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# Effect of self-consistency and crystalline potential in the solid state on nuclear quadrupole Sternheimer antishielding factors in closed-shell ions

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The Sternheimer quadrupole antishielding factor $\gamma_\infty$ including self-consistency effects have been studied for several closed-shell ions isoelectronic with He, Ne, A, Kr, Xi, $Cu^+$, and $Ag^+$ in both free state as well as in ionic solid-state systems. Solid-state effects have been included using the Watson sphere model for ionic solids. The self-consistency contributions $\gamma_\infty^{(1)}$ are found to be in general less than 30% of the zero-order antishielding factor $\gamma_\infty^{(0)}$. The net free ionic $\gamma_\infty (=\gamma_\infty^{(0)}+\gamma_\infty^{(1)})$ results agree very well with the results of corresponding coupled Hartree-Fock and polarized orbital calculations wherever available. For negative ions, $\gamma_\infty^{(0)}$ decreases significantly in going from the free ion to the solid state. For positive ions the opposite holds good. The solid-state effect on $\gamma_\infty^{(0)}$ is usually more important than the consistency effects $\gamma_\infty^{(1)}$ for the negative ions. For positive ions, the two effects are comparable except in some cases where the consistency effects are larger in magnitude. These trends in the relative importance of $\gamma_\infty^{(1)}$ as compared to solid-state effects are discussed in terms of the relative changes in the respective radial charge-density distributions in going from free ions to solid state. The possible influence of many-body correlations effects on $\gamma_\infty$ is considered. Finally, the utility of the $\gamma_\infty$ obtained in the present work for the net field gradients in ionic crystals, for which overlap and covalency effects between immediate neighbors have also to be considered, is discussed.

## I. INTRODUCTION

For the understanding of the origin of the nuclear quadrupole interaction in ionic crystals, it is important to have a good knowledge of the Sternheimer antishielding factor[1] $\gamma_\infty$. This factor describes the influence of the additional field gradient induced at the site of the nucleus by the polarization effect produced by the external field gradient on the electronic states of the ion. A major part of the efforts in the past in investigating $\gamma_\infty$ have been directed towards the direct response of the electrons on free ions (as contrasted to ions in a solid) to the influence of the external-field gradient, which has been studied by both differential equation[1] and variational[2] procedures. However, there are two important effects that need to be considered for the quantitative analysis of field gradients for ions in solid state: firstly, the influence of the crystal field on the radial character of the electronic orbitals and the consequent alteration in their response to the external electric field and, secondly, the influence of the interaction of the electrons among themselves on $\gamma_\infty$, a factor that must also be considered for free ions. For the former effect, a useful approach to employ is the Watson sphere model[3] and this has been utilized in the past for the study of the influence of crystalline fields on $\gamma_\infty$ for a number of ions,[4,5] without incorporation of electron-electron interactions. The influence of the latter can be incorporated in a number of ways. One approach is to use a fully coupled Hartree-Fock (CHF) perturbation procedure[6] which includes all the one-electron consistency effects.

Another procedure involves the linked-cluster many-body perturbation theory (LCMBPT) approach[7] which can include both consistency and correlation effects and provide information on the relative importance of these effects to various orders through the consideration of appropriate perturbation diagrams. However, both these methods are rather involved. The CHF method requires the use of very flexible variational functions with a substantial number of parameters to incorporate electron-electron interaction effects satisfactorily. In the differential equation procedure, the CHF method leads[8] to a coupled set of inhomogeneous second-order differential equations to be integrated numerically over several mesh points. The LCMBPT procedure,[7] on the other hand, requires a determination of a complete set of basis states and rather time-consuming evaluations of two-electron matrix elements involving both the occupied and excited states, which occur in the perturbation summations over excited states represented by diagrams. With respect to the calculations of $\gamma_\infty$, the largest atomic system dealt with so far using the CHF perturbation procedure has been[9] argon in the closed-shell configuration. LCMBPT calculations of $\gamma_\infty$ have been reported for[7] $Na^+$ and $Fe^{3+}$ and very recently[10] $Pr^{3+}$. To incorporate electron-electron interaction effects in a satisfactory manner without unduly elaborate efforts, a method has been devised[11] recently which utilizes the essence of the many-body perturbation procedure, but uses perturbed wave functions in lowest order from differential equation or variational approaches to the first-order perturbation equation describing the influence of the quadrupole moment (or external field gradient) on the electronic states. This procedure has recently been applied[12] to calculate the dipole and quadrupole polarizabilities of the closed-shell ionic systems as large as xenon in both free ions and ions in crystals treated by the Watson sphere model. In the present work we shall apply this procedure to calculate $\gamma_\infty$ for both free ions and ions in crystals.

The aim of the present work is twofold. The first is to obtain an understanding of the nature of the consistency effects on $\gamma_\infty$ which arise from the interaction between the perturbed electron states in the presence of the nuclear quadrupole moment and external-field gradient. The relative importance of direct and exchange-type consistency effects will be considered in a whole set of closed-shell positive and negative ions and neutral rare-gas atoms. Additionally, we shall also analyze the relative contributions from different multipoles of the Coulomb interactions, $e^2/r_{12}$, between the perturbed electrons. The second aim of the present work is to analyze, as in the case of polarizabilities discussed earlier, the influence of the crystal-field effects, as represented by the Watson sphere model, on $\gamma_\infty$, including the consistency effect, something that is being done for the first time in the present work. Such an analysis will allow one to draw conclusions regarding the relative importance of the electron-electron interaction effects of the consistency type and the crystal-field effects as well as the influence of one on the other.

In Sec. II we briefly discuss the procedures utilized for the incorporation of crystal-field effects through the Watson sphere model[3-5,11] and of consistency effects[11-14] including a discussion of the origin of the various multipolar terms of the Coulomb interaction between electrons contributing to the total consistency term in $\gamma_\infty$. In Sec. III we report the results of our calculations of $\gamma_\infty$ for both free ions and ions in ionic crystals and discuss them. Wherever available, the results of earlier calculations of $\gamma_\infty$ in the free ionic cases including the consistency effect have been compared with our results in this section. Also the importance of many-body correlation effects are discussed using the results of some of the ions for which such calculations have been performed.[7] The nature of crystal-field effects beyond that covered by the Watson sphere model on the field gradients in ionic crystals is also discussed.

## II. THEORY AND PROCEDURE

In this section we shall briefly present the theory of crystal-field and self-consistency effects on the Sternheimer antishielding factor $\gamma_\infty$ along with the details of the procedure adopted in the present work.

### A. Unperturbed wave functions for free and crystal ions

Throughout this work we shall be concerned with closed-shell atomic systems. The many-electron unperturbed-state wave function $\Phi_0$ in the present work is assumed to be the eigensolution of $\mathcal{H}_0$, the Hartree-Fock (HF) Hamiltonian for the system concerned, that is,

$$\mathcal{H}_0\Phi_0 = E_0\Phi_0 \ , \tag{1}$$

$\Phi_0$ being a single determinantal wave function comprised of the one-electron orbitals $\phi_{nlm_lm_s}$. For atoms and free ions, the radial HF one electron equations may be written as

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{r^2}+V_0^{\mathrm{HF}}(nl)\right]u_0(nl)=\epsilon_0^{nl}u_0(nl) \ , \tag{2}$$

where $V_0^{\mathrm{HF}}(nl)$ is the potential experienced by an electron in state $(nlm_lm_s)$ in the Hartree-Fock approximation, the potential for a closed-shell ion being independent of the magnetic quantum numbers of $m_l$ and $m_s$, and $u_0(nl)$ being the radial component of the wave function $\phi_{nlm_lm_s}$ defined by

$$\phi_{nlm_lm_s}(\vec{r}) = r^{-1}u_0(nl)Y_l^m(\theta\phi)\alpha_{m_s} \ , \tag{3}$$

$\alpha_{m_s}$ representing the spin component of the wave function.

For ions in crystals we have used the Watson sphere model[3] to represent the electrostatic potential due to the ionic lattice. In this model the ion $A^{+q}$ (with charge $+q$) is placed at the center of a uniformly charged hollow sphere of radius $r_{\mathrm{ion}}$ equal to the Pauling ionic radius[15] of the ion, the total charge carried by the sphere being taken as $-q$ units. The radial one-electron HF equations (2) for the ion in the crystal now includes an additional potential term due to the Watson sphere which may be written as

$$V_w = \begin{cases} qe^2/r_{\mathrm{ion}}, & r \leq r_{\mathrm{ion}} \\ qe^2/r, & r \geq r_{\mathrm{ion}} \ . \end{cases} \tag{4}$$

### B. Perturbed wave functions

The perturbation Hamiltonian $\Delta\mathcal{H}$ describing closed-shell atomic systems, under the combined influence of the nuclear quadrupole moment $eQ$ and the electric field gradient resulting from an external charge $+e$ situated at a distance $R$ from the nucleus, may be written as[7,11] a sum of three parts, $\mathcal{H}'$, $\mathcal{H}''$, and $\mathcal{H}'''$, respectively, given by

$$\mathcal{H}'=\sum_{i>j}\frac{e^2}{r_{ij}}-\sum_i V_{0i}^{\mathrm{HF}}(nl) \ , \tag{5}$$

$$\mathcal{H}''=-\frac{e^2}{R^3}\sum_i r_i^2 P_2(\cos\theta_i) \ , \tag{6}$$

and

$$\mathcal{H}'''=-e^2Q\sum_i\frac{P_2(\cos\theta_i)}{2r_i^3} \ , \tag{7}$$

respectively, with $\theta_i$ being measured with respect to the line joining the nucleus and the external charge. Thus, $\mathcal{H}'$ and $\mathcal{H}''$ represent the perturbation potential due to the external point charge $e$ and the nuclear quadrupole moment $eQ$, respectively. $\mathcal{H}'$ defines the difference[7] in the instantaneous electron-electron interaction potential and its average in the HF approximation. The total perturbation energy due to the influence of the perturbation Hamiltonian $\Delta\mathcal{H}$ is given by[7] the linked cluster expansion

$$\delta E=\sum_{n=0}^{\infty}\left\langle\Phi_0\left|\Delta\mathcal{H}\left[\frac{\Delta\mathcal{H}}{E_0-\mathcal{H}_0}\right]^n\right|\Phi_0\right\rangle_L \ . \tag{8}$$

The leading term of $\delta E$ gives the Sternheimer ionic antishielding factor in the uncoupled approximation,[16] namely,

$$\gamma_\infty^{(0)}=-\delta E_0/(2e^2Q/R^3) \ , \tag{9}$$

where $\delta E_0$ denotes the perturbation energy to first order each in $\mathcal{H}''$ and $\mathcal{H}'''$ and zero order in $\mathcal{H}'$. In the present work we have evaluated Eq. (9) using the moment perturbed differential equation (DE) method[13] as well as the variational equivalent[2,17] of the charge perturbed DE method. The perturbed one-electron wave functions are written in the form

$$\phi_{nlm_lm_s}+\sum_{l'}\delta\phi_{nlm_lm_s}(l\to l')=\left[\frac{u_0(nl)}{r}Y_l^{m_l}(\theta,\phi)+\sum_{l'}b(l\to l';m_l)\frac{\bar{u}_1'(nl\to l')}{r}Y_{l'}^{m_{l'}}(\theta,\phi)\right]\alpha_{m_s} \ , \tag{10}$$

where the angular factors $b(l\to l';m_l)$ are given by Sternheimer.[16]

The perturbation (charge perturbed) equation satisfied by $\bar{u}_1'(nl\to l')$ is given in the uncoupled approximation by

$$\left[-\frac{d^2}{dr^2}+\frac{l'(l'+1)}{r^2}+V_0^{\mathrm{HF}}(nl)-\epsilon_0^{nl}\right]\bar{u}_1'(nl\to l')=u_0(nl)(r^2-\langle r^2\rangle_{nl}\delta_{ll'}) \ . \tag{11}$$

In the variational method $\bar{u}_1'(nl\to l')$ is expanded in the form

$$\bar{u}_1'(nl\to l')=u_0(nl)r^2\sum_{s=0}^{m}a_sr^s \ , \tag{12}$$

where the $a_s$ are variational parameters. All the quadrupolar perturbations[16] $|l\to l'|=0,2$ have been considered. The appropriate second-order energy functional to be minimized is given by[18]

$$\begin{aligned}J_{nl}(\bar{u}_1'(nl\to l'))=&\left\langle\bar{u}_1'(nl\to l')\left|-\frac{d^2}{dr^2}+\frac{l'(l'+1)}{r^2}+V_0^{\mathrm{HF}}(nl)-\epsilon_0^{nl}\right|\bar{u}_1'(nl\to l')\right\rangle+2\langle\bar{u}_1'(nl\to l')|r^2|u_0(nl)\rangle\\&-\sum_{n''}\omega(n''l')[(\epsilon_0^{n''l'}-\epsilon_0^{nl})|\langle\bar{u}_1'(nl\to l')|u_0(n''l')\rangle|^2\\&+2\langle\bar{u}_1'(nl\to l')|u_0(n''l')\rangle\langle u_0(nl)|r^2|u_0(n''l')\rangle] \ ,\end{aligned} \tag{13}$$

where $\omega(n''l')$ denote the occupation number in the $n''l'$ shell.

The variational equivalent of Eq. (11) would not have the terms involving the summations over the other occupied shells $n''l'$. These terms take account of nonorthogonality effects between the perturbations $\delta\phi_{nlm_lm_s}(l\to l)$ and unperturbed functions $\phi_{n''l'm_lm_s}$ and would have their $nlm_lm_s$ counterparts in the perturbation Eq. (11), if one wanted to include the influence of the nonorthogonality effects in the DE approach. It has been shown in the literature that one in fact does not need to include these terms in Eq. (11) because the influences on $\gamma_\infty$ of nonorthogonality terms associated with the perturbations of different shells mutually cancel.[13] In the variational approach, however, one needs to incorporate these terms in the energy functional in Eq. (13) to prevent divergences associated with effects such as, for example,[17] the perturbed function $\phi_{3p}+\delta\phi_{3p}$ in $K^+$ tending towards the lowest state of $p$ symmetry such as $\phi_{2p}$ as one increases the number of variation parameters as in Eq. (12).

For the calculation of the self-consistency contribution to $\gamma_\infty$ it is convenient to have the perturbed wave functions $u_1$ orthogonal to the unperturbed states. Therefore for the calculation of $\gamma_\infty$ we have replaced $\bar{u}_1'$ by $\bar{u}_1$,

$$\bar{u}_1(nl\rightarrow l')=\bar{u}_1'(nl\rightarrow l') - \sum_{n'} u_0(n'l')\int u_0(n'l')\bar{u}_1'(nl\rightarrow l')dr' \ . \tag{14}$$

The perturbed functions $\bar{u}_1$ for all the atoms and ions considered in this work are essentially the same as those generated during recent calculations[12] of dipole and quadrupole polarizabilities including self-consistency effects. With the knowledge of $\bar{u}_1$, $\gamma_\infty^{(0)}$ is calculated according to

$$\gamma_\infty^{(0)}=\sum_{nl,l'} c(nl\rightarrow l')\int_0^\infty u_0(nl)\bar{u}_1(nl\rightarrow l')r^{-3}dr \ , \tag{15}$$

where the $c$'s denote factors resulting from angular integrations[16] occurring in the expression for $\delta E_0$ in Eq. (9) using the zero-order and perturbation components of the wave function in Eq. (13).

In the differential equation method of calculating $\gamma_\infty^{(0)}$, the perturbations in the one-electron wave functions due to the influence of the nuclear quadrupole moment perturbation are described by the one-electron radial wave functions $u_1'(nl\rightarrow l')$ which are determined by solving the following inhomogeneous differential equations[16]

$$\left[-\frac{d^2}{dr^2}+\frac{l'(l'+1)}{r^2}+V_0^{\mathrm{HF}}(nl)-\epsilon_0^{nl}\right]u_1'(nl\rightarrow l') = u_0(nl)(r^{-3}-\langle r^{-3}\rangle_{nl}\delta_{ll'}) \ . \tag{16}$$

$\gamma_\infty^{(0)}$ is then obtained from the relation

$$\gamma_\infty^{(0)}=\sum_{nl,l'} c(nl\rightarrow l')\int_0^\infty u_0(nl)u_1(nl\rightarrow l')r^{2}dr \ , \tag{17}$$

where the $u_1$ are obtained from the functions $u_1'$ by orthogonalization similar to that in Eq. (14).

In principle, Eqs. (15) and (17), as will be pointed out in the next section, should give rise to identical results. The small differences $\Delta\gamma_\infty^{(0)}$ (that are sometimes seen) are mainly caused by the fact that two different perturbations ($\mathcal{H}''$ and $\mathcal{H}'''$) are used to calculate the perturbed wave functions, which lead to different accuracies for the $u_1$ and $\bar{u}_1$.

The equivalent expressions corresponding to Eqs. (11) and (17), involving summations over the excited bound and continuum states in the many-body perturbation theory (MBPT),[7] can be obtained by setting

$$-\tfrac{1}{2}Q\langle u_{1p}|=\sum_i \frac{\langle p|\mathcal{H}'''|i\rangle\langle i|}{\epsilon_p-\epsilon_i} \tag{18}$$

and

$$-\frac{1}{R^3}\langle \bar{u}_{1p}|=\sum_i \frac{\langle p|\mathcal{H}''|i\rangle\langle i|}{\epsilon_p-\epsilon_i} \ , \tag{19}$$

respectively.

The consistency correction[11–14] $\gamma_\infty^{(1)}$ is defined as

$$\gamma_\infty^{(1)}=-\delta E_1/(e^2Q/2R^3) \ , \tag{20}$$

where $\delta E_1$ represents the sum of all the terms in Eq. (8) that contain one order each of $\mathcal{H}'$, $\mathcal{H}''$, and $\mathcal{H}'''$. The right-hand side in Eq. (20) is composed of three summation terms of type $A$, $B$, and $C$ defined, respectively, as

$$A=4\sum_{q>p}\left[\left\langle q\,p\left|\frac{1}{r_{12}}\right|\bar{u}_{1q}u_{1p}\right\rangle+\left\langle q\,p\left|\frac{1}{r_{12}}\right|u_{1q}\bar{u}_{1p}\right\rangle\right] \ , \tag{21}$$

$$B=-2\sum_{q>p}\left[\left\langle q\,p\left|\frac{1}{r_{12}}\right|\bar{u}_{1p}u_{1q}\right\rangle+\left\langle q\,p\left|\frac{1}{r_{12}}\right|u_{1p}\bar{u}_{1q}\right\rangle\right] \ , \tag{22}$$

and

$$C=-2\sum_{q>p}\left[\left\langle q\bar{u}_{1p}\left|\frac{1}{r_{12}}\right|pu_{1q}\right\rangle+\left\langle qu_{1p}\left|\frac{1}{r_{12}}\right|p\bar{u}_{1q}\right\rangle\right] \ , \tag{23}$$

where the summation is carried over all the occupied spin orbitals taking account of the Pauli exclusion principle. The integrals $A$ are Coulomb integrals and $B$ and $C$ are exchange integrals. The equivalent expressions for [i.e., Eqs. (6)–(8) in Ref. 14] $\gamma_\infty^{(1)}$ in linked-cluster many-body perturbation theory (LCMBPT) may be obtained by substituting Eqs. (18) and (19) in Eqs. (21)–(23), respectively.

We would like to make a few remarks about the terms $A$, $B$, and $C$ in Eq. (20) before proceeding to the presentation of results and discussion for $\gamma_\infty^{(0)}$, $\gamma_\infty^{(1)}$, and their sum, both for free ions and ions in the solid state with the solid-state effect incorporated[3–5, 12] through the Watson sphere model.

First, the Eqs. (21)–(23) are identical to those used recently for dipole and quadrupole polarizability calculations, but with $u_{1p}$ and $u_{1q}$ replaced by $\bar{u}_{1p}$ and $\bar{u}_{1q}$, respectively, the solution of the first-order perturbation equation involving the operator $\mathcal{H}''$ in Eq. (6) for quadrupole polarizabilities and the corresponding operator $-e^2\sum_i r_iP_i(\cos\theta_i)/R^2$ for dipole polarizabilites.

Also, the same expressions have been used in both earlier[7,19] and recent[10] calculations in LCMBPT for a number of ions and in earlier adaptations[11,13,14] of the LCMBPT diagram expression for study of consistency effects on $\gamma_\infty$. However, there is an important difference between the contribution $A$ in Eq. (21) to $\gamma_\infty^{(1)}$ and earlier LCMBPT calculations,[7,19] and associated consistency calculations (referred to compositely as I) on the one hand and more recent LCMBPT calculations on the other[10] (referred to compositely as II). Considering the comparison with I first, the main difference between the expressions used in the present calculation and in I, is that in the $A$ terms one finds finite contribution from terms involving the monopole term $k=0$ in the multipole expansion for

$$\frac{1}{r_{12}}=4\pi \sum_{kmk} \frac{1}{(2k+1)} \frac{r_<^k}{r_>^{k+1}} Y_k^{m_k *}(1) Y_k^{m_k}(2) \ . \tag{24}$$

These terms occur for radial excitation terms $u_{1q}$ (like, for instance, $p \rightarrow p$ for $d \rightarrow d$) with $p$ and $q$ [Eq. (21)] belonging to the same shell, representing intrashell self-consistency effects. These monopole terms $k=0$ can, in principle, also occur for intershell consistency terms involving radial excitations but vanish when one sums over a complete interacting shell. The intrashell monople consistency terms were inadvertently omitted in I and their effects will be shown to provide significant corrections to $\gamma_\infty^{(0)}$ of comparable order of magnitude and often of larger size and of opposite sign than the $k \neq 0$ terms. In both the present work and in I, no monopole terms occur for intrashell consistency effects ($p$ and $q$ belonging to the same shell) for $B$ and $C$ terms, but small intershell $k=0$ monopole terms do occur for $B$ and $C$.

Considering comparison with II, in the latter work, monopole terms associated with intrashell radial excitations were found for the consistency terms $B$ in contrast to the present work where no such monopole terms were found. As discussed elsewhere[20] this difference between the present work on the one hand and II on the other is associated with the use of different types of Hartree-Fock potentials for the LCMBPT calculations in I and II, namely,[21] the $V^{N-1}$ and $V^N$ potentials, the latter including self-Coulomb and self-exchange interactions. The former potential is more physical for excited states, leading to an effective asymptotic charge at large distances of unity in the case of neutral atoms, $+2$ for singly charged positive ions and so on. The Sternheimer approximation involving the zero-order Hamiltonian $\mathcal{H}_{0i}$ in the perturbation equation

$$\mathcal{H}_{0i}=-\tfrac{1}{2}\nabla^2+(\nabla^2\phi_i)/\phi_i+\epsilon_0^i \tag{25}$$

gives an effective potential of $1/r$ at large distances as in the case of the $V^{N-1}$ potential.

## III. RESULTS AND DISCUSSION

Our results for the values of $\gamma_\infty^{(0)}$ and $\gamma_\infty^{(1)}$ for both the free ions and ions in the Watson sphere are listed in Table I, including the ratios

$$\frac{(\gamma_\infty^{(0)}+\gamma_\infty^{(1)})_{\text{crystal}}}{(\gamma_\infty^{(0)})_{\text{free}}},\quad \frac{(\gamma_\infty^{(0)}+\gamma_\infty^{(1)})_{\text{free}}}{(\gamma_\infty^{(0)})_{\text{free}}} \ .$$

The first of these ratios represents the fractional correction to the $\gamma_\infty^{(0)}$ for the free ion due to the combined effects of the crystal field and consistency effect and the latter due to consistency effects alone.

### A. Free ions

In discussing the results in Table I we would like first to discuss the systematics of the results for $\gamma_\infty^{(0)}$ and $\gamma_\infty^{(1)}$ for free ions and subsequently of the same quantitites for the solid state involving the influence of the Watson sphere. We shall make comparisons between the results for the two cases to gain insight into the influence of crystal field on $\gamma_\infty^{(0)}$ and also on $\gamma_\infty^{(1)}$, the latter providing insight into the interplay of crystal field and consistency effects.

Considering first the free-ion results, as far as the $\gamma_\infty^{(0)}$ are concerned, our results are in good agreement with those from earlier uncoupled calculations[18,22] (which do not include consistency effects) by either variational or differential equation technique based on Hartree-Fock wave functions. In comparing with calculations involving Hartree-Fock-Slater wave functions,[23,24] in a number of cases,[5,25] there is reasonable agreement with our $\gamma_\infty^{(0)}$, but in a number of other cases (F$^-$, Ne, Cl$^-$, A, Br$^-$, Kr) there seems to be an overestimation of $\gamma_\infty^{(0)}$ by the Hartree-Fock-Slater calculation,[5,25] as compared to our results and other Hartree-Fock wave function results.[18,22] The good agreement between our results and earlier uncoupled Hartree-Fock calculations supports the accuracy of our computational procedure for obtaining the perturbed wave functions $u_1$ and $\bar{u}_1$. This is important for having confidence in the accuracy of our results for crystal-field and consistency effects and their interplay, for which practically no results of earlier calculations are available for comparison except for a few cases for free ions where results of variational calculations, using what is referred to[6] as method a in the literature, are available,[6,8] and which can be compared with our results for $\gamma_\infty^{(0)}+\gamma_\infty^{(1)}$. In a few other instances for free ions, results from many-body perturbation-theoretic calculations,[7,19] as well as consistency-effect calculations by the present procedure, have been carried out,[11,13,14] and we shall, of course, make comparisons with them. It should be pointed out, however, that from Table II, where we

TABLE I. List of results for the antishielding factor for free ions and ions in the Watson sphere in solid state. ($\gamma_\infty^{(0)}$, $\gamma_\infty^{(1)}$, and $\gamma_\infty$ refer to zero order, consistency, and net results for the antishielding factors.)

| | | Free | | | Crystal | | | | Watson sphere radius |
|---|---|---|---|---|---|---|---|---|---|
| Ion | $\gamma_\infty^{(0)}$ | $\gamma_\infty^{(1)}$ | $\gamma_\infty$ | $\gamma_\infty^{(0)}$ | $\gamma_\infty^{(1)}$ | $\gamma_\infty$ | $\frac{(\gamma_\infty)_{\text{free}}}{(\gamma_\infty^{(0)})_{\text{free}}}$ | $\frac{(\gamma_\infty)_{\text{crystal}}}{(\gamma_\infty^{(0)})_{\text{free}}}$ | [$r_{\text{ion}}$ in Eq. (4)] (Å) |
| He | 0.423 | − 0.025 | 0.398 | . . . | . . . | . . . | 0.941 | . . . | . . . |
| $Li^+$ | 0.259 | − 0.010 | 0.249 | 0.265 | − 0.010 | 0.255 | 0.961 | 0.985 | 0.060 |
| $Be^{2+}$ | 0.187 | − 0.005 | 0.182 | 0.206 | − 0.006 | 0.200 | 0.973 | 1.070 | 0.34 |
| $B^{3+}$ | 0.146 | − 0.003 | 0.143 | 0.195 | − 0.005 | 0.190 | 0.979 | 1.301 | 0.20 |
| $C^{4+}$ | 0.120 | − 0.002 | 0.118 | 0.185 | − 0.005 | 0.180 | 0.983 | 1.500 | 0.15 |
| $N^{5+}$ | 0.102 | − 0.001 | 0.101 | 0.185 | − 0.005 | 0.180 | 0.990 | 1.765 | 0.11 |
| $N^{3-}$ | . . . | . . . | . . . | − 11.317 | − 2.864 | − 14.181 | . . . | . . . | 1.59 |
| $O^{2-}$ | . . . | . . . | . . . | − 11.287 | − 2.498 | − 13.785 | . . . | . . . | 1.32 |
| $F^-$ | − 22.104 | − 6.505 | − 28.609 | − 10.307 | − 2.151 | − 12.458 | 1.294 | 0.564 | 1.33 |
| Ne | − 8.063 | − 1.391 | − 9.454 | . . . | . . . | . . . | 1.173 | . . . | . . . |
| $Na^+$ | − 4.640 | − 0.621 | − 5.261 | − 4.804 | − 0.648 | − 5.452 | 1.134 | 1.175 | 0.95 |
| $Mg^{2+}$ | − 3.145 | − 0.358 | − 3.503 | − 3.688 | − 0.430 | − 4.118 | 1.114 | 1.309 | 0.65 |
| $Al^{3+}$ | − 2.350 | − 0.239 | − 2.589 | − 3.269 | − 0.344 | − 3.613 | 1.102 | 1.537 | 0.50 |
| $S^{2-}$ | . . . | . . . | . . . | − 41.259 | − 10.956 | − 52.215 | . . . | . . . | 1.84 |
| $Cl^-$ | − 54.421 | − 14.390 | − 68.811 | − 34.721 | − 7.278 | − 41.999 | 1.264 | 0.772 | 1.81 |
| Ar | − 24.540 | − 4.063 | − 28.603 | | | | 1.166 | | |
| $K^+$ | − 17.583 | − 2.374 | − 19.957 | − 19.089 | − 2.693 | − 21.782 | 1.135 | 1.239 | 1.33 |
| $Ca^{2+}$ | − 12.638 | − 1.419 | − 14.057 | − 16.659 | − 2.132 | − 18.791 | 1.112 | 1.487 | 0.99 |
| $Sc^{3+}$ | − 10.401 | − 0.987 | − 11.388 | − 20.460 | − 2.644 | − 23.104 | 1.095 | 2.221 | 0.73 |
| $Cu^+$ | − 16.584 | − 4.954 | − 21.538 | − 18.242 | − 6.967 | − 25.209 | 1.299 | 1.520 | 0.96 |
| $Zn^{2+}$ | − 11.930 | − 2.159 | − 14.089 | − 16.267 | − 5.631 | − 21.898 | 1.181 | 1.836 | 0.74 |
| $Ga^{3+}$ | − 9.928 | − 1.379 | − 11.307 | − 13.445 | − 3.541 | − 16.986 | 1.139 | 1.711 | 0.62 |
| $Se^{2-}$ | . . . | . . . | . . . | − 76.543 | − 10.812 | − 87.355 | . . . | 0.633 | 1.98 |
| $Br^-$ | − 135.16 | − 30.83 | − 165.99 | − 75.675 | − 9.842 | − 85.517 | 1.228 | . . . | 1.95 |
| Kr | − 68.914 | − 8.830 | − 77.744 | . . . | . . . | . . . | 1.128 | . . . | . . . |
| $Rb^+$ | − 45.056 | − 2.608 | − 47.664 | − 49.448 | − 3.333 | − 52.781 | 1.058 | 1.171 | 1.48 |
| $Sr^{2+}$ | − 36.776 | − 2.117 | − 38.893 | − 47.620 | − 2.208 | − 47.828 | 1.058 | 1.301 | 1.13 |
| $Y^{3+}$ | − 29.778 | − 1.242 | − 31.020 | − 47.528 | − 4.459 | − 51.985 | 1.042 | 1.746 | 0.93 |
| $Ag^+$ | − 35.188 | − 7.952 | − 43.140 | − 35.835 | − 8.687 | − 44.522 | 1.226 | 1.265 | 1.26 |
| $Cd^{2+}$ | − 28.391 | − 4.959 | − 33.350 | − 31.562 | − 6.854 | − 38.416 | 1.175 | 1.353 | 0.97 |
| $I^-$ | − 248.56 | − 50.24 | − 298.80 | − 148.44 | − 13.98 | − 162.42 | 1.202 | 0.653 | 2.16 |
| $Cs^+$ | − 90.871 | − 4.290 | − 95.161 | − 103.27 | − 7.54 | − 110.81 | 1.047 | 1.219 | 1.69 |
| $Ba^{2+}$ | − 75.085 | − 1.139 | − 76.224 | − 103.01 | − 7.71 | − 110.72 | 1.015 | 1.475 | 1.35 |

have listed the values of $\gamma_\infty^{(0)}$ calculated from $u_1$, the perturbation by the nuclear quadrupole moment, and from $\bar{u}_1$, the perturbation by the external charge, there are found to be small differences between the two sets of values. The differences are usually in the neighborhood of 5% (with about 10% difference for doubly and triply charged negative ions and as low as 3% for triply positive ions), with the value from $\bar{u}_1$ always the lower one in magnitude. We have no physical explanation for this latter feature but use the difference of 5% between the two values of $\gamma_\infty^{(0)}$ as our confidence limit for $\gamma_\infty^{(1)}$ and $\Delta\gamma_\infty = \gamma_\infty$(free ion) $- \gamma_\infty$(solid), because these consistency and crystal-field effects are bilinear in $\bar{u}_1$ and $u_1$ like $\gamma_\infty$(free ion).

We turn next to the results for consistency contributions to the antishielding effect for free ions. Before discussing $\gamma_\infty^{(1)}$ *per se,* we would like to consider the contributions $A$ and $(B+C)$ to the latter. The terms $B$ and $C$ are grouped together both because they represent exchange-type effects, while $A$ represents a direct effect and also because $A$ contains the important intrashell monopole ($k=0$) term while $B$ and $C$ do not. From Table III, we find the following overall trends in $A$ and $(B+C)$. The sign of $(B+C)$ remains negative for all the systems studied,

TABLE II. Comparison of $\gamma_\infty^{(0)}$ calculated by $q$- and $Q$-perturbed methods.

| Ion | Free ions perturbation | | Ions in the crystal perturbation | |
|---|---|---|---|---|
| | $Qe$ | $e/R$ | $Qe$ | $e/R$ |
| He | 0.423 | 0.414 | . . . | . . . |
| $Li^+$ | 0.259 | 0.257 | 0.265 | 0.262 |
| $Be^{2+}$ | 0.187 | 0.186 | 0.206 | 0.205 |
| $B^{3+}$ | 0.146 | 0.145 | 0.195 | 0.186 |
| $C^{4+}$ | 0.120 | 0.119 | 0.185 | 0.168 |
| $N^{5+}$ | 0.102 | 0.101 | 0.185 | 0.169 |
| $N^{3-}$ | . . . | . . . | − 11.317 | − 12.866 |
| $O^{2-}$ | . . . | . . . | − 11.287 | − 10.771 |
| $F^-$ | − 22.104 | − 21.974 | − 10.307 | − 10.156 |
| Ne | − 8.063 | − 7.904 | . . . | . . . |
| $Na^+$ | − 4.640 | − 4.484 | − 4.804 | − 4.649 |
| $Mg^{2+}$ | − 3.145 | − 2.974 | − 3.688 | − 3.527 |
| $Al^{3+}$ | − 2.350 | − 2.209 | − 3.269 | − 3.129 |
| $S^{2-}$ | . . . | . . . | − 41.259 | − 41.061 |
| $Cl^-$ | − 54.421 | − 52.845 | − 34.721 | − 32.643 |
| Ar | − 24.540 | − 23.750 | . . . | . . . |
| $K^+$ | − 17.583 | − 16.198 | − 19.089 | − 17.749 |
| $Ca^{2+}$ | − 12.638 | − 11.829 | − 16.659 | − 15.766 |
| $Sc^{3+}$ | − 10.401 | − 9.656 | − 20.460 | − 19.615 |
| $Cu^+$ | − 16.584 | − 16.088 | − 18.242 | − 17.761 |
| $Zn^{2+}$ | − 11.930 | − 11.545 | − 16.267 | − 15.858 |
| $Ga^{3+}$ | − 9.928 | − 9.273 | − 13.445 | − 13.575 |
| $Se^{2-}$ | . . . | . . . | − 76.543 | − 75.692 |
| $Br^-$ | − 135.16 | − 132.65 | − 75.675 | − 73.369 |
| Kr | − 68.914 | − 67.322 | . . . | . . . |
| $Rb^+$ | − 45.056 | − 46.091 | − 49.448 | − 50.250 |
| $Sr^{2+}$ | − 36.776 | − 35.015 | − 47.620 | − 45.855 |
| $Y^{3+}$ | − 29.778 | − 28.182 | − 47.528 | − 45.622 |
| $Ag^+$ | − 35.188 | − 35.225 | − 35.835 | − 35.993 |
| $Cd^{2+}$ | − 28.391 | − 29.301 | − 31.562 | − 31.332 |
| $I^-$ | − 248.56 | − 244.77 | − 148.44 | − 141.81 |
| $Cs^+$ | − 90.871 | − 93.473 | − 103.27 | − 105.71 |
| $Ba^{2+}$ | − 75.085 | − 75.544 | − 103.01 | − 99.55 |

with $A$ of the same sign and losing in relative importance in going along isoelectronic negative ions to successively lesser charge and on to positive ions up to the argonlike ion series and changing sign beyond $Rb^+$ for kryptonlike and all the positive ions for xenonlike ions. For the negative ions, while $A$ always has negative sign, same as $(B+C)$, its fractional importance decreases in going to heavier ions, from predominance for heliumlike ions to about comparable to $(B+C)$ in the xenonlike ions $I^-$. For the positive $3d^{10}$ shell we have studied, $A$ is positive in sign and always smaller in magnitude than $(B+C)$ which is negative, so that the total $\gamma_\infty^{(1)}$ is negative. These observations will be seen later in this section to help in the physical understanding of trends in $\gamma_\infty^{(1)}$ for free ions and also for ions in Watson sphere.

We consider next the net results for $\gamma_\infty^{(1)}$ for free ions. These are listed for all the ions we have studied in the third column of Table I. In examining these results for $\gamma_\infty^{(1)}$ we would like first to remark on the relative importance of the monopole, $k=0$ and other multipole, $k\neq 0$ contributions, since the former contribution was left out in earlier studies[11,13,14] based on the procedure similar to the present one. In Table IV we have compared the $k=0$ and $k\neq 0$ contributions for $F^-$. It is seen from the results in Table IV that the major contribution to $\gamma_\infty^{(1)}$ comes from the $k=0$ term arising from the intrashell radial excitations, namely, the consistency interaction between $2p\rightarrow p$ excitations for $F^-$ listed. This appears to be a general feature of all the ions studied, the most important $k=0$ contributions always arising from the

TABLE III. Contributions $A$ and $(B+C)$ [$A$, $B$, and $C$ are given by Eqs. (21) through (23)] to $\gamma_\infty^{(1)}=A+B+C$ for free ions and ions in crystals.

| Ion | Free ions |  | Ions in the crystal |  |
|---|---|---|---|---|
|  | $A$ | $(B+C)$ | $A$ | $(B+C)$ |
| He | $-0.0254$ | ... | ... | ... |
| $Li^+$ | $-0.0096$ | ... | $-0.0100$ | ... |
| $Be^{2+}$ | $-0.0050$ | ... | $-0.0060$ | ... |
| $B^{3+}$ | $-0.0031$ | ... | $-0.0053$ | ... |
| $C^{4+}$ | $-0.0020$ | ... | $-0.0047$ | ... |
| $N^{5+}$ | $-0.0014$ | ... | $-0.0047$ | ... |
| $N^{3-}$ | ... | ... | $-2.089$ | $-0.776$ |
| $O^{2-}$ | ... | ... | $-1.767$ | $-0.731$ |
| $F^-$ | $-5.810$ | $-0.695$ | 1.620 | $-0.531$ |
| Ne | $-1.032$ | $-0.359$ | ... | ... |
| $Na^+$ | $-0.391$ | $-0.229$ | $-0.416$ | $-0.232$ |
| $Mg^{2+}$ | $-0.199$ | $-0.159$ | $-0.259$ | $-0.170$ |
| $Al^{3+}$ | $-0.120$ | $-0.119$ | $-0.206$ | $-0.138$ |
| $S^{2-}$ | ... | ... | $-5.125$ | $-5.831$ |
| $Cl^-$ | $-8.724$ | $-5.666$ | $-3.176$ | $-4.102$ |
| Ar | $-1.382$ | $-2.681$ | ... | ... |
| $K^+$ | $-0.535$ | $-1.839$ | $-0.758$ | $-1.935$ |
| $Ca^{2+}$ | $-0.142$ | $-1.277$ | $-0.604$ | $-1.528$ |
| $Sc^{3+}$ | $-0.012$ | $-0.976$ | $-1.137$ | $-1.507$ |
| $Cu^+$ | 9.621 | $-14.575$ | 14.195 | $-21.162$ |
| $Zn^{2+}$ | 3.848 | $-6.007$ | 10.339 | $-15.970$ |
| $Ga^{3+}$ | 2.268 | $-3.646$ | 6.940 | $-10.481$ |
| $Se^{2-}$ | ... | ... | $-2.151$ | $-8.660$ |
| $Br^-$ | $-19.326$ | $-11.501$ | $-2.196$ | $-7.646$ |
| Kr | $-2.550$ | $-6.280$ | ... | ... |
| $Rb^+$ | $-1.431$ | $-1.118$ | $-1.788$ | $-1.545$ |
| $Sr^{2+}$ | 1.209 | $-3.326$ | $-4.021$ | $-4.229$ |
| $Y^{3+}$ | 1.388 | $-2.630$ | $-0.576$ | $-3.883$ |
| $Ag^+$ | 14.435 | $-22.385$ | 15.694 | $-24.383$ |
| $Cd^{2+}$ | 9.340 | $-14.299$ | 11.952 | $-18.806$ |
| $I^-$ | $-26.411$ | $-23.824$ | 1.529 | $-15.509$ |
| $Cs^+$ | 4.282 | $-8.572$ | 1.861 | $-9.405$ |
| $Ba^{2+}$ | 5.890 | $-7.029$ | 1.223 | $-8.937$ |

consistency between $np \rightarrow p$ excitations, with $np$ representing the outermost shell. It is seen from Table IV, that the $k=0$ and $k\neq 0$ terms have opposite sign, with the $k\neq 0$ contribution being about 40% of the $k=0$ contribution for $F^-$ and of opposite sign. The sign of $k=0$ contribution is the same as $\gamma_\infty^{(0)}$. In view of the smaller magnitudes of the $k\neq 0$ contributions compared to $k=0$, the net $\gamma_\infty$ has a negative sign in this case. In fact, in all the cases listed in Table I, $\gamma_\infty^{(1)}$ has a negative sign and this indicates that the $k=0$ terms, which are always negative, dominate over the $k\neq 0$ terms in all cases where the latter have opposite sign.

TABLE IV. Contributions to $\gamma_\infty^{(1)}$ from $k=0$ and $k\neq 0$ to multipole components of $1/r_{12}$ for $F^-$.

|  | $A$ | $B+C$ | $\gamma_\infty^{(1)}$ |
|---|---|---|---|
| $k=0$ | $-10.682$ | 0.001 | $-10.681$ |
| $k\neq 0$ | 4.872 | $-0.696$ | 4.176 |
| Total | $-5.810$ | $-0.695$ | $-6.505$ |

From Table I it is seen from the results for $\gamma_\infty^{(1)}$ for the free ions we have studied that for each of the series, heliumlike through xenonlike and the $3d^{10}$ and $4d^{10}$ shell ions, $\gamma_\infty^{(1)}$ decreases rapidly as one goes towards more positive charges, this decrease being significantly faster than $\gamma_\infty^{(0)}$. This trend of significant decrease of $\gamma_\infty^{(1)}$ with increase of positive charge is physically expected since the $1/r_{12}$ perturbation line that occurs in the perturbation diagrams[7,19] for $\gamma_\infty^{(1)}$ relative to $\gamma_\infty^{(0)}$ and whose effect is represented by Eqs. (21)–(23) does involve a type of polarizability effect exerted by the field of one electron (including monopole field) on the other. In earlier work,[14] it had been concluded that this trend would be much less pronounced, this conclusion apparently having been a consequence of the neglect of $k=0$ contributions to $A$ in the earlier results for $F^-$ and $Na^+$ on which it was based.

Another interesting trend in the nature of $\gamma_\infty^{(1)}$ is observed in going from light to heavy in the negative halogen ion series, $F^-$ through $I^-$, the ratio $\gamma_\infty^{(1)}/\gamma_\infty^{(0)}$ decreasing steadily. The decrease is expected in view of the decrease in fractional importance of the $A$ term (Table III) in going to heavier ions. This trend is also different from that observed in earlier work[14] on the consistency effect in halogen negative ions where $\gamma_\infty^{(1)}$ was found to change sign in going from $F^-$ to $Cl^-$ and was a consequence of the neglect of the $k=0$ terms in $A$. A significant decrease in $\gamma_\infty^{(1)}/\gamma_\infty^{(0)}$ is also observed in Table I in going through the series $Na^+$, $K^+$, $Rb^+$, and $Cs^+$, the decrease being both a consequence of the decrease in relative importance of $A$ as compared to $(B+C)$ as discussed earlier and seen from Table III as well as the change of sign in $A$ for $Cs^+$, leading to cancellation between $A$ and $(B+C)$.

Finally, we consider the net $\gamma_\infty=\gamma_\infty^{(0)}+\gamma_\infty^{(1)}$ for free ions which are tabulated in the fourth column of Table I. For the $\gamma_\infty^{(1)}$ in Table I we have taken the $Q$-perturbed values but if one prefers the $q$-perturbed values which are slightly different, they could be used from Table II. As just discussed, $\gamma_\infty^{(1)}$ comes out as negative, which adds to the antishielding factors $\gamma_\infty^{(0)}$ for all of the ions considered, except for the heliumlike ions where the $\gamma_\infty^{(0)}$ are positive, that is shielding in nature. The $\gamma_\infty^{(1)}$ in this latter case reduce the magnitudes of the shielding factors, but the effects are less than 5% for helium and $Li^+$ and as low as 1% for $N^{5+}$. For the rest of the ions, of course $\gamma_\infty^{(1)}$ adds to $\gamma_\infty^{(0)}$ and the $\gamma_\infty^{(1)}$ enhance the net $\gamma_\infty$ by no more than 25% for the non-transition-metal ions as compared to $\gamma_\infty^{(0)}$, the 25% figure applying for the singly negative ions, diminishing to about 15% or less for the singly positive alkali ions and close to 10% or less for the triply positive ions. The $\gamma_\infty^{(1)}$ for the ions with $d$ shells as outermost ones influence the $\gamma_\infty$ somewhat more than for the other ions considered, enhancing it, for example, by about 30% of $\gamma_\infty^{(0)}$ for $Cu^+$ and 23% for $Ag^+$, both figures being substantially larger than for the monovalent alkali ions, and in the case of $Cu^+$, larger than for the halogen negative ions. It should be noted that in these $d$-shell ions, both the outermost $d$ shells and $p$ shells contribute comparably to $\gamma_\infty^{(0)}$ and both shells also produce comparable amounts of $\gamma_\infty^{(1)}$, while in the case of non-transition-metal ions, only the outermost $p$ shells make the main contribution, except in the case of the heliumlike ions where the outermost shells are $s$ ones.

Our total $\gamma_\infty$ for the free ions in the fourth column of Table I can be compared in some of the cases we have studied with results available from other procedures including the fully coupled variational procedure,[6,8] the orbitally polarized Hartree-Fock procedure,[26] and the effective-field procedure.[27] The first of these uses[6] the method in which the influence of the perturbation of one orbital (by external-field gradient) on another orbital is obtained by forming a determinant out of the perturbed states and minimizing the total energy of the system including the many electron Hamiltonian as well as the perturbation $\mathcal{H}''$ in Eq. (6) and keeping energy terms up to second order in $\mathcal{H}''$. This leads to coupled differential equations which can be solved either by integration or by variational procedures. With the perturbed orbitals obtained, one than calculates the field gradient at the nucleus to get the antishielding factor. In the orbitally polarized procedure,[26] the total energy of the system including $\mathcal{H}''$ was minimized with respect to the radial and angular characters of the one-electron orbitals without handling $\mathcal{H}''$ as a perturbation. The field gradient at the nucleus based on such polarized orbitals are then employed to obtain the antishielding factor. In the effective-field approach,[27] the perturbed orbitals obtained variationally by the uncoupled Hartree-Fock procedure were used to generate additional polarizing potentials at the electron sites which would in principle incorporate self-consistency effects except that by the nature of the procedure adopted only $k=2$ (the leading $k\neq 0$ term) type effects of the electron-electron interaction were included. We shall remark a little later on this and the comparison of effective-field-procedure results[27] and many-body perturbation approach results[7,19] where also only the $k=2$ effects of $1/r_{12}$ alone were included.

Considering the systems Ar, $K^+$, $Ca^{++}$, $F^-$, Ne, $Na^+$, $Mg^{++}$, and $Al^{3+}$ for which fully coupled Hartree-Fock (CHF) variation perturbation results are available,[8] there is very good agreement with our results. Since the CHF results involve, in principle, consistency effects to all orders, the good agreement between our results and the CHF results lends support to the conclusion that one would make from our results for free ions in Table I, that consistency effects in general contribute up to 30% of $\gamma_\infty^{(0)}$ or less. For the $Cl^-$ ion, our result differs from the corresponding CHF estimate by a somewhat larger amount (about 12%). We cannot think of any specific reason for this difference between the two values. It is, however, interesting to note that our value lies between the CHF and polarized orbital results.

For the ions $Br^-$, $Rb^+$, $I^-$, $Cs^+$, and $Cu^+$, polarized orbital Hartree-Fock values[26] are also included in Table V for comparison with our results. Of these, for $Rb^+$, $Cs^+$, and $Cu^+$, the two results are found to be in good agreement with each other. For $Br^-$ and $I^-$, however, our values appear to be substantially

TABLE V. Comparison of net results in present work with available results of earlier work.

| Ion | Coupled Hartree-Fock[a] | Polarized orbitals[b] | Effective field[c] | Present work | |
|---|---|---|---|---|---|
| | | | | $Qe$[d] | $e/R$[e] |
| He | 0.396 | | 0.407 | 0.398 | 0.387 |
| $Li^+$ | 0.246 | | 0.254 | 0.249 | 0.247 |
| $Be^{2+}$ | 0.180 | | 0.184 | 0.182 | 0.181 |
| $B^{3+}$ | 0.142 | | 0.143 | 0.143 | 0.142 |
| $F^-$ | − 29.88 | | − 25.072 | − 28.609 | − 28.479 |
| Ne | − 9.213 | | − 7.340 | − 9.454 | − 9.295 |
| $Na^+$ | − 5.178 | | − 3.974 | − 5.261 | − 5.105 |
| $Mg^{2+}$ | − 3.485 | | − 2.598 | − 3.503 | − 3.332 |
| $Al^{3+}$ | − 2.570 | | − 1.887 | − 2.589 | − 2.448 |
| $Cl^-$ | − 63.21 | − 87.0 to −84.9 | − 67.411 | − 68.811 | − 67.235 |
| Ar | − 28.62 | | − 28.773 | − 28.603 | − 27.813 |
| $K^+$ | − 18.27 | | − 18.140 | − 19.957 | − 18.572 |
| $Ca^{2+}$ | − 13.32 | | − 12.844 | − 14.057 | − 13.248 |
| $Cu^+$ | | − 17.0 | | − 21.538 | − 21.02 |
| $Br^-$ | | − 100.0 | − 161.928 | − 165.99 | − 163.48 |
| Kr | | | − 83.852 | − 77.744 | − 76.152 |
| $Rb^+$ | | − 50.0 | − 75.850 | − 47.664 | − 48.699 |
| $I^-$ | | − 175 | | − 290.80 | − 287.01 |
| $Cs^+$ | | − 100 | | − 95.161 | − 97.763 |

[a] Coupled Hartree-Fock results. Results for helium series refer to Langhoff, Karplus, and Hurst (Ref. 6), others to Lahiri and Mukherji (Ref. 8).

[b] Polarized orbital results: Watson and Freeman (Ref. 26).

[c] Effective-field method: Litt (Ref. 27).

[d] Refers to net $\gamma_\infty$ obtained using $\gamma_\infty^{(0)}$ from $Q$-perturbed wave functions $u_1$, which are solutions of equations of the form (16).

[e] Refers to net $\gamma_\infty$ obtained using $\gamma_\infty^{(0)}$ from charge-perturbed wave functions $\bar{u}_1$ which are solutions of equations of the the form (13).

higher by about 65%. Again, we do not know the precise reasons for the difference. Our $\gamma_\infty^{(0)}$ by the $q$ and $Q$ perturbation procedures for these two ions differ by only 0.5%, so the difference does not appear to be due to significant error in $\gamma_\infty^{(0)}$. It is also unlikely from the systematics of variation of $A$ and $(B+C)$ in Table III that the consistency effect $\gamma_\infty^{(1)}$ could be significantly different than what we have obtained in Table VI. However, other than these few exceptions, the good agreement of CHF and polarized HF values of $\gamma_\infty$ for the ions where they are available with our results for these ions indicates that our results are reasonably accurate and that consistency effects are significant and are up to 30% of $\gamma_\infty^{(0)}$.

The values obtained by Litt[27] for a number of ions, tabulated in Table I, differ from both our values and the CHF or polarized orbital Hartree-Fock values. The reason for this, as mentioned earlier, is that the effective field in principle includes the $k=2$ component of $1/r_{12}$ and not the sizable $k=0$ monopole effect. In fact, good agreement was found between the effective field value of $\gamma_\infty$ for $Na^+$ and the many-body perturbation-theoretic value[19] which also did not include the $k=0$ contribution.

A similar reason is also responsible for the difference between earlier results[14] for $\gamma_\infty$ including self-consistency effects and ours for the free ions, $Rb^+$,

TABLE VI. Dependence of $\gamma_\infty^{(0)}$ and $\gamma_\infty^{(1)}$ on the Watson sphere radius $r_{\text{ion}}$ for $Cl^-$.

| $r_{\text{ion}}$ (Å) | $\gamma_\infty^{(0)}$ | $\gamma_\infty^{(1)}$ | $\gamma_\infty$ |
|---|---|---|---|
| ∞ | −54.421 | −14.390 | −68.811 |
| 1.99 | −39.165 | −8.702 | −47.867 |
| 1.81 | −34.721 | −7.278 | −41.999 |
| 1.63 | −30.229 | −5.908 | −36.137 |

$Cs^+$, $F^-$, $Cl^-$, and $Br^-$, as we have discussed earlier. We have compared the radial integrals that went into the calculation of $k \neq 0$ consistency effects in these earlier calculations[14] and find good agreement with the integrals used in the present work, although the earlier work used perturbed wave functions obtained independently by the DE procedure. Additionally our results for $F^-$ agree very well with a recent value[28] of $\gamma_\infty$ obtained using the same $u_1$ and $\bar{u}_1$ functions that were used in the earlier consistency calculations,[14] but including the $k=0$ effect. These comparisons confirm that the differences between our results and the earlier perturbation results[14] for $Rb^+$, $Cs^+$, $F^-$, $Cl^-$, and $Br^-$ can be ascribed mainly to the neglect of $k=0$ terms in earlier work.

We would like to make one last remark about our free-ion results before proceeding to antishielding results for ions in solid state subject to the influence of the Watson sphere. Our conclusion about the consistency effect being about 30% or less as confirmed by comparison with the CHF (Ref. 8) and polarized orbitals HF calculations[26] is in agreement with the conclusions from recent LCMBPT calculations[20] on $Gd^{3+}$ and $Eu^{2+}$ ions where consistency effects less than 10% of $\gamma_\infty$ were obtained. On the other hand, a recent study[10] of the consistency effect in $Pr^{3+}$ by the LCMBPT technique gave a contribution twice as large as $\gamma_\infty$. Since the consistency effect in $Eu^{2+}$ and $Gd^{3+}$ also arises as in $Pr^{3+}$ mainly from the intrashell $k=0$ effect for the $5p \rightarrow p$ perturbation, the $Pr^{3+}$ result[10] appears anomalous.

### B. Ions in solid state

We consider next the results for the antishielding effects for ions in the presence of the Watson sphere[3] both with and without consistency. The first feature one notices from Table II concerns $\gamma_\infty^{(0)}$ and is the same as in the case of the free ions, namely, that the results using the $Q$ and $q$ perturbations, involving $u_1$ and $\bar{u}_1$, respectively, have small differences, with the $q$-perturbation result always lower. Again, we have presented the $Q$-perturbation result for $\gamma_\infty^{(1)}$ and the corresponding $\gamma_\infty^{(0)}+\gamma_\infty^{(1)}$ but one could, if one desires, replace the $\gamma_\infty^{(0)}$ in Table I by the $q$-perturbed values in Table II.

The most important point about the $\gamma_\infty^{(0)}$ results for the Watson sphere model is that the values of $\gamma_\infty^{(0)}$ decrease in magnitude for the negative ions in going from free ion to the Watson sphere systems while those for the positive ions increase. However, the changes are larger than the consistency effect $\gamma_\infty^{(1)}$ for the negative ions and smaller for the positive ions. The first observation regarding the direction of change due to the influence of the Watson sphere, namely, the decrease of $\gamma_\infty^{(0)}$ for negative ions and increase for positive ions is in keeping with the trend observed[12] for dipole and quadrupole polarizabilities and results from the tightening of the diffuse wave function for the negative ions by the Watson sphere and loosening of the tightly bound wave functions for the positive ions. This direction of change would also be expected in a real ionic crystal since the positive ion is surrounded by negative-ion ligands which repel the electrons of the central ion and the opposite situation applies to the negative ion. The greater change in $\gamma_\infty^{(0)}$ for the negative ions compared to $\gamma_\infty^{(1)}$ and the reverse situation for the positive ions can be understood by noting that the negative-ion electrons being more diffuse are subject to greater amounts of contraction and therefore greater reduction in $\gamma_\infty^{(0)}$ as compared to the corresponding expansion and consequent increase in $\gamma_\infty^{(0)}$ for the tightly bound positive-ion electrons.

One more observation needs to be made about the $\gamma_\infty^{(0)}$ before passing on to the $\gamma_\infty^{(1)}$ results in the presence of the Watson sphere. This is the question of the sensitiveness of the $\gamma_\infty^{(0)}$ in the solid to the radius assumed for the Watson sphere. In Table VI, we have presented results for $\gamma_\infty^{(0)}$ and $\gamma_\infty^{(1)}$ for the relatively loose $Cl^-$ ion for two other Watson sphere radii besides the choice of Pauling radius made for it in the results presented in Table I. These additional radii, were, respectively, 10% larger and smaller as compared to the Pauling radius. Our results show that while there is about 15% variation in both $\gamma_\infty^{(0)}$ and $\gamma_\infty^{(0)}+\gamma_\infty^{(1)}$ in going either way in the Watson sphere radius, these changes are substantially smaller than the difference between the free ion and Pauling radius choice for the Watson sphere. It thus appears that small changes in the Watson sphere radii, the uncertainties in these being expected to be significantly less than 10% of the Pauling radii, will not cause the results for $\gamma_\infty^{(0)}$ and $\gamma_\infty^{(1)}$ to change drastically, a feature expected to be even more valid for the tightly bound positive ions. Consequently, the results in Table I with the Pauling-radius choice for the Watson sphere can be considered to be quite meaningful. For the trivalent ions, $Sc^{3+}$ and $Y^{3+}$, the Pauling radii are not as well known as for the singly and doubly charged positive and negative ions. We have actually found that the choices of $r_{\text{ion}}$ made for these trivalent ions are not very satisfactory, because a substantial electron density resides outside the Watson sphere in these cases. Different choices for the Watson sphere radius would be desirable in future work and this may remove some of the apparent anomalies in the trends showing up in Table I for the $\gamma_\infty^{(1)}$ for these ions.

We consider next the consistency contributions $\gamma_\infty^{(1)}$ for the Watson sphere systems. Considering the $A$ and $(B+C)$ contributions in Table III, it should be noted that the changes in these contributions in going from free ion to the Watson sphere show the same trend for negative ions as is obtained earlier in going from free negative to free positive ions and the opposite trend is observed for the changes in going from free ion to Watson sphere for the positive ions. This is understandable because for a negative ion, which, in an ionic crystal, is surrounded by positive ions whose influence is simulated by the Watson sphere potential in Eq. (4), the latter leads to a tightening of the orbitals as happens in going from a free negative ion to a positive ion. A corresponding explanation applies to the case of positive ions where the Watson sphere potential is expected to lead to a loosening of the orbitals. Thus, considering Xe-like systems, for the $I^-$ ion, in going from the free ion to the Watson sphere system, the value of $A$ changes from negative to a small positive value and $(B+C)$ also decreases in magnitude substantially while remaining negative. This is the same trend that is observed in Table III in going from the free $I^-$ ion to the $Cs^+$ ion and was discussed earlier in this section in considering free-ion results. For the $Cs^+$ and $Ba^{2+}$ ions, in going to the Watson sphere from the free ion, a decrease is seen in their positive values of $A$, while their negative $(B+C)$ contributions increase in magnitude, a direction similar to that found in going from the free $Cs^+$ ion to the $I^-$ ion or from the double positive free $Ba^{2+}$ ion to $Cs^+$. The same trend is observed for the krypton, argon, and neon series, the changes observed in going from the free ion to the ion in Watson sphere being progressively smaller as one goes to the smaller ions. For the $3d^{10}$ and $4d^{10}$ series, the values of $A$, which are positive for free ions, increase in going to the ions in Watson sphere and $(B+C)$ which are negative get more negative, again the same trend as in going from a free positive ion to one with a lesser positive charge.

Having analyzed the component contributions $A$ and $(B+C)$, it becomes easier to understand the trends observed in Table I for the net consistency contributions $\gamma_\infty^{(1)}$ in going from the free ion to ions in the Waston sphere. Thus the $\gamma_\infty^{(1)}$ are seen to increase for positive ions and decrease for negative ions in going to the Watson sphere systems as expected from the changes in $A$ and $(B+C)$ in Table III. One thus has here a clear manifestation of the interplay of solid-state and consistency effects. Also, in going successively from the smaller ions such as the neonlike ones to argonlike, kryptonlike, and xenonlike ions, the solid-state effect on the electron distribution increases in importance as observed from the trends in $A$ and $(B+C)$ in Table III and this is reflected in the larger changes in $\gamma_\infty^{(1)}$ seen in Table I in going from the free ions to Watson sphere systems.

We conclude this discussion by summarizing the main features of our results. The net $\gamma_\infty$ including solid-state effects in the Watson sphere model and consistency effects are shown in the seventh column of Table I. The next column represents the ratio of $\gamma_\infty$ to $\gamma_\infty^{(0)}$ for the free ion, representing the correction from consistency effects alone. The following column gives the ratio of $\gamma_\infty$ for the solid to $\gamma_\infty^{(0)}$ for the free ion, this ratio reflecting the importance of the combination of solid-state and consistency effects.

The results of our investigation over an extensive set of ions indicate that solid-state effects are rather important for both positive and negative ions. Percentagewise, solid-state effects on $\gamma_\infty^{(0)}$ are larger in magnitude for negative ions (as much as 50% for $I^-$) than for positive ions, the signs of the effect being opposite in the two cases as expected, since the negative-ion contract in the solid and positive ions expand. The absolute solid-state effect on $\gamma_\infty^{(0)}$ increases as one goes from neonlike ions to xenonlike ions but the percentagewise effect diminishes along the series for negative ions and increases for positive ions (see Table I).

The consistency effect $\gamma_\infty^{(1)}$ is comparable in order of magnitude with the solid-state effect on $\gamma_\infty^{(0)}$, as represented by the difference in $\gamma_\infty^{(0)}$ between the solid and the corresponding free ion, the latter being usually more important than $\gamma_\infty^{(1)}$ for negative ions and in some of the positive ions (with relatively reduced importance in the latter) while in some other positive ions, $\gamma_\infty^{(1)}$ is more important.

The influence of solid-state effects on $\gamma_\infty^{(1)}$, representing an interplay of consistency and solid-state effects, is clearly demonstrated by our results in Table I. Thus there are significant changes (and trends in changes) in going from the free ion to the solid, there being an increase in $\gamma_\infty^{(1)}$ for positive ions which become more expanded from the free-ion state in going to the solid and a decrease in $\gamma_\infty^{(1)}$ for negative ions which become contracted.

The consistency contributions $\gamma_\infty^{(1)}$ in both free ions and ions in Watson sphere are all found to be up to 30% or less of $\gamma_\infty^{(0)}$ even after the $k=0$ terms representing the monopole component of electron-electron interaction $1/r_{12}$, omitted in earlier work, were included. Many-body effects have not been investigated extensively, but for a few ions[7,19] where such investigations have been carried out by linked-cluster many-body perturbation-theoretic techniques, the ratio of consistency and correlation contributions indicate that correlation effects are not expected to be more than 25% of consistency effects.

Finally, we would like to point out that while the results for $\gamma_\infty$ for ions in a Watson sphere represent reasonable approximations to the appropriate $\gamma_\infty$ for the field gradients due to an external point charge at the nuclei of ions in an ionic crystal, some additional important considerations are necessary in calculating the net field gradient at a nuclear site in an ionic crystal. This has to do with the influence of the immediate neighbors or ligands of the central ion containing the nucleus under study. The field gradient due to the nuclear charges and electrons on these neighboring ions cannot be handled as arising from external point charges but instead the influence of their overlap and covalent binding with the central ion electrons has to be taken into account, including their appropriate antishielding effects (which can be rather different from either $\gamma_\infty$ or atomic valence-type antishielding factors) due to the various electronic and nuclear sources associated with the neighboring ions. Some useful steps in this direction have been taken in recent work[29,30] on $Fe_2O_3$ and $Al_2O_3$. However, the net field gradient at a nucleus in an ionic crystal also involves the field gradient due to all the distant ions beyond the immediate ligands and in evaluating the field-gradient contributions due to these, the values of $\gamma_\infty$ obtained in the seventh column of Table I are directly applicable.

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