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Antishielding effects of atomic core states from nonorthogonal Hartree-Fock perturbation theory

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The quadrupole antishielding factors γ_∞ for the ions Na^+, Mg^{2+}, and Cl^- have been calculated by solving differential equations in nonorthogonal Hartree-Fock perturbation theory. The results are compared with the values of γ_∞ obtained in other calculations. The agreement in all the cases except $\gamma_\infty(3p \rightarrow p)$ of Cl^- is quite satisfactory. It is believed that the discrepancy in the latter case is perhaps due to the different zero-order wave function used in the present calculation.

I. INTRODUCTION

For a better understanding of quadrupole coupling constants in crystals, a good knowledge of the electric field gradient at the nucleus in the system is essential. While in ionic crystals the field gradient at a given nucleus is due to the remaining lattice ions, in metals it is due both to the lattice ions and the conduction electrons. In either type of crystal the core states, perturbed by both the quadrupole moment of the nucleus and the external lattice ions, enhance the field gradient in most cases. The factor by which the field gradient is enhanced is known as the antishielding factor.[1] Thus, for a quantitative interpretation of the field-gradient data in these crystals, a knowledge of the proper antishielding factor is very important.

There is, however, a subtle difference between the antishielding factor for a metal[2] and that for an ionic crystal. Since in both these crystals the lattice consists of ions of the respective kind, it may appear at first sight that the appropriate antishielding factor will be the one calculated by using the core wave functions of the respective ions. While this is true for ionic crystals, it is not so for metals because of the presence of conduction electrons in the latter. Since the conduction electrons provide some screening of the potential experienced by the core electrons in metal, the latter electrons are more loosely bound in metals than in the isolated ions. Thus the core wave functions which will perhaps be more appropriate for obtaining γ_∞ in metals are those of the isolated neutral atom rather than of the free ion. For example, the γ_∞ for Na^+ in the ionic crystal NaCl should be calculated by using the core functions of the free Na^+ ion, and the γ_∞ for Mg^{2+} in magnesium metal should be obtained by using the core functions of the neutral magnesium atom. However, in spite of this difference, in most of the field-gradient calculations in metals, the values of γ_∞ obtained by using the core functions of the ions have been used. The difference in γ_∞ resulting from the use of core wave functions of the ion on the one hand, and the core wave functions of the neutral atom on the other, has been shown[2,3] in the case of the Zn^{2+} ion to be less than 10%. It may, however, be larger in the case of heavier ions.

The motivation of the present paper has been, first, to calculate the proper antishielding factors for ionic crystals and metals, and second, to test the accuracy of the nonorthogonal Hartree-Fock perturbation theory[4,5] (HFPT) by applying it to calculate γ_∞ for the negative ion Cl^-, which is more polarizable than some of the positive ions studied[3] before. We would like to remark here that in the past the nonorthogonal HFPT[4,5] has been very successful in obtaining γ_∞ for relatively less polarizable positive ions.[3]

In Sec. II, we derive the relevant perturbation equations for the perturbed-core wave functions and the expression for the antishielding factor in the nonorthogonal HFPT.[3] Section III discusses the results of the present investigation. Our conclusions are given in Sec. IV.

II. WAVE-FUNCTION CALCULATION

The perturbed-core wave functions in first order can be obtained by solving the appropriate perturbation equation. For this purpose, we denote the zeroth-order atomic wave function by ψ^0_{nlm}, which belongs to the state characterized by the quantum numbers n, l, and m. Let H_0 and H_1 be, respectively, the unperturbed Hamiltonian and the perturbation due to the nuclear quadrupole moment Q. In atomic units (a.u.), we have

$$H_0 = -\nabla^2 + V_0\,, \tag{1}$$

$$H_1 = -(\tfrac{4}{5}\pi)^{1/2} Q Y_{20}/r^3\,. \tag{2}$$

To ascertain the angular dependence of $\delta\psi$, the change in ψ^0_{nlm} due to perturbation, we write the familiar first-order perturbation expansion for $\delta\psi$ in the usual notation, namely,

$$\delta\psi = {\sum_{n'l'm'}}' \frac{\langle \psi^0_{n'l'm'} | H_1 | \psi^0_{nlm}\rangle}{E^0_{nl} - E^0_{n'l}} \psi^0_{n'l'm'} \,. \tag{3}$$

The prime over the summation sign in Eq. (3) indicates that the summation is to be taken over all the quantum states except the one for which $n' = n$, $l' = l$, and $m' = m$. In view of the given angular dependence of the perturbation H_1, it follows from Eq. (3) that the function $\delta\psi$ can be written as

$$\delta\psi = (\tfrac{4}{5}\pi)^{1/2} \langle lm | 20 | lm\rangle Q V_1(nl \to l)/r Y_{lm} \,, \tag{4}$$

for the radial excitation $(l \to l)$ process and as

$$\delta\psi = (\tfrac{4}{5}\pi)^{1/2} \langle l+2m | 20 | lm\rangle Q V_1(nl \to l+2)/r Y_{l+2m} \,, \tag{5}$$

for the angular excitation $(l \to l+2)$ process. The factor $\langle lm | 20 | lm\rangle$ is the angular integral and is given by

$$\langle lm | 20 | lm\rangle = \int Y^*_{lm} Y_{20} Y_{lm} d\Omega \,. \tag{6}$$

The functions $V_1(nl \to l)$ in Eq. (4) and $V_1(nl \to l+2)$ in Eq. (5) are, respectively, r times the radial parts of $\delta\psi$ for the radial and angular excitation processes.

The function $\delta\psi$ is obtained by solving the following differential equation derived in the nonorthogonal HFPT discussed previously in the literature:[3-5]

$$\begin{aligned}(H_0 - E^0_{nl})\delta\psi = {} & -H_1\psi^0_{nlm} + \langle \psi^0_{nlm} | H_1 | \psi^0_{nlm}\rangle \psi^0_{nlm} \\ & + \sum_{\substack{n' \\ n' \neq n}} \langle \psi^0_{n'lm} | H_1 | \psi^0_{nlm}\rangle \psi^0_{n'lm} \\ & + \sum_{\substack{n' \\ n' \neq n}} \langle \psi^0_{n'lm} | \delta\psi\rangle (E^0_{n'l} - E^0_{nl}) \psi^0_{n'lm} \,. \end{aligned} \tag{7}$$

The respective differential equations for the radial functions $V_1(nl \to l)$ and $V_1(nl \to l+2)$ are obtained from Eq. (7) by substituting the form of $\delta\psi$ successively from Eq. (4) for the radial excitation and from Eq. (5) for the angular excitation. These equations are

$$\begin{aligned}\left(-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_0 - E^0_{nl}\right) V_1(nl \to l) = {} & [1/r^3 - \langle U_0'(nl) | 1/r^3 | U_0'(nl)\rangle] U_0'(nl) \\ & - \sum_{\substack{n' \\ n' \neq n}} \langle U_0'(nl) | 1/r^3 | U_0'(n'l)\rangle U_0'(n'l) \\ & + \sum_{\substack{n' \\ n' \neq n}} \langle U_0'(n'l) | V_1(nl \to l)\rangle (E^0_{n'l} - E^0_{nl}) U_0'(n'l) \,, \end{aligned} \tag{8}$$

$$\left(-\frac{d^2}{dr^2} + \frac{(l+2)(l+3)}{r^2} + V_0 - E^0_{nl}\right) V_1(nl \to l+2) = \frac{1}{r^3} U_0'(nl) \,, \tag{9}$$

where $U_0'(nl)$ is r times the radial part of the atomic zeroth-order function ψ^0_{nlm}, and the quantity $\langle U_0'(nl) | 1/r^3 | U_0'(n'l)\rangle$ is given by the integral

$$\langle U_0'(nl) | \frac{1}{r^3} | U_0'(n'l)\rangle = \int_0^\infty U_0'(nl) \frac{1}{r^3} U_0'(n'l) dr \,. \tag{10}$$

Comparing Eqs. (8) and (9) with the corresponding equations of Sternheimer,[1] we note that, as far as the radial excitation process is concerned, the equation in the nonorthogonal HFPT[3] differs from the equation of Sternheimer[1] by having two additional terms, namely, the second and the third on the right-hand side of Eq. (8). For the angular excitation process, there is no difference between Eq. (9) and the corresponding one of Sternheimer.[1] The reason why Eq. (9) does not have terms similar to the second and third terms on the right-hand side of Eq. (8), even though both Eqs. (8) and (9) are derived from Eq. (7), is that the angular part of $\delta\psi$ for the angular excitation process is orthogonal to the zeroth-order wave function ψ^0_{nlm}.

The total antishielding factor γ_∞ is the sum of the contributions from radial excitation and angular excitation processes. First, we consider the contribution from the radial excitation process. The solution $\delta\psi$ obtained from Eqs. (8) and (4) is not orthogonal to other occupied core states of the same l and m value as that of ψ^0_{nlm} under perturbation. The necessary orthogonalization is accomplished by the Schmidt procedure,[3] and the resulting solution $\delta\psi'$ is given by

$$\delta\psi' = \delta\psi - \sum_{\substack{n' \\ n' \neq n}} \langle \psi^0_{n'lm} | \delta\psi\rangle \psi^0_{n'lm} \,, \tag{11}$$

where the summation is taken over all the other occupied core states of the same l and m value as that of ψ^0_{nlm}. Having obtained the properly orthogonalized solutions, we may then calculate the induced quadrupole moment due to radial excitation. The antishielding factor $\gamma_\infty(nl \to l)$ for the radial excitation process is then obtained by taking the ratio of the induced quadrupole moment to Q and is given by

$$\gamma_\infty(nl \rightarrow l) = \frac{4}{Q}\sum_m \int \psi^{0\,*}_{nlm}\delta\psi' r^2(3\cos^2\theta - 1)d^3r\,, \tag{12}$$

where, out of the factor 4, a factor of 2 is due to the electron spin degeneracy and the remaining factor of 2 is due to the expression of induced charge. The function $\delta\psi'$ obtained from Eqs. (4), (8), and (11) is substituted into Eq. (12) to give

$$\gamma_\infty(nl \rightarrow l) = C^{(2)}_{ll}\int_0^\infty U_0'(nl)V_1'(nl \rightarrow l)r^2\,dr\,, \tag{13}$$

where

$$V_1'(nl \rightarrow l) = V_1(nl \rightarrow l) - \sum_{\substack{n' \\ n' \neq n}} \langle U_0'(n'l)|\,V_1(nl \rightarrow l)\rangle U_0'(n'l)\,, \tag{14}$$

$$C^{(2)}_{ll} = \tfrac{32}{5}\pi\sum_m (\langle lm|\,20\,|lm\rangle)^2\,. \tag{15}$$

For a filled p core, $C^{(2)}_{11} = 48/25$ and for a filled d core, $C^{(2)}_{22} = 16/7$. In a similar way, by using Eqs. (5), (9), and (12), the angular contribution to the antishielding factor is obtained as

$$\gamma_\infty(nl \rightarrow l+2) = C^{(2)}_{l+2\,l}\int_0^\infty U_0'(nl)\;V_1(nl \rightarrow l+2)r^2\,dr\,, \tag{16}$$

where

$$C^{(2)}_{l+2\,l} = \tfrac{32}{5}\,\pi\sum_m (\langle l+2m|\,20\,|lm\rangle)^2\,. \tag{17}$$

Since the value of γ_∞ from angular excitation,[1] $\gamma_\infty^{\text{ang}}$, is usually much smaller than that from the radial excitation, we have obtained the former not from Eq. (16) but from a relatively simpler but less accurate model of charge distribution namely, the Thomas-Fermi model.[1,3] The latter model has been used in the past[1,3] for a number of systems.

III. RESULTS AND DISCUSSION

The functions $V_1(nl \rightarrow l)$ are solved for Na^+, Mg^{2+}, and Cl^- ions from Eq. (8) by a noniterative procedure.[3,4] For this purpose the zeroth-order wave functions used for all three systems are the analytic Hartree-Fock (HF) functions of Clementi.[6] The solutions of the differential equations were carried out on the IBM 370 computer at the Indian Inst. of Technology, Madras. The individual shell contributions to $\gamma_\infty(nl \rightarrow l)$ and the $\gamma_\infty^{\text{ang}}$ for these three systems are summarized in Table I. This table also lists the results for γ_∞ from other calculations for comparison.

We first discuss the antishielding factor for magnesium. Although results for γ_∞, obtained by using ionic core functions, are available in the literature[7,8] for the Mg^{2+} ion, the result for γ_∞ by using the core functions of the neutral magnesium atom is not available. Since it is the latter γ_∞ which is more appropriate for the quantitative interpretation of the field-gradient data in magnesium metal, we have calculated it by using the core functions of the neutral Mg atom. For the part $\gamma_\infty^{\text{ang}}$ we have estimated the value from the Thomas-Fermi model following exactly the same procedure as has been adopted in our earlier work.[3]

In order to see how much the present result differs from the γ_∞, obtained by using the core functions of the Mg^{2+} ion, we have compared our results with those of others.[7,8] From Table I, it is clear that the γ_∞ in this work is slightly larger in magnitude than those previously reported.[7,8] This is expected, since the core wave functions, particularly for the $2p$ state, used in this work are more loosely bound and hence more polarizable than the core functions used in other calcula-

TABLE I. Values of γ_∞ for Na^+, Mg^{2+}, and Cl^- from different calculations.

	Na^+				Mg^{2+}			Cl^-	
γ_∞	Ref. 9	Ref. 10	Ref. 9[a]	This work	Ref. 8[b]	Ref. 7[b]	This work[c]	Ref. 12	This work
$2p \rightarrow p$	−4.7	−5.23	−5.18	−5.38			−3.88	−1.51	−1.10
$3p \rightarrow p$								−57.0	−66.20
Angular	0.60	0.69	0.60	0.60			+0.36	1.40	1.40
Total	−4.1	−4.54	−4.58	−4.78	−3.20	−3.35	−3.52	−57.11	−65.90

[a] The zero-order wave functions used are the same as in Ref. 10.

[b] These results are obtained for the Mg^{2+} ion by using the core functions of the free ion Mg^{2+}.

[c] The core functions used were those of the neutral Mg atom.

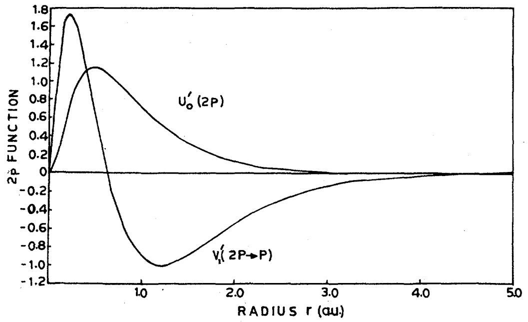

FIG. 1. Perturbed function $V_1'(2p \to p)$ and $2p$ function $U_0'(2p)$ for Mg.

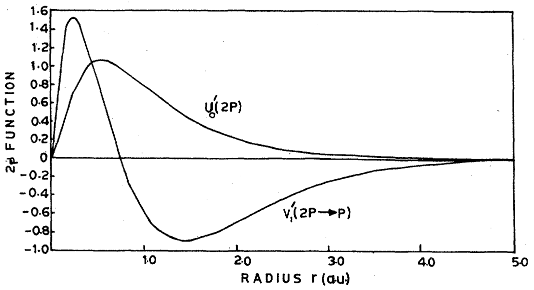

FIG. 2. Perturbed function $V_1'(2p \to p)$ and $2p$ function $U_0'(2p)$ for the Na^+ ion.

tions.[7,8] A similar difference in the values of γ_∞ was previously[2,3] noted in the case of the Zn^{2+} ion. The radial part of the zeroth-order $2p$ function, $U_0'(2p)$, as well as the radial part of the perturbed $2p$ function, $V_1'(2p \to p)$, are plotted against r in Fig. 1. The latter function shows the expected behavior with regard to the number of nodes.

In the case of the Na^+ ion, the value of γ_∞ obtained in the present work is compared with that of Sternheimer and Foley (SF)[9] and with those of Das and Bersohn.[10] While the method of calculation used by the former author[9] is perturbation, that of the latter[10] is variational. By using a HF function[11] for the zeroth-order core function Sternheimer and Foley obtained a value -4.71 for $\gamma_\infty (2p \to p)$, which is smaller than the value -5.23 obtained by Das *et al.*[10] The difference in the two values was attributed by SF[9] to the different zeroth-order wave functions used in the calculations. In fact, by repeating his calculation with the wave function of Das *et al.*[10] SF[9] did obtain a value -5.18 for $\gamma_\infty(2p \to p)$ which is very close to the value of Das *et al.*[10]

On comparing the $\gamma_\infty(2p \to p)$ for Na^+ in this work with those of SF[9] and of Das *et al.*[10] we find that the present result is larger than theirs[9,10] by about 4%. We ascribe this difference to the different zeroth-order wave functions[6] used in the present calculation. For the $\gamma_\infty^{\text{ang}}$, we have used the SF value,[9] which is better than the value estimated from the Thomas-Fermi model. Both the functions $U_0'(2p)$ and $V_1'(2p \to p)$ are plotted in Fig. 2. As in the case of Mg^{2+}, the function $V_1{}'(2p \to p)$ shows the expected variation with distance.

Comparing the γ_∞ for Mg^{2+} with that for Na^+, we find from Table I that the latter is larger in magnitude than the former. This is understandable because the p electrons in the Na^+ ion, in view of its smaller nuclear charge, are more external than the p electrons in the neutral Mg atom. This fact is further confirmed by noting from Figs. 1 and 2 that the function $V_1'(2p \to p)$ of Na^+ spreads out to a longer distance than $V_1'(2p \to p)$ of Mg.

The third system for which we have calculated γ_∞ is the Cl^- ion. Before discussing its results, we would like to say why, out of the four halogen ions, we have chosen Cl^- for the present investigation. The F^- ion, having only one closed p shell, would have been the simplest of the halogen ions to study. But since the nonorthogonal HFPT[3] shows features distinct from conventional perturbation theory[1] only for systems having more than one closed shell of nonzero l, the Cl^- will be the simplest halogen ion to investigate by the present method. The ion F^-, having only one closed p shell, leads to the same differential equation for $V_1(2p \to p)$ in nonorthogonal HFPT[3] as in the conventional perturbation theory[1] and is thus unsuitable to show the distinctive features of the former theory.

The antishielding factor of Cl^- has been calculated by several authors. Sternheimer and Foley[9,12] have calculated both the first- and second- order effects of the perturbation by the nuclear quadrupole moment on the atomic core states. Beri *et al*[13] have calculated the higher-order correction arising out of the consistency effect. Watson and Freeman[14] (WF) have calculated γ_∞ by the unrestricted Hartree-Fock method. Since our motivation is to test the nonorthogonal HFPT approach for obtaining γ_∞ for negative halogen ions, as a first step in this direction we have calculated to first order the γ_∞ for the Cl^- ion. It will be pertinent therefore to compare our result with the first-order result of SF.[9] However, we also estimate somewhat empirically in the present investigation the contribution to γ_∞ up to second-order perturbation by using Sternheimer's data.[12] The exact calculations to include a second-order effect on antishielding in Cl^- as well as the calculations for the total antishielding factors for other halogen ions are in progress; the results will be reported as soon as they are available.

In order to compare the individual shell contributions $\gamma_\infty(nl \to l)$ obtained to first order in this work with that of SF,[9] we must first account for the exclusion-principle-violating[3] (EPV) correction to γ_∞, as has been done in Ref. 3. The latter correction arises owing to the fact that the SF[9] results for $\gamma_\infty(2p\rightarrow p)$ and $\gamma_\infty(3p\rightarrow p)$ include the contributions $\gamma_\infty(2p\rightarrow 3p)$ and $\gamma_\infty(3p\rightarrow 2p)$, respectively. The latter two contributions, in view of the closed $2p$ and $3p$ cores in the Cl$^-$ ion, are referred to as the EPV corrections.[3] The values of $\gamma_\infty(nl\rightarrow l)$ in this work do not include such EPV contributions because of the orthogonalization of $\delta\psi$ to other occupied states of same l and m as that of ψ^0_{nlm} under perturbation. The EPV corrections for $2p$ and $3p$ states were calculated by using the formula[3]

$$\gamma_\infty(nl\rightarrow n'l)=C^{(2)}_{ll}\langle U_0'(nl)\,|\,r^2\,|\,U_0'(n'l)\rangle\langle U_0'(n'l)\,|\,1/r^3\,|\,U_0'(nl)\rangle/(E^0_{n'l}-E^0_{nl})\,. \tag{18}$$

From Eq. (18), $\gamma_\infty(2p\rightarrow 3p)$ is found to be -0.38 and $\gamma_\infty(3p\rightarrow 2p)$, being equal and opposite to $\gamma_\infty(2p\rightarrow 3p)$, is 0.38. Adding these corrections to $\gamma_\infty(2p\rightarrow p)$ and $\gamma_\infty(3p\rightarrow p)$, respectively, in the present work, we have found that the resulting $\gamma_\infty(2p\rightarrow p)=-1.48$ and $\gamma_\infty(3p\rightarrow p)=-65.82$. Since $\gamma^{\text{ang}}_\infty$ is very small, we have used the value of $\gamma^{\text{ang}}_\infty$ of SF.[9] Now comparing the individual shell contributions with SF,[9] we find that the $\gamma_\infty(2p\rightarrow p)$ compares well with the value[12] of -1.51. But the value of $\gamma_\infty(3p\rightarrow p)$ is quite different from Sternheimer's value[12] of -57.0. We believe that the discrepancy in the values of $\gamma_\infty(3p\rightarrow p)$ is perhaps due to the different zeroth-order wave functions used in the present calculation. While SF[9] have used the numerical HF functions,[15] we have used the analytical HF functions.[6]

A similar discrepancy in the values of $\gamma_\infty(3p\rightarrow p)$ due to the use of different zeroth-order HF wave functions, was previously[12] noted by Sternheimer between his result for the Cl$^-$ ion and that of WF.[14] The latter authors had used an analytical HF function in their calculation of γ_∞ for the Cl$^-$ ion. On repeating his calculations of $\gamma_\infty(3p\rightarrow p)$ by using the analytic HF functions of WF,[14] Sternheimer[12] had obtained a value of -68.4. The latter value is closer to our result of -65.82. Sternheimer[12] concluded that the analytic HF functions of WF[14] were more external than the numerical HF functions[15] used in his calculations. In view of the difference between the analytical and numerical HF functions, we also conclude that the analytical HF functions[6] used in this work, similar to analytic HF functions of WF,[14] are perhaps more external than the numerical HF functions[15] used in Sternheimer's calculation.[12] Of course the best way of confirming this conclusion would have been to repeat our calculation by using the zeroth-order wave functions[15] of Sternheimer.[12] However, since the latter wave function[15] is not available to us at present, we could not carry this out.

Assuming that the analytic HF functions used in the present work are more external than the numerical HF functions,[15] one would have then expected, as in the case of $\gamma_\infty(3p\rightarrow p)$, a significant difference in the values of $\gamma_\infty(2p\rightarrow p)$ obtained in both the calculations. On the contrary, the agreement in the latter, as shown before, is quite satisfactory. The reason why the agreement in $\gamma_\infty(2p\rightarrow p)$ is so good, in spite of the use of the different zeroth-order wave functions, is perhaps due to the greater localization of the $2p$ electron compared to the $3p$ electron. The antishielding factor is heavily weighted in regions of large r ($\sim r^2$). Since the $2p$ function is localized in a smaller-r region, the contribution to $\gamma_\infty(2p\rightarrow p)$ is much smaller than $\gamma_\infty(3p\rightarrow p)$. For the same reason, even if the analytic $2p$ function is more external than the numerical $2p$ function, the region in r over which the spreading out of the former occurs, being small, the difference in contributions to $\gamma_\infty(2p\rightarrow p)$ is not significant. Adding the radial and angular contributions to γ_∞, we have obtained for the total γ_∞ a value equal to -65.90. Compared to the latter value, the result of Sternheimer[12] is -57.11.

In a later calculation[12] Sternheimer has included the effect of the second-order perturbation by the nuclear Q. He has observed that the latter effect is to reduce the magnitude of γ_∞ obtained in first order to 80% of the latter value. Including the second-order effect, the total γ_∞ in Sternheimer's calculation is -50.45. We would like to remark here that in a subsequent paper[13] Sternheimer and co-workers report a value of γ_∞ quoted for

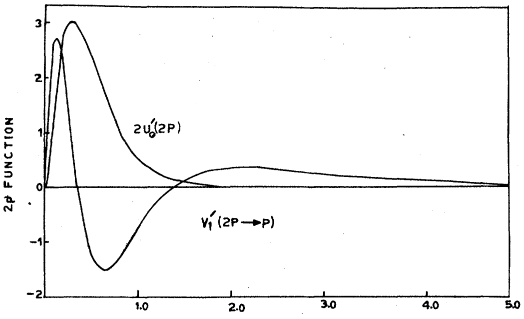

FIG. 3. Perturbed function $V_1'(2p\rightarrow p)$ and $2p$ function $U_0'(2p)$ for the Cl$^-$ ion.

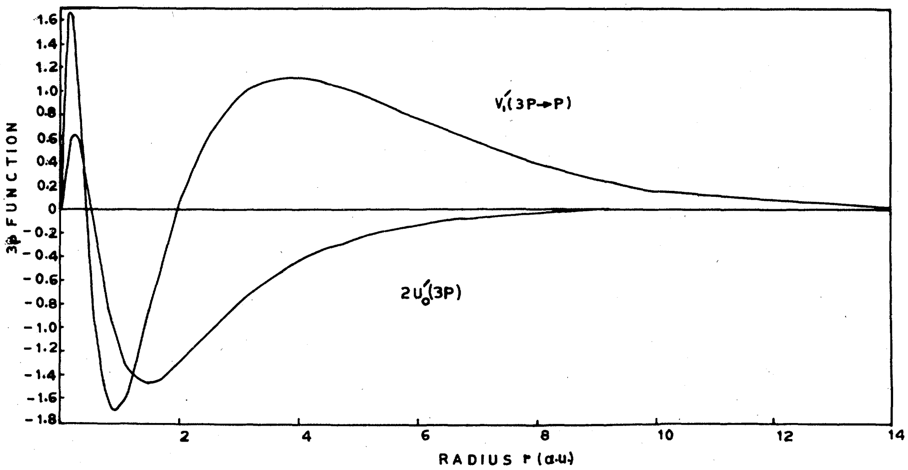

FIG. 4. Perturbed function $V_1'(3p \rightarrow p)$ and $3p$ function $U_0'(3p)$ for Cl^- ion.

Cl^- of −55.1. By looking at the suggested[13] reference from which the latter value is quoted, we found the listed[12] value of −57.11. We are unable to resolve this difference. Now supposing that the factor of reduction, namely 0.8, remains the same in our case, the value of γ_∞ including contributions up to second order, is estimated to be −53.20. The latter value is closer to Sternheimer's value[12] −50.45. Of course in our case the exact factor of reduction may be different from 0.8 and can be determined accurately only after calculating the second-order effect in our procedure. Such calculations, as indicated above, are in progress.

For the Cl^- ion, we have plotted the functions $U_0'(2p)$ and $V_1'(2p \rightarrow p)$ in Fig. 3, and $U_0'(3p)$ and $V_1'(3p \rightarrow p)$ in Fig. 4. Both figures are quite instructive and show why $\gamma_\infty(3p \rightarrow p)$ is much larger than $\gamma_\infty(2p \rightarrow p)$. In case of the $2p$ electron, the function $U_0'(2p)$ extends to a distance of about 2 a.u., while $V_1'(2p \rightarrow p)$ extends to roughly 5 a.u. But in the case of the $3p$ electron, the function $U_0'(3p)$ extends to 10 a.u., and $V_1'(3p \rightarrow p)$ extends to nearly 20 a.u. (It is shown only to 15 a.u. in Fig. 4.) In addition, both the functions $V_1'(2p \rightarrow p)$ and $V_1'(3p \rightarrow p)$ have the expected behavior with regard to the number of nodes.

IV. CONCLUSION

We have calculated the antishielding factors γ_∞ in first order for the ions Na^+, Mg^{2+}, and Cl^- in the nonorthogonal HFPT.[3-5] While the γ_∞ obtained by using the core functions of the neutral Mg atom is more appropriate in the calculation of the electric field gradient in magnesium metal the values of γ_∞ for Na^+ and Cl^- are appropriate for ionic crystals such as NaCl. The values of γ_∞ for Na^+ and Mg^{2+} obtained in this work are in good agreement with the corresponding results obtained in other calculations.[7,8,12] However, a discrepancy is noted between $\gamma_\infty(3p \rightarrow p)$ obtained in this work and that in Sternheimer's calculation.[12] It is believed that the latter discrepancy is perhaps due to the different zeroth-order wave functions[6] used in the present calculation. The calculations, including the second-order effect of the nuclear Q on the core states of the Cl^- ion, as well as the calculations of the total γ_∞ for other halogen ions, are in progress and will be reported when available.

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