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Theory of Quadrupole Polarizability and Antishielding of Nuclear Quadrupole Moments of Many-Electron Ions

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Important corrections are proposed to earlier procedures for the calculation of quadrupole polarizabilities and antishielding factors of ions. A generalized formulation of the second-order perturbation theory for many-electron atoms and ions by Dalgarno is applied to K^+ and Cl^- ions leading to increases of about 30 and 11%, respectively, over results of earlier variational calculations of the antishielding factors for these ions.

INTRODUCTION

THE theory of quadrupole polarizability and the nuclear quadrupole antishielding property of ions was first worked out by Foley, Sternheimer, and Tycko,[1] and subsequently by a number of other authors.[2–4] All these calculations made use of second-order perturbation theory but while Sternheimer and his collaborators obtained the first-order perturbations in the electronic wave functions by setting up the requisite differential equations, the others[3,4] used variational forms for the perturbed wave functions and minimized the second-order energy for the ion when placed in an external electric field gradient. Dalgarno[5] and Allen[6] have recently formulated in general terms the second-order energy of a many-electron atom subject to a perturbation. The many-electron nature of the atom leads to a number of exchange terms in the second-order perturbation energy in the same manner as exchange terms arise in the Hartree-Fock procedure for the ground-state wave functions of the atom. One can compare Dalgarno's general procedure with the earlier calculations[1–4] of the quadrupole polarizabilities and antishielding factors of ions. It can be seen that the exchange terms in Dalgarno's general theory have been neglected completely in the differential equation procedure and only partially considered in the variational calculations. In the present paper, we have applied the Dalgarno formalism to the variational calculation of quadrupole polarizabilities and antishielding factors for K^+ and Cl^- ions and find that the inclusion of the exchange terms cause only a small change in the quadrupole polarizabilities but a substantial change in the antishielding factors. In Sec. II, the adaptation of Dalgarno's procedure to the variational calculation is described and corrected forms of the differential equations for the perturbations in the electronic wave functions are listed. In Sec. III, the results of our calculation are listed and their significance is discussed.

II. DALGARNO VARIATIONAL PROCEDURE

The general form of the variational problem is the following: We have an atomic system described by a zero-order Hamiltonian given by (1) and we assume that the ground-state determinantal wave function Ψ_0 is known in the Hartree-Fock approximation.[7]

$$H_0=-\sum_i \nabla_i^2-\sum_i \frac{2Z}{r_i}+\sum_{i>j}\frac{2}{|\mathbf{r}_i-\mathbf{r}_j|}, \qquad (1)$$

$$\Psi_0=\frac{1}{(n!)^{\frac{1}{2}}}\sum_P (-)^P P\prod_i \psi_i^0(\mathbf{r}_i), \qquad (2)$$

where P is the permutation operator and the ψ_i^0 are the one-electron eigenfunctions which are solutions of the one-electron wave equations

$$(H_i-\epsilon_i^0)\psi_i^0(\mathbf{r})=0,$$

where

$$H_i=-\nabla_i^2-\frac{2Z}{r_i}+\sum_{k\neq i}(\beta_{ik}-\alpha_{ik}), \qquad (3)$$

$$\beta_{ik}=2\int\frac{|\psi_k^0(\mathbf{r}_k)|^2}{|\mathbf{r}_i-\mathbf{r}_k|}d\tau_k,$$
$$\alpha_{ik}=\frac{2\psi_k^0(\mathbf{r}_i)}{\psi_i^0(\mathbf{r}_i)}\int\frac{\psi_k^{0*}(\mathbf{r}_k)\psi_i^0(\mathbf{r}_k)}{|\mathbf{r}_i-\mathbf{r}_k|}d\tau_k, \qquad (4)$$

and ϵ_i^0 is the one-electron energy for the state ψ_i^0. The system of electrons is subject to two perturbing sources

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[1] H. M. Foley, R. M. Sternheimer, and D. Tycko, Phys. Rev. **93**, 734 (1954).

[2] R. M. Sternheimer and H. M. Foley, Phys. Rev. **102**, 731 (1956); R. M. Sternheimer, *ibid.* **115**, 1198 (1959).

[3] T. P. Das and R. Bersohn, Phys. Rev. **102**, 733 (1956); E. G. Wikner and T. P. Das, *ibid.* **109**, 360 (1958).

[4] G. Burns, Phys. Rev. **115**, 357 (1959); J. Chem. Phys. **31**, 1255 (1959). G. Burns and E. G. Wikner, Phys. Rev. **121**, 155 (1961).

[5] A. Dalgarno, Proc. Roy. Soc. (London) **A251**, 282 (1959).

[6] L. C. Allen, Phys. Rev. **118**, 167 (1960).

[7] Throughout this paper, atomic units are used, namely unit of length a_0, the Bohr radius, unit of charge e and unit of energy Rydberg ($e^2/2a_0$).

described by the perturbing Hamiltonians H_1' and H_2' given by Eqs. (5) and (6) below:

$$H_1'=\sum_i h_1(i)=-\frac{1}{R^3}\sum_i (3\cos^2\theta_i-1)r_i^2, \tag{5}$$

and

$$H_2'=\sum_i h_2(i)=-Q\sum_i \frac{(3\cos^2\theta_i-1)}{r_i^3}, \tag{6}$$

where $h_1(i)$ arises out of the interaction between the field gradient due to a point charge at a distance R from the nucleus and an electron at a point $(r_i\theta_i)$ with respect to the nucleus. $h_2(i)$ arises out of the interaction of the quadrupole moment of the nucleus with the electron. Dalgarno[5] obtains the following expressions for the second-order energy $\mathcal{E}_{11}$ due to H_1' alone and $\mathcal{E}_{12}$ due to first order in H_1' and first order in H_2':

$$\begin{aligned}\mathcal{E}_{11}=\sum_i \langle\psi_i^{(1)}|H_i-\epsilon_i^0|\psi_i^{(1)}\rangle &-\sum_{i\neq j}(\epsilon_j^0-\epsilon_i^0)|\langle\psi_j^0|\psi_i^{(1)}\rangle|^2\\ &+2\{\sum_i\langle\psi_i^{(1)}|h_1|\psi_i^0\rangle\\ &-\sum_{i,j}\langle\psi_j^0|h_1|\psi_i^0\rangle\langle\psi_i^{(1)}|\psi_j^0\rangle,\end{aligned} \tag{7}$$

$$\begin{aligned}\mathcal{E}_{12}=\sum_i 2\langle\psi_i^{(2)}|H_i-\epsilon_i^0|\psi_i^{(1)}\rangle &-\sum_{i\neq j}(\epsilon_j^0-\epsilon_i^0)\{\langle\psi_j^0|\psi_i^{(1)}\rangle\langle\psi_i^{(2)}|\psi_j^0\rangle\\ &+\langle\psi_j^0|\psi_i^{(2)}\rangle\langle\psi_i^{(1)}|\psi_j^0\rangle\}\\ &+2[\sum_i(\langle\psi_i^{(1)}|h_2|\psi_i^0\rangle+\langle\psi_i^{(2)}|h_1|\psi_i^0\rangle)\\ &-\sum_{i,j}\{\langle\psi_j^0|h_1|\psi_i^0\rangle\langle\psi_i^{(2)}|\psi_j^0\rangle\\ &+\langle\psi_j^0|h_2|\psi_i^0\rangle\langle\psi_i^{(1)}|\psi_j^0\rangle\}],\end{aligned} \tag{8}$$

where $\psi_i=\psi_i^0+\psi_i^{(1)}+\psi_i^{(2)}$ is the perturbed-state wave function resulting from ψ_i^0 due to the action of h_1 and h_2 and the perturbed many-electron wave function has been taken as

$$\Psi=\frac{1}{(n!)^{\frac{1}{2}}}\sum_P(-)^P P\prod_i\psi_i(\mathbf{r}_i). \tag{9}$$

From Eq. (7), the differential equation for $\psi_i^{(1)}$ will be given by $\partial\mathcal{E}_{11}/\partial\psi_i^{(1)}=0$, that is,

$$\begin{aligned}(H_i-\epsilon_i^0)\psi_i^{(1)}-\textstyle\sum_j(\epsilon_j^0-\epsilon_i^0)\langle\psi_j^0|\psi_i^{(1)}\rangle\psi_j^0\\ =-h_1\psi_i^0+\textstyle\sum_j\langle\psi_j^0|h_1|\psi_i^0\rangle\psi_j^0.\end{aligned} \tag{10}$$

For the $l\rightarrow l'$ and $l\rightarrow l$ excitations that Sternheimer has discussed, Eqs. (10) would reduce, respectively, to

$$\begin{aligned}-\frac{d^2u_i^{(1)}}{dr^2}+\frac{l'(l'+1)-l(l+1)}{r^2}u_i^{(1)}\\ -\sum_j(\epsilon_j^0-\epsilon_i^0)\langle u_j^0|u_i^{(1)}\rangle u_j^0\\ +\frac{u_i^{(1)}}{u_i^0}\frac{d^2u_i^0}{dr^2}=+u_i^0r^2\\ -\sum_{j\neq i}\langle u_j^0|r^2|u_i^0\rangle u_j^0,\end{aligned} \tag{11}$$

where

$$\begin{aligned}\psi_i^{(1)}&=K_{ll'm}\frac{u_i^{(1)}(r)}{r}Y_{l'}^m,\\ \psi_j^0&=\frac{u_j^0(r)}{r}Y_{l'}^m,\\ K_{ll'm}&=\frac{1}{R^3}\int_0^\pi\int_0^{2\pi}Y_{l'}^{m*}(3\cos^2\theta-1)Y_l^m\sin\theta d\theta d\phi;\end{aligned} \tag{12}$$

$$\begin{aligned}-\frac{d^2u_i^{(1)}}{dr^2}-\sum_j(\epsilon_j^0-\epsilon_i^0)\langle u_j^0|u_i^{(1)}\rangle u_j^0\\ +\frac{u_i^{(1)}}{u_i^0}\frac{d^2u_i^0}{dr^2}=+u_i^0r^2-\sum_j\langle u_j^0|r^2|u_i^0\rangle u_j^0,\end{aligned} \tag{13}$$

where

$$\begin{aligned}\psi_j^0&=[u_j^0(r)/r]Y_l^m,\\ \psi_i^{(1)}&=K_{llm}[u_i^{(1)}(r)/r]Y_l^m,\\ K_{llm}&=\frac{1}{R^3}\int_0^\pi\int_0^{2\pi}Y_l^{m*}(3\cos^2\theta-1)Y_l^m\sin\theta d\theta d\phi.\end{aligned}$$

On comparing with the corresponding equations in Sternheimer's formulation, we find that the terms $\sum_j(\epsilon_j^0-\epsilon_i^0)u_j^0\langle u_j^0|u_i^{(1)}\rangle$ on the left and $\sum_{j\neq i}\langle u_j^0|r^2|u_i^0\rangle u_j^0$ on the right were dropped. This is the result that one would get if one used a simple Hartree product wave function in the perturbed state instead of the determinantal wave function (9).

In the variational method,[3,4] the terms $\sum_{i\neq j}(\epsilon_j^0-\epsilon_i^0)\times|\langle\psi_j^0|\psi_i^{(1)}\rangle|^2$ and $\sum_{i\neq j}\langle\psi_j^0|h_1|\psi_i^0\rangle\langle\psi_i^{(1)}|\psi_j^0\rangle$ were made to vanish by imposing the condition that in the perturbed state the one-electron wave functions are orthogonal,[3] that is,

$$\langle\psi_i^0|\psi_j^{(1)}\rangle+\langle\psi_i^{(1)}|\psi_j^0\rangle=0. \tag{15}$$

This condition, however, imposes a restriction on the variational functions $\psi_i^{(1)}$ and $\psi_j^{(1)}$ and therefore might also lead to errors. Using Eqs. (12), (14), and (7), for the $np\rightarrow p$ perturbations of the p electrons in an ion with closed shells, the second-order perturbation energy

TABLE I. Quadrupole polarizabilities and antishielding factors from $2p\rightarrow p$ perturbation.[a]

Author	Sternheimer[b]		Wikner and Das[c]		Burns[d]		This paper	
Ion	α_Q (A^5)	γ_∞	α_Q (A^5)	γ_∞	α_Q (A^5)	γ_∞	α_Q (A^5)	γ_∞
K$^+$		-1.219	0.828×10^{-4}	-1.225		-1.161	0.419×10^{-4}	-0.831
Cl$^-$		-1.5	2.200×10^{-4}	-1.531		-1.522	1.345×10^{-4}	-0.992

[a] The separation into contributions from $2p\rightarrow p$ excitations and $3p\rightarrow p$ excitations is made depending on whether the contribution depends on $u_{2p}^{(1)}$ or $u_{3p}^{(1)}$, respectively.

[b] The value of γ_∞ for Cl$^-$ ion is from reference 1 and for K$^+$ ion from R. M. Sternheimer, Phys. Rev. **115**, 1198 (1959).

[c] The quoted values are values recalculated by us because of an error discovered in the earlier value [Phys. Rev. **109**, 360 (1958)] of $\gamma_\infty(2p\rightarrow p)$ for Cl$^-$ ion. The recalculated value is now in good agreement with Burns' value.

[d] G. Burns, J. Chem. Phys. **31**, 1255 (1959).

TABLE II. Quadrupole polarizabilities and antishielding factors from $3p\rightarrow p$ perturbation.

Author	Sternheimer[a]		Wikner and Das[b]		Burns[c]		This paper	
Ion	α_Q (A^5)	γ_∞	α_Q (A^5)	γ_∞	α_Q (A^5)	γ_∞	α_Q (A^5)	γ_∞
K$^+$	0.183	-17.15	0.190	-12.97	-0.185	-12.81	0.181	-16.906
Cl$^-$	5.38	-56.5	5.029	-50.01	5.322	-50.07	4.956	-56.246

[a] Results for Cl$^-$ are from R. M. Sternheimer and H. M. Foley, Phys. Rev. **102**, 731 (1956), and for K$^+$ from R. M. Sternheimer, Phys. Rev. **115**, 1198 (1959); **107**, 1565 (1957).

[b] Quoted values have been obtained by a recalculation although they are very close to E. G. Wikner and T. P. Das' value [Phys. Rev. **109**, 360 (1958)] except for α_Q for K$^+$ ion where Wikner and Das' value was 0.222.

[c] Values of α_Q are from Phys. Rev. **115**, 357 (1959) and the γ_∞ are from J. Chem. Phys. **31**, 1255 (1959).

due to h_1 reduces to[3]

$$\mathcal{E}_{11}=\frac{48}{25}\Big[\sum_n \langle u_n^{(1)}|H_n-\epsilon_n^0|u_n^{(1)}\rangle -\sum_{n,n'}(\epsilon_{n'}^0-\epsilon_n^0)|\langle u_{n'}^0|u_n^{(1)}\rangle|^2 -2\Big\{\sum_n \langle u_n^{(1)}|r^2|u_n^0\rangle -\sum_{n,n'}\langle u_{n'}^0|r^2|u_n^0\rangle\langle u_n^{(1)}|u_{n'}^0\rangle\Big\}\Big]. \quad (16)$$

In Eq. (16) n' refers to the other occupied $n'p$ orbitals in the ion. In the case of K$^+$ and Cl$^-$ ions, the occupied p orbitals are $2p$ and $3p$, so while considering the perturbation of the $2p$ state, that is $u_{2p}^{(1)}$, the exchange interaction of this perturbation with the $3p$ state will have to be considered and for $u_{3p}^{(1)}$, the interaction with the $2p$ state will have to be considered. In Das and Bersohn's calculation[3] on Na$^+$ and Al^{3+} ions, the only occupied orbitals were $2p$ orbitals and so there are no interaction terms with other p states to be considered. Their calculations are therefore free of errors due to exchange effects which calculations on the heavier ions are subject to. As variational functions for the $u_{np}^{(1)}$, functions of the type employed in earlier variational calculations were used, namely,

$$u_{np}^{(1)}=u_{np}^0 r^2(\kappa_n r^{-1}+\alpha_n+\beta_n r+\gamma_n r^2). \quad (17)$$

The results for the minimum value of the second-order energy differed in each case by less than 1% on including or excluding γ_n, therefore, additional variation parameters were not used. From the minimum value of $\mathcal{E}_{11}$ in atomic units $(e^2/2a_0)$, the quadrupole polarizability is obtained (in A^5) using the relation

$$\alpha_Q=-\mathcal{E}_{11}a_0^5.$$

Using the calculated $u_{np}^{(1)}$, the value of the antishielding factor was obtained from the following equation which follows from Eq. (8), namely

$$\gamma_\infty=\frac{48}{25}\Big[\sum_n \langle u_n^{(1)}|r^{-3}|u_n^0\rangle -\sum_{n,n'}\langle u_{n'}^0|r^{-3}|u_n^0\rangle\langle u_n^{(1)}|u_{n'}^0\rangle\Big]. \quad (18)$$

It is to be noticed again that in earlier variational calculations[3,4] on ions except for the neon-like and helium-like ions, the second term in the brackets on the right-hand side of Eq. (18) was dropped because of the orthogonality condition imposed on the perturbed states.

III. RESULTS AND DISCUSSION

The values obtained by us for the contributions to the quadrupole polarizabilities and antishielding factors γ_∞ from the $2p\rightarrow p$ and $3p\rightarrow p$ perturbations are compared in Tables I and II with corresponding values by Sternheimer's method and also by earlier variational calculations.[8] It is seen that for the $2p\rightarrow p$ perturbation

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[8] In the subsequent discussions in this section the values of γ_∞ and α_Q calculated in this paper will be compared with the results of earlier variational calculations (references 3 and 4) and not with Sternheimer's results obtained by numerical solution of the first-order perturbation equation without considering the mixing between $2p$ and $3p$ states (reference 2). These latter results can be more appropriately compared with the results that would be obtained by solving Eqs. (11) and (13) when and if they become available. However, from earlier experience with the comparison between results of variational calculations for the Na$^+$ ion and the

the quadrupole polarizabilities are affected most strongly by the inclusion of the exchange terms considered in Sec. II. The antishielding factors γ_∞, though altered significantly, are relatively less affected. The opposite trends are found for the contributions from $3p \rightarrow p$ perturbations, the quadrupole polarizabilities being affected very little while the values of γ_∞ are increased quite significantly.

One can explain the origin of this trend qualitatively. From Eq. (7), we find that the correction terms due to the exchange between the perturbed $2p$ and $3p$ states depends on the overlap between the perturbed states. So the effect of the correction terms will be most significant in the region where the $2p$ and $3p$ functions overlap the most. This region is the peripheral region for the $2p$ wave function and internal for the $3p$ wave function. Now, the value of γ_∞ according to Eq. (18) depends on the expectation values of negative powers of r while the quadrupole polarizability depends on the expectation values of positive powers of r. Hence, a large part of the contribution to the quadrupole polarizability comes from the outer regions of the wave function and is therefore altered relatively more for the $2p$ state than for the $3p$ state. The opposite trend is expected for the antishielding factor, as is actually observed.

Our results show that the effect of exchange between the perturbed states as obtained by taking a determinantal wave function for the perturbed state of the atom is important in the calculation of the antishielding factor γ_∞. The effect of this exchange is seen to be to increase the calculated $(1-\gamma_\infty)$ for the free ion. This trend is in agreement with that expected from experimental data as shown by recent careful calculations[9] of field gradients on solid solutions. Earlier conclusions[4] that experimental data tended to show that the values of $(1-\gamma_\infty)$ in crystals were smaller than in free ions were based on rather approximate calculations of the field gradients. In Table III we have tabulated the total values of α_Q and γ_∞ for K^+ and Cl^- ions including the contributions from angular excitations which were evaluated by Burns.[4] These values will not be affected by the exchange effect considered for the $np \rightarrow p$ excitations, because there are no occupied d and f states for these ions. In addition to K^+ and Cl^-, Hartree-Fock wave functions are available for the three other ions Cu^+, Ga^{3+}, and Fe^{3+}, for which nuclear quadrupole interaction data are available. Our experience with K^+ and Cl^- ions indicates that substantial changes due to the inclusion of the exchange effect, may be expected in the calculated values of γ_∞ for these other ions.[3,4] No wave functions including exchange are available for the ground states of Br^-, I^-, Rb^+, or Cs^+ ions, so it would not be meaningful to correct for exchange effects in the perturbed states of these ions.

TABLE III. Total values of α_Q and γ_∞.

	Contributions from[a] angular perturbations		Contributions from radial perturbation		Total	
Ion	α_Q (A^5)	γ_∞	α_Q (A^5)	γ_∞	α_Q (A^5)	γ_∞
K^+	0.536	+1.414	0.181	−17.737	0.717	−16.323
Cl^-	8.397	+1.724	4.956	−57.238	13.053	−55.514

[a] These values are taken from G. Burns, J. Chem. Phys. 31, 1255 (1959).

In conclusion, it should be mentioned that all the methods which have been used for quadrupole polarizabilities and antishielding factors in the past,[1–4] whose most correct form is the one outlined in this paper, come under what Dalgarno[5] terms his method II. In this method, as contrasted to[5,6] method I, the requirement of self-consistency is not satisfied in the perturbed state of the ion. A calculation by method I should be attempted in order to obtain the most correct values of polarizabilities and antishielding factors. Such a calculation would be rather complicated because of the large number of two-electron integrals involved. Dalgarno[4] has shown that method II gives a value for α_Q for helium atom differing by only 0.7% from that obtained by method I. It is still not clear without actual calculation, whether similar small differences between the results with the two methods is to be expected also for the values of α_Q and γ_∞ of other ions.

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helium-like ions (references 2 and 3) we hope that our present results will be comparable to the results that would be obtained using solutions of Eq. (13) in Eqs. (16) and (18). The variational calculations on K^+ and Cl^- ions in references 3 and 4 required the use of the restrictive condition that the perturbed $2p$ and $3p$ states be orthogonal, to prevent the second-order energy of the perturbed $3p$ state from collapsing to a value comparable to the zero-order energy of the $2p$ state on minimization (p. 362 of the second paper in reference 3). It was not necessary to invoke any such orthogonality condition in reference 2. It is not surprising, therefore, that the results in references 3 and 4 for K^+ and Cl^- ions do not agree closely with the results for these ions in reference 2.

[9] T. P. Das and B. G. Dick (to be published); briefly reported at the Conference on Chemical Physics of Non-Metallic Crystals, Evanston, Illinois, August 28–31, 1961 [W. A. Benjamin Inc., New York (to be published)].