Thus the perturbation $\bar{u}_{1,3p}$ of the $3p$ orbital due to the external point charge gives a perturbation which is mainly confined to the external regions of the ion. This causes the major contribution to those terms to come from the external regions of the $2p$ orbital where the $2p$ and $3p$ orbitals have opposite signs due to the extra node in the $3p$ radial function in contrast with the square of the $3p$ or $2p$ radial functions occurring in the case of the intrashell effect. The relative signs for angular excitations are somewhat harder to understand since the radial functions belonging to different angular functions are not as simply related. The resultant cancellation between sizeable intershell and intrashell terms leads to the small antishielding contribution from the consistency effect in the case of Cl^- in contrast with the situation for F^-.

C. Br^-

From Table IV we notice that the trend followed by various individual terms in going from Cl^- to Br^- is in agreement with the trend from F^- to Cl^-. The greater size of the Br^- ions leads to greater Δ deformability of the outer orbitals and hence the observed enhancement in the individual consistency terms. Also, since there are more intershell terms in Br^- because of the presence of three p shells ($2p$, $3p$, $4p$), the total intershell effect is seen to be larger, and the net consistency contribution in Table I is antishielding in nature and stronger than for Cl^-.

IV. SUMMARY

From the results and discussions in the last section one can conclude that intershell and intrashell interactions both play important roles in consistency corrections to γ_∞. For Cl^- and Br^-, the intershell effect is opposite in sign to the intrashell and dominates, giving rise to net antishielding from consistency, as opposed to the net shielding contributed by the electron-electron interaction in F^-. For I^-, one expects the results to follow the trends observed in the three negative ions studied here, namely, larger intershell and intrashell interactions, with the former dominating and negative, giving rise to a total antishielding effect significantly larger than for Br^-. From our present analysis and that for positive ions,[7,8] where most of these interactions also occur, we can conclude that the consistency effect should not in general exceed about 15% of $(\gamma_\infty)_0$ in most ions. It would be interesting to check this conclusion by carrying out similar investigations in some other ions, with different charges and different numbers of shells. Calculations already available for divalent[10] and trivalent[7] $3d$-group ions indicate that the consistency effects do lie within the 15% limit.

We have not studied correlation effects in negative ions, which involve two orders of the $1/r_{12}$ interaction, but analysis of correlation contributions to γ_∞ in Na^+ and other positive ions[7,11] indicates that usually these higher-order perturbations are weaker than the consistency effect and follow the same relative trends from one ion to another.

It should be remarked that in ionic crystals, the γ_∞ factors may be somewhat different in magnitude than for the free ions considered here due to differences in the electronic wave functions. However the results in the various negative and positive ions studied so far, which represent a wide spectrum of deformabilities, suggest that the consistency effects for ions in crystals should also lie within about 15% of $(\gamma_\infty)_0$. A knowledge of the total γ_∞ including $(\gamma_\infty)_1$ is important for quantitative interpretation of nuclear quadrupole coupling data in ionic crystals, particularly in evaluating the contributions to the field gradient from non-nearest-neighbor ions which could be treated as point multipoles. For the contributions to the field gradient from nearest-neighbor ions, a quantitative analysis of overlap[2,12] and charge-transfer covalency effects[13] will be necessary.

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