PHYSICAL REVIEW VOLUME 115, NUMBER 2 JULY 15, 1959

Antishielding and Polarizabilities in Alkali Halide Gases

GERALD BURNS
International Business Machines Research Laboratory, Poughkeepsie, New York

(Received February 20, 1959)

The ionic model that has been used in an attempt to explain eQq/h data in ionic gases and solids is examined, extended, and applied to alkali halide gases. It is shown that the antishielding factor, γ_∞, multiplies the unshielded value of q, $(\partial^2V/\partial Z^2)$, produced not only by an external charge but by all the external moments, and some of these effects are important in alkali halide gases. In order to estimate the magnitude of the contributions to q of such moments, polarizabilities are calculated that apply to alkali halide internuclear distances. These polarizabilities are often much smaller than those calculated for the free ion. Polarizabilities and γ_∞'s are calculated using both Hartree and Hartree-Fock wave functions and are compared. The values obtained using the Hartree-Fock wave functions are consistently smaller. Some second order calculations of the polarizabilities and antishielding factors are calculated by a direct substitution method. The results indicate that for the alkali halide gas calculations perturbation theory is applicable to the alkali ions but not to the easily deformable halide ions for the situation considered here. This is probably the reason the ionic model has always yielded poor results for the halide ions. When the ionic model is extended, as described in this paper, and applied to the alkali ions, a set of antishielding factors is found for which there is agreement between theory and experiment or would be if Hartree-Fock wave functions were available to calculate γ_∞. From this model the nuclear quadrupole moment, Q, of Li^7 is found to be -0.016×10^{-24} cm^2.

I. INTRODUCTION

THE nuclear quadrupole coupling constant (eQq/h) has been measured in many alkali halide gases and ionic solids. To understand the results one would like to be able to calculate the second derivative of the electrostatic potential evaluated at the nucleus, q. This can then be compared to experimental values of q obtained from eQq/h if the value of the nuclear quadrupole moment, Q, is independently known. However, if one is confident of the calculation of q, values of Q can be obtained from these measurements. Much of this paper is devoted to calculations that are shown to be required if one is to compare experimental values of q to calculated ones. Then in the case of Li the procedure is reversed and a value of Q is obtained from the measured eQq/h and the calculated q.

Foley, Sternheimer, and Tycko[1] have shown that q of an ion, due to an external charge, c, a distance R away can be much larger than the value $2c/R^3$ which is found by ignoring the effect of the electrons on the ion. Enhancement comes from the perturbation of the ion's electrons by the external charge. Considering the perturbation for this ionic model, they showed that q can be written as $(2c/R^3)(1-\gamma_\infty)$, where γ_∞ is the antishielding factor for the particular ion. They applied this model to some nuclear quadrupole coupling data of alkali halide gases and showed that the data gave some support to the calculations.

The antishielding factor has been used in explaining other experimental data with various measures of success. For example, Proctor and co-workers have induced nuclear spin transitions in crystals by ultrasonic waves.[2] In ionic crystals one can calculate the q produced by the ultrasonic waves. This calculation involves the enhancement factor. It is difficult to make precise comparisons with the measured quantities because one must know the ultrasonic energy density which involves some uncertain terms. However, the experiments indicate that q is larger than one would expect from a simple ionic calculation where antishielding effects are omitted.

The requirement that one know the energy density in this type of experiment has been eliminated by Jennings *et al.*[3] by measuring the ratio of quadrupole coupling of sodium and iodine in a NaI crystal. By applying the ionic model and using known values of Q for Na and I they obtain a ratio of the antishielding factor of iodine to that of sodium which is of the order of magnitude of the theoretical ratio.[4]

Nuclear quadrupole spin lattice relaxation times, T_1's, have also been interpreted in terms of the ionic model[5] by Van Kranendonk. Wikner *et al.*[5] have measured a number of T_1's in alkali halide crystals and have shown that calculated relaxation times based on the ionic model are in agreement with some of the data and the antishielding factors are close to the theoretical values. However, for other crystals, covalent effects are more important in determining the relaxation mechanism than the ionic effects.

Bersohn[6] has shown, in a number of ionic solids, that there is reasonable agreement between measured values of eQq/h and those calculated from the ionic model.

In general, experimental evidence indicates that the antishielding factor exists but there is little quantitative agreement between the measured values and those theoretically calculated. The object of this paper is to

---

[1] Foley, Sternheimer, and Tycko, Phys. Rev. **93**, 734 (1954); R. M. Sternheimer and H. M. Foley, Phys. Rev. **102**, 731 (1956); R. M. Sternheimer, Phys. Rev. **84**, 244 (1951).

[2] W. G. Proctor and W. H. Tanttila, Phys. Rev. **98**, 1854 (1955); **101**, 1757 (1956); W. G. Proctor and W. Robinson, Phys. Rev. **104**, 1344 (1956).

[3] Jennings, Tanttila, and Kraus, Phys. Rev. **109**, 1059 (1958).

[4] They obtain a ratio of 10.9. Using γ_∞ for I of -179 (see reference 8) and γ_∞ for Na from reference 1 or 7, 32.5 and 35 is obtained.

[5] J. Van Kranendonk, Physica **20**, 781 (1954); Wikner, Blumberg, and Hahn (to be published).

[6] R. Bersohn, J. Chem. Phys. **29**, 326 (1958).

re-evaluate the ionic model and to apply it to alkali halide gases to compare the values of q measured to those predicted by this model. To make this comparison, several extensions of the model are shown to be required.

First, it is shown that $(1-\gamma_\infty)$ multiplies not only the effect of an external spherical charge but the effects of all the external moments. These terms can be important when considering the alkalies in alkali halide gases. To see the effects of these terms, the polarizabilities (dipole α_D, quadrupole α_Q, octupole α_O, and hexadecapole α_H) of Cl^- and F^- are calculated for the case R equal to alkali halide internuclear distances. It is shown that using these values the calculated values of eQq/h are now in good agreement with the experimentally measured ones for Na^+ and K^+ but not for Rb^+ and Cs^+. However, investigation of the values of γ_∞ calculated from both the Hartree-Fock and Hartree wave functions shows that the agreement would be good for all four alkalies if Hartree-Fock wave functions were available for Rb^+ and Cs^+. The polarizabilities are also dependent on which type of wave function is used.

Finally, the applicability of perturbation theory is examined. Certain second order terms in the polarizability and antishielding factor are calculated by a direct substitution method and considered with other second order calculations.[1] The results indicate that in this situation perturbation theory is applicable to the alkali ions but is not to the easily deformed halide ions. Thus, it is reasonable that theory and experiment are in good agreement for the alkali ions but not for the halide ions.

II. ANTISHIELDING

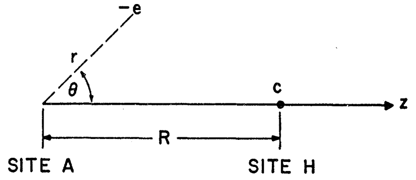

FIG. 1. Electron on ion A in field of charge c.

One can attempt to explain the alkali halide gas data by considering the molecule to be strongly ionic and that higher order interactions between the ions can be treated as perturbations on the spherical ions. The zero-order wave functions (ψ_0) used are those of the Hartree (H.) or Hartree-Fock (H.F.) type for free ions. In this case q at site A, q_A, equals $2c/R^3$, where c is the charge of the ion at site H. (See Fig. 1.) The spherical distribution of A's electrons contribute nothing to q_A. However, the charge, c, interacts with the electrons on A. The potential energy of the interaction is

$$-ec\left[\frac{1}{R}+\frac{r\cos\theta}{R^2}+\frac{r^2}{R^3}\frac{3\cos^2\theta-1}{2}+\frac{r^3}{R^4}P_3(\cos\theta)+\frac{r^4}{R^5}P_4(\cos\theta)+\cdots\right]_{r<R}, \qquad (1)$$

where $P_i(\cos\theta)$ is the ith Legendre polynomial. If (1) is considered as a perturbation on ψ_0 to first order, only the term $r^2P_2(\cos\theta)$ contributes to antishielding.[1] This term has matrix elements connecting states with s orbital angular momentum and those with d, and p orbital states are connected to other states with p and f orbital angular momentum ($s\rightarrow d$, $p\rightarrow p$, and $p\rightarrow f$). The contribution of this perturbation to the field gradient is given by

$$\Delta q_A=\int\psi^*\frac{3\cos^2\theta-1}{r^3}\psi d\tau,$$

where $\psi(=\psi_0+\psi_1)$ is the wave function of A's electrons. The result is given by $-(2c/R^3)\gamma_\infty$. The antishielding factor, γ_∞, is a pure number depending only on the wave functions of the ion being perturbed. Hence, to first order,

$$q_A=(2c/R^3)(1-\gamma_\infty). \qquad (2)$$

This antishielding factor has been evaluated for a number of ions by solving numerically the first-order perturbed Schrödinger equation.[1] It has also been evaluated by a variation-of-parameters method.[7,8]

Now consider the effect of a dipole μ, oriented along the z axis at site H. Besides having a direct contribution to the field gradient given by $q_A=6\mu/R^4$, it also interacts with A's electrons. The potential energy of this interaction is

$$-e\mu\left[\frac{1}{R^2}+\frac{2r}{R^3}\cos\theta+\frac{3r^2}{R^4}P_2(\cos\theta)+\cdots\right]_{r<R}. \qquad (3)$$

The $r^2P_2(\cos\theta)$ connects the ground states to the same excited states as the point charge calculation of Eq. (1). Since the same excited states are involved, one need only consider the difference in the constants when using (1) and (3) in an antishielding calculation to get the difference between (2) and its counterpart for an external dipole. The result is

$$q_A=(6\mu/R^4)(1-\gamma_\infty) \qquad (4)$$

where this is the same γ_∞ as in the point charge case.[9] In a similar manner the effect of any axial symmetric moment at H will be multiplied by the same $(1-\gamma_\infty)$.[10]

---

[7] T. P. Das and R. Bersohn, Phys. Rev. **102**, 733 (1956).

[8] E. G. Wikner and T. P. Das, Phys. Rev. **109**, 360 (1958).

[9] G. Burns, Bull. Am. Phys. Soc. Ser. II, **3**, 147 (1958).

[10] One can arrive at (4) directly from (2) by placing a positive and a negative charge along the z axis, applying (2) for each and then going to the proper limit to get a dipole. Since $(1-\gamma_\infty)$ is a pure number it factors out and one gets (4). In a similar manner one gets the same type of result for any moment that can be represented by an axial charge distribution. One can also get estimates of the effect of the nonideal character of the moments by allowing the charges to remain apart. The effects of the nonideal character of the moments are much smaller than the effects of the moments. This can, of course, be treated more formally with equations similar to (3).

Thus, the total q at site A is

$$q_A=(1-\gamma_{\infty A})\left[\frac{2c}{R^3}+\frac{6\mu}{R^4}+\frac{6e\bar{Q}}{R^5}+\frac{10eO}{R^6}+\frac{30e\bar{H}}{8R^7}+\cdots\right]_H, \quad (5)$$

where the subscripts refer to the properties of the particular electron distribution[11] and the moments have their usual definition.[12] The moments μ, $\bar{Q}$, etc., are those induced in the H-ion electron distribution by the ion A.

To facilitate the comparison of this model with experimental results, a quantity κ is defined as

$$\kappa_A=\frac{(\text{measured coupling constant})_A}{(e/h)Q_A[2c/R^3+6\mu/R^4+6e\bar{Q}/R^5+10eO/R^6+30e\bar{H}/8R^7+\cdots]_H}. \quad (6)$$

The quantities κ and $(1-\gamma_\infty)$ should be equal if the theory applies to the alkali halides.

Considering only the contribution κ from an external charge, as has been done in the past, the agreement for the alkalies between κ and $(1-\gamma_\infty)$ is only approximate. However, the κ's are internally consistent. That is, the κ for a given alkali is relatively independent of its neighboring halide. (See column P in Table III.) However, the contributions to κ of the alkalies from the μ and $\bar{Q}$ terms are large and it was not apparent that additional terms would cause κ to converge. The investigation of this point was thus undertaken.

On the other hand, κ for the halides is affected only slightly by the μ, $\bar{Q}$, etc., terms because the polarizabilities of the alkalies are relatively small. However, the agreement between κ and $(1-\gamma_\infty)$ for the halides is extremely poor and the values of κ in this case are not internally consistent. A simple application of the Townes and Dailey[13] covalent theory does not help to understand q for the halides in alkali halide gases. Some calculations of second order effects in Sec. IV show why this simple ionic model is inadequate for the easily deformable halides.

III. MOMENTS

As mentioned in the last section κ for the alkalies did not appear to converge as the effects of the μ, $\bar{Q}$, etc., moments of the halides were added. It must converge if the model is to be useful. Higher order polarizabilities were therefore calculated to test this. If the κ does not converge, either the model must be abandoned or the reason that the calculated moments are too large must be found.

Two methods of calculation are used here to determine the polarizabilities. They are the variation-of-parameters method, similar to that used by Das and Bersohn,[7] and a numerical solution of the first order perturbed Schrödinger equation similar to that used by Sternheimer.[14,1] In all cases, where both methods are used to calculate the same polarizabilities, the agreement is good. The polarizabilities are calculated for application to alkali halide gases where $R\approx 2.5$ A.

For details of the type of variation-of-parameters procedure used, reference 7 should be consulted where α_Q and γ_∞ are calculated. To calculate a polarizability, one need only select the proper term from Eq. (1) to use as a perturbation. For example, the $P_1(\cos\theta)$ term will connect the ground state wave functions to excited state wave functions that have the correct angular dependence to give first order contributions to α_D. The $P_2(\cos\theta)$ term acts as a perturbation for α_Q, etc. The energies associated with the quadrupole perturbation are given in reference 7. The others are in the Appendix.

Following Das and Bersohn the form of the radial perturbed wave function used is $(\alpha+\beta r+\gamma r^2)H_1(r)u_0'$, where $H_1(r)$ is the radial form of the perturbation, u_0' is the radial ground state wave function, and α, β, and γ are variation parameters to be obtained from the minimization-of-energy procedure. To see if the assumed form of the wave function is a good one the polarizabilities are first calculated using α only, then using α and β, and finally using α, β and γ. The addition of the parameter γ always had negligible effects. When the polarizabilities calculated here could be compared with other published calculations, the agreement was good.[7,14–16] The results of these calculations are in Table I. In this table the contribution from each type of excited state wave function is listed for the outer electron shell and the polarizability is found by summing the contributions from the appropriate states. The contribution from the inner shells is negligible. Also one can see that the use of Hartree-Fock rather than Hartree wave functions has a large effect in reducing the values of the polarizabilities. It must be remembered that the polarizabilities are obtained by using the appropriate terms in Eq. (1) as perturbations and it will be shown that one cannot always apply these to ions in alkali halide molecules, since Eq. (1) is good only for $r<R$.

The second method used to calculate u_1' is the numerical solution of a differential equation in a manner similar to that described by Sternheimer.[14,1] The perturbed radial wave function with orbital angular

---

[11] For the sake of clarity and simplicity, liberties have been taken with the sign of some of the effects of the moments in (5) and similar equations that follow. The sign of the effects of all the induced moments is the same as the sign of the $2c/R^3$ term. Thus, the moments in the electron distribution can be calculated without regard to sign. The sign of the contribution to q from all the moments at H can then be taken as the same as the sign of the charge, c, effect.

[12] $\mu=\langle r\cos\theta\rangle=\int\psi^* r\cos\theta\psi d\tau$, $e\bar{Q}=\langle r^2(3\cos^2\theta-1)\rangle$, $eO=\langle r^3(5\cos^3\theta-3\cos\theta)\rangle$, $e\bar{H}=\langle r^4(35\cos^4\theta-30\cos^2\theta+3)\rangle$.

[13] C. H. Townes and B. P. Dailey, J. Chem. Phys. **17**, 782 (1949).

[14] R. M. Sternheimer, Phys. Rev. **96**, 951 (1954).

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

[16] See Table I of reference 8. However, the angular factors have been left out and their values of E_2 must be multiplied by the proper numbers as in reference 7.

TABLE I. Contributions to the polarizabilities from the outer shell electrons.[a]

Ion (type of wave function used)[b]	α_D(A^3)	α_Q(A^5)			α_O(A^7)			α_H(A^9)		
	$p\to d$	$s\to d$	$p\to f$	$p\to p$	$s\to f$	$p\to d$	$p\to g$	$s\to g$	$p\to f$	$p\to h$
F$^-$(H.)	3.432	0.110	10.52	11.24	0.0738	45.01	35.41	0.42	904.0	745.1
F$^-$(H.F.)	1.237	0.076	1.493	1.384	0.0256	2.340	1.787	0.0527	14.81	11.85
K$^+$(H.)	1.371	0.1587	0.7541	0.3713	0.0431	0.5275	0.3731	0.0651	1.276	1.015
K$^+$(H.F.)	0.9719	0.1211	0.4149	0.1851	0.0294	0.2254	0.1569	0.0396	0.4066	0.3211
Cl$^-$(H.)	12.233	0.6067	43.422	37.350	0.2997	214.92	167.24	0.877	4745.3	3879.4
Cl$^-$(H.F.)	5.026	0.6174	7.780	5.322	0.3202	16.44	12.54	0.975	149.5	122.3
Na$^+$(H.F.)	0.1320	0.01013	0.03217	0.02262	0.001375	0.009807	0.007227	0.001065	0.01141	0.009192
Rb$^+$(H.)	2.775	0.3405	1.898	0.7892	0.1080	1.665	1.152	0.1920	4.758	3.742
Cs$^+$(H.)	5.787	1.037	5.057	1.766	0.4291	5.747	3.882	0.957	20.51	16.08

[a] The inner shells contribute negligibly.

[b] References to original calculation of the Hartree and Hartree-Fock wave functions are conveniently summerized in R. S. Knox, Solid-State Physics edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 4, p. 413. For the F$^-$(H.F.) results see C. Froese, Proc. Cambridge Phil. Soc. **53**, 206 (1957).

momentum l' which is connected to the ground state radial wave function, u_0', with orbital angular momentum l satisfies Eq. (7) when $E_1=0$.

$$\left[-\frac{d^2}{dr^2}+\frac{l(l+1)}{r^2}+V_0-E_0\right]u_1'=-H_1(r)u_0'. \tag{7}$$

By using

$$V_0-E_0=\frac{1}{u_0'}\left[\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}\right]u_0', \tag{8}$$

and

$$\frac{d^2u_1'(r)}{dr^2}=\frac{u_1'(r+\delta)-2u_1'(r)+u_1'(r-\delta)}{\delta^2} \tag{9}$$

for the second derivative, where δ is the interval between the listed values of u_0', one obtains

$$u_1'(r+\delta)=u_1'(r)\left\{2+\delta^2\left[\frac{l'(l'+1)-l(l+1)}{r^2}+\frac{d^2u_0'(r)/dr^2}{u_0'(r)}-\frac{H_1(r)u_0'(r)}{u_1'(r)}\right]\right\}-u_1'(r-\delta). \tag{10}$$

This gives u_1' at all values of r if two starting values are known. The solution is started with $u_1'(r-\delta)$ equal to zero at the origin and $u_1'(r)$ at $r=0.01$ is varied until u_1' behaves properly at infinity. In practice, solutions of (10) are used that diverge slowly to $+\infty$ or $-\infty$. The difference over the region of interest could be made negligibly small and the polarizabilities are then the same for the two solutions. The polarizabilities obtained by this method are in good agreement with those calculated by the variation of parameters method.

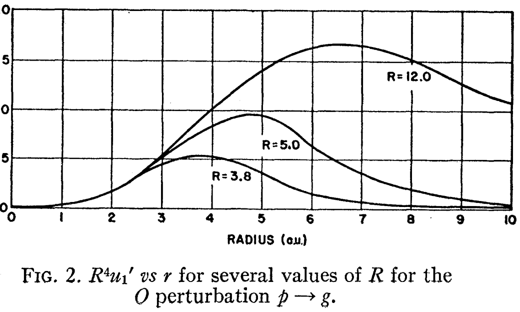

FIG. 2. R^4u_1' *vs* r for several values of R for the O perturbation $p\to g$.

Upon examination, the higher the moment under consideration, the larger the contribution to the polarizabilities from the outer part of the electron distribution. For example, the Hartree-Fock wave function for Cl$^-$ has only 2% of the $3p$ electron distribution at distances greater than 5 a.u., yet more than 50% of the contributions to α_Q in Cl$^-$ come from the region past 5 a.u. This percentage increases rapidly for higher moments. Thus a calculation of polarizability that does not treat the problem accurately for large r will yield incorrect results.

If the polarizabilities are to be applied to alkali halide internuclear distances, it must be remembered that Eq. (1) is good only for $r<R$. For $r>R$ the perturbation is

$$-ec\left[\frac{1}{r}+\frac{R\cos\theta}{r^2}+\frac{R^2}{r^3}P_2(\cos\theta)+\cdots\right]_{r>R}. \tag{11}$$

This is much smaller than (1) for $r>R$ and gives smaller u_1''s and polarizabilities.

To get polarizabilities that apply to alkali halide internuclear distances, so that the proper moments can be substituted in (6), u_1' is obtained from (10) as before, but the value of $H_1(r)$ from (1) or (11) is used depending on whether r is smaller than R or larger than R. (See Fig. 2.) Then, for example, the quadrupole polarizability is calculated from

$$\alpha_Q=Y_Q\left[\int_0^R u_0'r^2u_1'dr+R^5\int_R^\infty u_0'\frac{1}{r^3}u_1'dr\right], \tag{12}$$

and similar equations for the other polarizabilities where the Y's are the angular parts of the integrations.[17]

---

[17] The definitions of the polarizabilities are: $\mu=-\alpha_D\partial V/\partial z=\alpha_D E$, $eQ=\alpha_Q\partial^2V/\partial^2z$, $eO=-\alpha_O\partial^3V/\partial z^3$, $eH=\alpha_H\partial^4V/\partial z^4$. This makes the polarizabilities independent of R. The Y's are angular factors that appear in the expressions for the polarizabilities in the Appendix.

TABLE II. Contributions to the polarizabilities from the outer electron shells for several values of R.

	R (atomic units)	α_D(A^3)		α_Q(A^5)			α_O(A^7)			α_H(A^9)	
		$p \to d$	$s \to d$	$p \to f$	$p \to p$	$s \to f$	$p \to d$	$p \to g$	$s \to g$	$p \to f$	$p \to h$
F(H.F.)	2.8	0.4270	0.0522	0.1759	0.1180	0.00963	0.06585	0.04227	0.00814	0.05460	0.04037
	3.4	0.5498	0.0605	0.3079	0.2393	0.01446	0.1647	0.1057	0.0164	0.1945	0.1438
	3.6	0.5827	0.0624	0.3557	0.2870	0.01580	0.2113	0.1356	0.0195	0.2770	0.2047
	4.0	0.6669	0.0662	0.5222	0.4738	0.01916	0.4257	0.2733	0.0293	0.7748	0.5728
	4.5	0.7051	0.0674	0.6304	0.6078	0.02053	0.6202	0.3982	0.0349	1.3786	1.0183
Cl(H.F.)	3.8	2.308	0.4203	1.3442	0.5141	0.1256	0.7592	0.4874	0.1687	0.9888	0.7303
	4.5	3.010	0.5072	2.2497	0.9814	0.1880	1.7194	1.1038	0.3308	3.109	2.297
	5.0	3.372	0.5427	2.8648	1.5468	0.2237	2.6817	1.7216	0.4579	5.925	4.377
	5.5	3.635	0.5635	3.4723	1.8615	0.2502	3.8397	2.4650	0.5780	10.142	7.491

Polarizabilities were calculated for several values of R for Cl^- and F^- using Eqs. (10), (11), and (12). It was noted that the variation of parameters method gives good agreement with the above results if all the integrations are carried up to R instead of ∞. Thus, the electron distribution between R and ∞ ($\approx 2\%$) is ignored. It is reasonable to expect agreement between the two methods, since (11) and (12) strongly decrease the contribution of the electron distribution at $r > R$. The use of the variation of parameters method to find the polarizabilities for various R's is the simpler of the two.

Polarizabilities of F^- and Cl^- for several values of R calculated by the variation of parameters method are given in Table II. As can be seen, there sometimes is a large difference between the results in Table II and those in Table I. The results in Table I are applicable when the charge, c, is outside the electron distribution. Agreement between the two methods of obtaining polarizabilities, applicable to alkali halide internuclear distances, cannot be expected to be extremely precise, since many of the polarizabilities are strongly R-dependent and in the region of interest the δ's are relatively large. Also, the two methods only qualitatively have the same effects and there is an inexactness associated with the fact that the δ's in the region of interest are relatively large and approximations such as Eq. (9) and the use of the trapezoidal method of integration introduce errors. However, the numerical solution for a given R gave values of polarizability closest to the variation of parameters solution for the same R. Thus, the two methods are in agreement.

Some comments are appropriate at this point.

The polarizabilities calculated from this point charge model, as just described, vary with R. Thus, even α_D for an ion should vary slightly with R. A variation has been seen[18] but the variation is not in a consistent direction. It must be remembered that distortion effects, due to closed shell repulsion, are being neglected and this may not be reasonable for the easily deformable halides and it will be shown that other factors enter when second order perturbations are considered. The point charge model can be extended[19] but it was felt, for this problem, the return would not warrant the effort.

It has been pointed out[8] that in the presence of inner shells having the same orbital angular quantum number as the excited state, the variation of parameters procedure must be modified slightly to keep the wave functions orthogonal. For example, in the quadrupole $p \to p$ perturbation for a $3p$ electron, the perturbed state must be made orthogonal to not only the $3p$ state, which has been done, but to the $2p$ wave function also. This has not been done because this effect on the polarizabilities is small as can be seen by comparing the $p \to p$ contribution to α_Q in Table I to that obtained by Wikner and Das.[16] This effect on a γ_∞ calculation is, however, larger and has been taken into account for the values of γ_∞ quoted in the next section. In most polarizability calculations in this paper it is not necessary to consider this at all, since the perturbed state is orthogonal by virtue of its angular dependence.

The variation of parameters solution was tried for the dipole cases $s \to p$, $p \to s$, and $p \to d$. It worked well for all but the $p \to s$ where changing u_1' from $\alpha H_1(r) u_0'$ to $(\alpha + \beta r) H_1(r) u_0'$, etc., resulted in major changes in the dipole polarizability. When the numerical solution for this case is considered[20] it is seen that u_1' is much closer to the origin than u_0' and has more nodes. This type of function is not expressable in the form that has been chosen for the variation of parameters u_1'. It is fortunate that the $p \to s$ and $s \to p$ contributions to α_D as calculated numerically by Sternheimer[14] and this author almost cancel, with the $s \to p$ being a bit larger. The $s \to p$ contribution to α_D is decreased slightly by use of (11) as has been discussed. Thus, α_D is even more closely given by the $p \to d$ contribution alone. This $p \to d$ contribution is listed in Tables I and II.

The last point is that (11) should be used in calculations of γ_∞ also. However, the use of (1) only, leads to much less error than in the polarizability calculations

---

[18] W. Klemperer and S. A. Rice, J. Chem. Phys. **26**, 618 (1957); S. A. Rice and W. Klemperer, J. Chem. Phys. **27**, 573 (1957).

[19] See the references and work in Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), Chap. 12.

[20] See Fig. 2 of reference 14.

TABLE III. Values of κ for the alkali ions.

Mol.[a,b,c]	$(1-\gamma_\infty)$[d]	P	$P+D$[e]	$P+D+Q$	$P+D+Q+O$	$P+D+Q+O+H$
LiF	(0.74)	1.30	0.788	0.594	0.487	0.453
LiCl		1.43	0.681	0.485	0.388	0.348
LiBr		1.69	0.759			
LiI		2.11	0.875			
NaF	(5.1)	7.26	5.18	4.01	3.57	3.35
NaCl		10.21	5.94	4.55	3.81	3.49
NaBr		10.53	5.75			
NaI		11.12	5.64			
KF	(14)	15.71	12.03	9.433	8.11	7.47
KCl		22.60	14.56	11.93	10.54	9.91
KBr		23.04	14.08			
RbF	(72)	46.04	36.07	28.96	25.11	23.21
RbCl		66.02	43.91	36.78	32.72	30.91
CsF	(145)	76.57	59.90	48.28	42.19	38.95

[a] Values of eQq/h can be found in N. F. Ramsey, *Molecular Beams* (Oxford University Press, Oxford, 1956), p. 311 and in Logan, Cote, and Kusch, Phys. Rev. **86**, 280 (1952).

[b] The values of the internuclear distance, R, are obtained from Honig, Mandel, Stitch, and Townes, Phys. Rev. **6**, 629 (1954).

[c] The values of the nuclear quadrupole moment were obtained from the following sources: (1) Li^7: the value of Q is not known, -0.016 b is used since it makes κ agree with $1-\gamma_\infty$. See Sec. V. (2) Na^{23}: $+0.01$ b—Perl, Rabi, and Senitzky, Phys. Rev. **98**, 611 (1955). See also Bersohn's comment in reference 30. (3) K^{39}: $+0.07$ b—P. Buck and I. I. Rabi, Phys. Rev. **107**, 1291 (1957). See also K. Murakawa's comment, Phys. Rev. **110**, 393 (1958). (4) Rb^{87}: $+0.12$ b—B. Senitzky and I. I. Rabi, Phys. Rev. **103**, 315 (1958). (5) Cs^{133}: -0.003 b—Buck, Rabi, and Senitzky, Phys. Rev. **194**, 553 (1956); K. Althoff, Z. Physik **141**, 33 (1955).

[d] See references 1 and 8.

[e] Values of α_D are taken from reference 23.

since γ_∞ weights more heavily the internal part of the wave function which is relatively independent of R. Also, it is known that the self-consistent wave functions have too small a value at small r.[21] Thus, the use of (11) would make γ_∞ smaller and the use of better wave functions would make γ_∞ larger so the two errors may somewhat compensate.

IV. RESULTS AND SECOND ORDER EFFECTS

The polarizabilities applicable to alkali halide internuclear distances, as listed in Table II, can now be substituted in Eq. (6) so that κ can be compared to $(1-\gamma_\infty)$ for the alkali ions. Table III shows the results. The column labeled P shows κ when only a point charge is considered at the halide ion site, as has been done in the past. It is seen that the κ for a given alkali ion is relatively independent of its neighboring halide ion. The $P+D$ column shows κ for the alkali ions when a charge and induced dipole,[22] using experimental dipole polarizabilities,[23] are considered at the halide ion site.

Notice that the spread of κ for a given alkali ion is reduced considerably. The third column shows κ when the effects of a charge, induced dipole, and induced quadrupole are considered at the halide ion site where the polarizabilities are taken from Table II. The next two columns consider the addition of an octupole and hexadecapole. If the polarizabilities in Table I were used κ would clearly diverge.

The values of Q used are those obtained from molecular beam measurements except in the case of Li where no reliable value of Q exists. A value of -0.016×10^{-24} cm^2 was used. See the discussion in Sec. V.

A similar table for the halide ions would reveal that the addition of the dipole, etc., moment has little effect on κ because the alkali ions are not very polarizable. A table of κ for the halide ions for the charge effect alone is given in an article by Townes.[24] As pointed out, there is a large variation in the value of κ and the agreement with $1-\gamma_\infty$ is bad. Consideration of second order terms shows why this model is not applicable to the halide ions and thus agreement between κ and $1-\gamma_\infty$ would not be expected to be good.

Besides calculating γ_∞ by first order perturbation theory, certain second order terms were calculated by Foley, Sternheimer, and Tycko[1] in their original paper. They calculated the effect on q of Cl^- by applying the dipole perturbation, $r\cos\theta$, to the ground states to obtain excited state wave functions; then again applied the same perturbation to the excited state wave functions to obtain other excited state wave functions, ψ_2. They also calculated the effect of applying the quadrupole perturbation twice. The contribution of the second order effects evaluated for $R=4.46$ a.u., i.e., the NaCl internuclear distance, was 10.9 and 10.3, respectively, as compared to the first order effect of 46.5 $(=-\gamma_\infty)$. Thus, the second order effects are not negligible. They add to the first order effect for the negative ions and subtract for the positive ions.

It was felt that second order calculations of the antishielding factor and α_Q for several ions might be revealing. A direct substitution method proved simple and adequate. It was noticed in the variation of parameters solutions that it was not the α term that was important in u_1' but rather the βr term. If one calculated the energy or polarizability using the βr term, the addition of the α and γr^2 terms made little difference. Thus, a solution of the form $u_1'=\beta r H_1(r)u_0'$ was assumed, substituted in (7) and β calculated at a number of points. Over a range of r past the last peak in u_0', β was found to be approximately constant and

---

[21] T. Yamanouchi and H. Horie, J. Phys. Soc. (Japan) **1**, 52 (1952). G. C. Dousmanis [Phys. Rev. **97**, 967 (1955)] says the Hartree-Fock $\langle 1/r^3\rangle$ is 8% too low for oxygen. T. P. Das [J. Chem. Phys. **27**, 1 (1957)] calculates 0.216 (atomic unit) for $\langle 1/r^3\rangle$ and compares it to an experimental value of 0.323 (atomic unit). See also A. Mukherji and T. P. Das, Phys. Rev. **111**, 1479 (1958).

[22] The moments in one ion are induced by all the moments of the other ion [see S. Rittner, J. Chem. Phys. **19**, 1030 (1951)]. The effect of $\bar{Q}$, O, and $\bar{H}$ in inducing moments in the other ion was small and thus neglected. Rittner shows that a simple ionic model can give satisfactory results for the binding energy, vibration frequency, and dipole moment of alkali halide molecules.

[23] Tessman, Kahn, and Shockley, Phys. Rev. **92**, 890 (1953). These values are used even though they were obtained from solids. They are truly an experimental set of polarizabilities and they give better agreement with the measured dipole moments of the alkali halide gas than the often used Pauling values.

[24] C. H. Townes, *Handbuch der Physik* (Springer-Verlag, Berlin, 1958), Vol. 38.

TABLE IV. Comparison of values of $\langle r^n\rangle$ in atomic units, for K^+ and F^-. The value of $\langle r^0\rangle$ is 1. The trapezoidal method of integration is used.

	K^+(H.)		K^+(H.F.)		F^-(H.)		F^-(H.F.)	
	s	p	s	p	s	p	s	p
$\langle r^{-3}\rangle$	···	1.288×10^{1}	···	1.294×10^{1}	···	5.676	···	6.404
$\langle r^{-2}\rangle$	6.620	1.916	6.265	1.957	7.772	1.885	7.987	2.082
$\langle r^{-1}\rangle$	1.068	9.045×10^{-1}	1.076	9.425×10^{-1}	1.396	1.087	1.411	1.163
$\langle r^{1}\rangle$	1.319	1.538	1.275	1.429	1.065	1.446	1.037	1.257
$\langle r^{2}\rangle$	2.023	2.834	1.879	2.411	1.398	3.194	1.320	2.211
$\langle r^{3}\rangle$	3.516	6.077	3.124	4.684	2.222	10.39	2.022	5.248
$\langle r^{4}\rangle$	6.877	1.501×10^{1}	5.823	1.038×10^{1}	4.274	4.694×10^{1}	3.686	1.613×10^{1}
$\langle r^{5}\rangle$	1.506×10^{1}	4.221×10^{1}	1.211×10^{1}	2.597×10^{1}	10.10	27.71×10^{1}	7.901	6.168×10^{1}
$\langle r^{6}\rangle$	3.672×10^{1}	13.38×10^{1}	2.795×10^{1}	7.273×10^{1}	3.019×10^{1}	20.34×10^{2}	1.968×10^{1}	2.827×10^{2}
$\langle r^{7}\rangle$	9.890×10^{1}	4.724×10^{2}	7.114×10^{1}	2.257×10^{2}	11.66×10^{1}	17.87×10^{3}	5.634×10^{1}	1.502×10^{3}
$\langle r^{8}\rangle$	2.922×10^{2}	18.41×10^{2}	1.984×10^{2}	7.689×10^{2}	5.658×10^{2}	182.4×10^{3}	1.833×10^{2}	8.978×10^{3}
$\langle r^{9}\rangle$	9.398×10^{2}	7.846×10^{3}	6.027×10^{2}	2.851×10^{3}	32.22×10^{2}	211.2×10^{4}	6.711×10^{2}	5.893×10^{4}
$\langle r^{10}\rangle$	3.265×10^{3}	3.625×10^{4}	1.983×10^{3}	1.141×10^{4}	20.16×10^{3}	272.1×10^{5}	2.741×10^{3}	4.163×10^{5}

equal to the value obtained by the variation of parameters method. Since the nodes occur at small r the region of constant β is the region from which most of the contribution to the polarizabilities is obtained. For example, the contribution to α_D from $p\rightarrow d$ and α_Q from $p\rightarrow f$ for Na^+ and F^- is 0.132 A^3, 1.26 A^3, and 0.0321 A^5, 1.51 A^5, respectively, all of which are very close to the values in Table I.

The same type of guess was made for certain second order wave functions. The $p\rightarrow d\rightarrow p$ (ground p state perturbed to connect to excited d states which are perturbed to connect to other p states) and $p\rightarrow d\rightarrow f$ wave functions were obtained by applying the dipole perturbation twice. The $p\rightarrow f\rightarrow f$ and $p\rightarrow f\rightarrow p$ wave functions were obtained by applying the quadrupole perturbation twice. In these cases the coefficients were approximately constant over the important range. Using these second order wave functions, contributions to α_Q and the antishielding factors were calculated for Na^+ and F^-. The differential equations necessary to calculate the wave functions, and angular factors necessary to calculate α_Q and the antishielding factor can be found in reference 1. It was found that each of the calculated second order contributions (one contribution from $p\rightarrow d\rightarrow p$, etc.) to α_Q for F^- were approximately equal to the first order, $p\rightarrow f$ contribution, while for Na^+ they were at least a factor of ten smaller. Each of the second order contributions to the antishielding factor for F^- calculated was in approximately the same ratio to γ_∞ as the Cl^- results[1] (i.e., not negligible) while for Na^+ the second order contributions are 50 to 500 times smaller than the first order effects.[25]

Also, if one evaluates $[\langle\psi_1|\psi_1\rangle]^{\frac{1}{2}}$, where ψ_1 is the perturbed wave function for any of the perturbations considered in this paper, one gets 10% to 20% for F^- and Cl^- while for Na^+ and K^+ one gets 1% to 3%. Then the perturbed wave function is not small compared to the unperturbed one. Thus, for alkalies it does not appear to be necessary to extend the calculations beyond first order. However, it appears that perturbation theory may not be applicable to the easily deformable halides in this situation. This is, perhaps, the reason why there is no agreement between κ and $(1-\gamma_\infty)$ for the halide ions. This also leads one to the conclusion that the values of the polarizabilities of the halide ions, as calculated from first order perturbation theory, are open to question. Thus, it is felt that the κ's in the $P+D$ column are the safest to use since they are obtained from experimental polarizabilities, and it is these that are compared to $(1-\gamma_\infty)$.

When κ is compared to $1-\gamma_\infty$ it is seen that the agreement is good for Na^+ and K^+ but not for Rb^+ and Cs^+. It was noted that Hartree-Fock wave functions were used to calculate γ_∞ for Na^+ and K^+ while only Hartree wave functions were available for Rb^+ and Cs^+. Thus, calculations were made to see how sensitive γ_∞ is to the wave function used. The ratio of the Hartree to the Hartree-Fock contribution to γ_∞, for the $p\rightarrow p$ perturbation[26] for Al^{+3}, K^+, F^-,[27] and Cl^-,[27] is 1.15, 1.83, 2.88, and 3.14, respectively. From size and charge considerations one would expect the ratio for Rb^+ to be a little larger than K^+ and for Cs^+ to be even larger, perhaps as large as F^-. Thus, if Hartree-Fock wave functions were available for Rb^+ and Cs^+ it is expected that the agreement between κ and $(1-\gamma_\infty)$ would be good for these alkalies also.

Table IV shows how the moments calculated from the Hartree and Hartree-Fock wave functions differ for K^+ and F^-. As one can see there is very little difference between the wave functions at small r. However, the Hartree wave functions are more external than the Hartree-Fock so that the polarizabilities, which are

---

[25] This direct substitution method is not adequate for all the second order effects. For example, the "constant" in wave function for $p\rightarrow s\rightarrow p$ by applying the dipole perturbation twice was not constant over the important range.

[26] The difference between Hartree and Hartree-Fock wave functions had little effect on the angular contribution to γ_∞.

[27] The previously unreported contributions to γ_∞ for F^- are given here. The $s\rightarrow d$, $p\rightarrow f$ and $p\rightarrow p$ contribution to γ_∞ for Hartree and Hartree-Fock wave functions is 0.293, 0.312, -66.86, 0.416, 0.390, -23.22, respectively. Adding 0.10 for the $1s$ shell contribution, the best value of γ_∞ for F^- is -22.31. The $p\rightarrow p$ contribution to γ_∞ for Cl^- using Hartree wave functions is -158.5. This is compared to Wikner and Das' value of -50.43 (reference 8) since the two values were obtained in the same way.

strongly affected by the electron density in the outer regions, are thus much smaller when calculated using Hartree-Fock wave functions (see Table I).

V. SUMMARY AND DISCUSSION

1. The antishielding factor, $1-\gamma_\infty$ for an alkali or halide ion, multiplies not only the effect of an external charge but the effect of all the moments of the halide or alkali ion, respectively. The contributions to the field gradient of some of these moments are not negligible.

2. The agreement between the results of the variation of parameters and the numerical solution of the differential equation is good for the polarizabilities calculated here.

3. Previous calculations[14,28] of α_D gave results that were generally larger than the experimentally measured values. The use of Eq. (11) will reduce some of the values of α_D bringing them in better agreement with experiment. Also the use of Hartree-Fock rather than Hartree wave functions reduces α_D for F^- to bring it in better agreement with experiment. A similar effect would be noted in Rb^+ and Cs^+ if Hartree-Fock wave functions were available. The use of Eq. (11) has a large affect on the higher moments as can be seen by comparing the results in Tables I and II.

4. The ground-state wave functions used here are those calculated by the Hartree or Hartree-Fock method for a free ion. Second order calculations give non-negligible contributions to the halide ion's polarizabilities and antishielding factors in this situation but are negligible for the alkali ions. This is probably the reason the agreement between κ and $1-\gamma_\infty$ is poor for the halide ions. This is also the reason why the best value of κ for the alkali ions is taken from the $P+D$ column in Table III. These values do not require the use of the polarizabilities calculated for the easily deformable halide ions. A simple application of the Townes and Dailey[13] covalent theory does not help to understand q for the halides in alkali halide gases.[29]

5. When κ for the alkali ions from the $P+D$ column is compared to $1-\gamma_\infty$ the agreement is good provided Hartree-Fock wave functions are used to calculate γ_∞. Thus, when estimates of q for positive ions are made[6,30] an enhancement factor, κ, can be used for which agreement between theory and experiment is good.

6. Controversy exists about the value of the nuclear quadrupole moment of Li^7. Using the experimental observation for Li^7 in Li_2 of $eQq/h=+0.060$ Mc/sec,[31] several people have calculated q to obtain a value of Q. Harris and Melkanoff[32] have calculated q for three wave functions. They have 0.27 ev, 0.48 ev, and 0.51-ev dissociation energy and obtain for Q +0.035 b (barns), −0.120 b, and −0.042 b, respectively. Thus, the lowest dissociation energy predicts the smallest negative value for Q. Sternheimer and Foley[33] have considered the effects of shielding on the Li_2 wave functions. Mannari and Arai[34] have used a wave function with a dissociation energy of −0.96 ev and obtain −0.025 b for Q. If shielding effects were considered $|Q|$ would be $\approx 15\%$ smaller.[33,34]

Using the results of this paper the value for Q of Li^7 is −0.016 b. This is in agreement with the trend of the results from molecular wave function calculations. It is also in good agreement with the curve of the nuclear quadrupole moments obtained by Townes, Foley, and Low[35,24] and the value of −0.013 b obtained recently from nuclear calculations.[36] Then using the known ratio of the quadrupole moments of Li^6 to Li^7 [37,38] the value of Q of Li^6 is -0.30×10^{-4} b.

ACKNOWLEDGMENTS

The author is indebted to Dr. S. Triebwasser for many stimulating discussions and for a great deal of encouragement. Discussions and correspondence with Dr. R. Sternheimer, Professor C. Townes, and Dr. G. Wikner are gratefully acknowledged. Values of some excited state wave functions, enabling the r dependence of α_Q to be estimated, were generously supplied by Dr. R. Sternheimer. The programming was skillfully performed by Mr. A. Ferris of the Computing Center.

APPENDIX

The equations required to calculate the polarizabilities by the variation-of-parameters method are given here. Atomic units are used throughout.

The value of $\langle r^n\rangle$ is the expectation value of r^n over ground state wave functions $[=\int (u_0')^2 r^n dr]$. The energy, E, equals $\phi_1+\phi_2$ and for the value of α, β, and γ obtained, it can be shown that $\phi_1=-2\phi_2$.[7]

Dipole polarizability.—

$p\rightarrow d$:

$$\phi_1=-\frac{32}{3}\frac{1}{R^4}[\alpha\langle r^2\rangle+\beta\langle r^3\rangle+\gamma\langle r^4\rangle],$$

$$\phi_2=\frac{16}{3}\frac{1}{R^4}[5\alpha^2+8\beta^2\langle r^2\rangle+13\gamma^2\langle r^4\rangle+12\alpha\beta\langle r\rangle+14\alpha\gamma\langle r^2\rangle+20\beta\gamma\langle r^3\rangle],$$

$$\alpha_D=-\frac{R^4}{2}\phi_1.$$

---

[28] E. G. Wikner and T. P. Das, Phys. Rev. **107**, 497 (1957).

[29] See Sec. IV of reference 8. In that paper x should be $x<1-I$ rather than $x\leq I$ in their Eq. (11).

[30] G. Burns, Bull. Am. Phys. Soc. **3**, 371 (1958).

[31] Logan, Cote, and Kusch, Phys. Rev. **86**, 28 (1952).

[32] E. G. Harris and M. A. Melkanoff, Phys. Rev. **90**, 585 (1953).

[33] R. M. Sternheimer and H. M. Foley, Phys. Rev. **92**, 1460 (1953).

[34] I. Mannari and T. Arai, J. Chem. Phys. **28**, 28 (1958).

[35] Townes, Foley, and Low, Phys. Rev. **76**, 1415 (1949).

[36] A. N. Kushnerenko, Doklady Akad. Nauk U.S.S.R. **117**, 963 (1957) [translation: Soviet Phys. Doklady **2**, 568 (1957)].

[37] N. G. Cranna, Can. J. Phys. **31**, 1185 (1953).

[38] P. Kusch, Phys. Rev. **92**, 268 (1953).

Quadrupole polarizability.—See reference 7.

Octupole polarizability.—For each case

$$\alpha_O = -(R^8/6)\phi_1.$$

$s \rightarrow f$:

$$\phi_1 = -\frac{16}{7}\frac{1}{R^8}[\alpha\langle r^6\rangle + \beta\langle r^7\rangle + \gamma\langle r^8\rangle],$$

$$\phi_2 = \frac{8}{7}\frac{1}{R^8}[21\alpha^2\langle r^4\rangle + 28\beta^2\langle r^6\rangle + 37\gamma^2\langle r^8\rangle + 48\alpha\beta\langle r^5\rangle + 54\alpha\gamma\langle r^6\rangle + 64\beta\gamma\langle r^7\rangle].$$

$p \rightarrow d$:

$$\phi_1 = -\frac{144}{49}\frac{1}{R^8}[\alpha\langle r^6\rangle + \beta\langle r^7\rangle + \gamma\langle r^8\rangle],$$

$$\phi_2 = \frac{72}{49}\frac{1}{R^8}[13\alpha^2\langle r^4\rangle + 20\beta^2\langle r^6\rangle + 29\gamma^2\langle r^8\rangle + 32\alpha\beta\langle r^5\rangle + 38\alpha\gamma\langle r^6\rangle + 48\beta\gamma\langle r^7\rangle].$$

$p \rightarrow g$:

$$\phi_1 = -\frac{192}{49}\frac{1}{R^8}[\alpha\langle r^6\rangle + \beta\langle r^7\rangle + \gamma\langle r^8\rangle],$$

$$\phi_2 = \frac{96}{49}\frac{1}{R^8}[27\alpha^2\langle r^4\rangle + 34\beta^2\langle r^6\rangle + 43\gamma^2\langle r^8\rangle + 60\alpha\beta\langle r^5\rangle + 66\alpha\gamma\langle r^6\rangle + 76\beta\gamma\langle r^7\rangle].$$

Hexadecapole polarizability.—$\alpha_H = -(R^{10}/6)\phi_1$.

$s \rightarrow g$:

$$\phi_1 = -\frac{16}{9}\frac{1}{R^{10}}[\alpha\langle r^8\rangle + \beta\langle r^9\rangle + \gamma\langle r^{10}\rangle],$$

$$\phi_2 = \frac{8}{9}\frac{1}{R^{10}}[36\alpha^2\langle r^6\rangle + 45\beta^2\langle r^8\rangle + 56\gamma^2\langle r^{10}\rangle + 80\alpha\beta\langle r^7\rangle + 88\alpha\gamma\langle r^8\rangle + 100\beta\gamma\langle r^9\rangle].$$

$p \rightarrow f$:

$$\phi_1 = -\frac{64}{27}\frac{1}{R^{10}}[\alpha\langle r^8\rangle + \beta\langle r^9\rangle + \gamma\langle r^{10}\rangle],$$

$$\phi_2 = \frac{32}{27}\frac{1}{R^{10}}[26\alpha^2\langle r^6\rangle + 35\beta^2\langle r^8\rangle + 46\gamma^2\langle r^{10}\rangle + 60\alpha\beta\langle r^7\rangle + 68\alpha\gamma\langle r^8\rangle + 80\beta\gamma\langle r^9\rangle].$$

$p \rightarrow h$:

$$\phi_1 = -\frac{80}{27}\frac{1}{R^{10}}[\alpha\langle r^8\rangle + \beta\langle r^9\rangle + \gamma\langle r^{10}\rangle],$$

$$\phi_2 = \frac{40}{27}\frac{1}{R^{10}}[44\alpha^2\langle r^6\rangle + 53\beta^2\langle r^8\rangle + 64\gamma^2\langle r^{10}\rangle + 96\alpha\beta\langle r^7\rangle + 104\alpha\gamma\langle r^8\rangle + 116\beta\gamma\langle r^9\rangle].$$

The Y's are the numbers in the polarizability equations (i.e., the Y for α_D $p \rightarrow d$ is 16/3, etc.).