

Theory of the Electronic Polarizabilities of Ions in Crystals: Application to the Alkali Halide Crystals

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A theoretical estimate of the polarizabilities of ions in the alkali halides is made by means of a procedure based upon the product approximation which distinguishes the ionic constituents in the crystals but allows for their overlap and mutual interaction. Analysis by means of the Thomas-Kuhn sum rule is used allowing the sum representing the ionic polarizability to be represented by one effective parameter, which is calculated for the free ions from the Pauling theoretical values. The change in this parameter when the ion is transported into the crystalline environment is estimated by an energy level analysis used previously by Seitz. It is shown that this procedure accounts for most of the quantitative features of the polarizabilities of the alkali halides. Moreover, the implications of these results are strongly at variance with the usual view concerning the polarizabilities of ionic crystals, since the additivity rule appears as an accidental result of the qualitative similarity of the interactions in many crystals, and the possibility of large fluctuations in the polarizability of a given ion in different crystalline environments is made evident.

I. INTRODUCTION

ONE of the most striking physical properties of the ionic crystals is the fact that the electronic polarizabilities of these materials very nearly obey an additivity rule. The fact that the ionic constituents of these materials appear to have polarizabilities which are independent of their lattice environment lends indirect support to a physical picture of a lattice of weakly interacting atomic ions as descriptive of the ionic crystals. Two of the most recent and extensive empirical investigations of the validity of the additivity rule in ionic crystals are those of Roberts¹ and of Tessman, Kahn, and Shockley² (TKS). Roberts utilized the Lorentz-Lorentz local field correction and found that the additivity rule was obeyed by a large number of ionic materials. Using the least squares minimization technique, TKS demonstrated that when the additivity rule is applied to the alkali halides, the Lorentz factor gives the best fit of the experimental data. Moreover, the least square polarizabilities obtained in this manner reproduced the polarizabilities of the alkali halides, with the exception of the fluorides, to within 3%.

These investigations lend some credence to the additivity rule in the alkali halides and more or less establish the Lorentz factor as correctly giving the local field correction in isotropic crystals. However, several questions are left unanswered. First, as was pointed out by Shockley,³ the least square polarizabilities differ systematically by rather large percentage amounts from the Pauling⁴ theoretical values for the free ions; the differences are such that the least square cation values are consistently larger than the Pauling values, while the least square anion values are consistently smaller. These differences also exist, in general, when comparison is made with other determinations of the polariza-

bilities of gaseous ions such as those of Born and Heisenberg,⁵ Mayer and Mayer,⁶ and the examination of ions in aqueous solutions by Fajans and Joos.⁷ Second, large deviations from the additivity rule are observed in some materials other than the alkali halides. This is seen most clearly in the work of TKS in which the least square alkali and halide ion polarizabilities are used to obtain the polarizabilities of other ions. These fail in many materials to reproduce the empirical polarizabilities by, in some cases, large percentage amounts.

These questions confirm to a certain extent what one might suspect intuitively, namely, that the interactions among the constituents of the ionic crystals are too strong to enable one to consider these materials as being composed of lattices of weakly interacting ions. However, the fact that an additivity rule works at all, and actually works so well for a large number of materials, indicates that the electronic polarizabilities of these materials can, in an approximate sense, be associated with the polarizabilities of localized constituents in the lattice.

It has been the practice to discuss deviations from the additivity rule as well as the differences between polarizabilities deduced from the additivity rule and those calculated for free ions as due to a combination of a distortion of the ions in the crystal brought about by the interionic interactions and a transition to a situation in which homopolar binding plays a greater role. It is the purpose of this investigation to attempt to replace this rather vague analysis with a systematic examination of this problem from a more fundamental point of view. Based upon an analysis of the crystal properties by means of a procedure which distinguishes the ionic constituents but allows for their overlap and mutual interaction, it will be demonstrated that a relatively simple analysis can account for the main

¹ S. Roberts, *Phys. Rev.* **76**, 1215 (1949).

² J. R. Tessman, A. H. Kahn, and W. Shockley, *Phys. Rev.* **92**, 890 (1953).

³ W. Shockley, *Phys. Rev.* **70**, 105 (1946).

⁴ L. Pauling, *Proc. Roy. Soc. (London)* **A114**, 191 (1927).

⁵ M. Born and W. Heisenberg, *Z. Physik* **23**, 1 (1924).

⁶ J. E. Mayer and M. G. Mayer, *Phys. Rev.* **43**, 605 (1933).

⁷ M. Fajans and G. Joos, *Z. Physik* **23**, 1 (1924).

quantitative features of the polarizabilities of the alkali halide crystals. Moreover, the implications of this analysis yield conclusions which are strongly at variance with some of the usual concepts regarding ionic polarizabilities. It is hoped that these results will lend some insight into the problem of ionic polarizabilities which has hitherto not been available.

II. SUM RULE ANALYSIS OF FREE ION POLARIZABILITIES

We begin our discussion with an analysis of the polarizability of a system of noninteracting free ions. Considering one of the isolated ions for the moment, its static electronic polarizability may be obtained directly from the quadratic Stark effect since at ordinary temperatures the ground state of the ion is the only one having an appreciable probability of being occupied. If the electric field is in the x direction, second-order perturbation theory yields for the polarizability the result⁸

$$\alpha = 2e^2 \sum_{\gamma'} |\langle \gamma' | X | \gamma \rangle|^2 / E_{\gamma'\gamma}, \tag{2.1}$$

where $X = \sum_i x_i$, the x_i being the x coordinates of the individual electrons and $E_{\gamma'\gamma} = E_{\gamma'} - E_{\gamma}$. There is no first-order contribution since for free ions $\langle \gamma | X | \gamma \rangle = 0$. Evaluation of the expression (2.1) is complicated by the fact that it requires a knowledge of the energies and wave functions of all the states of the system, which is generally not available. Consequently, it is advantageous to find some means of surmounting the necessity of knowing the wave functions as well as the specific energies of all the quantum states.

Such a means is available in this case in the form of a sum rule which was discovered independently by Thomas⁹ and Kuhn¹⁰ from consideration of the dispersion formula for optical frequencies from the standpoint of the correspondence principle. It follows directly from the commutation relations

$$[q_i, p_i] = i\hbar\delta_{ij} \tag{2.2}$$

for the electronic coordinates and momenta and may be written in the following manner:

$$(8\pi^2 m / \hbar^2) \sum_{\gamma'} E_{\gamma'\gamma} |\langle \gamma | X | \gamma' \rangle|^2 = n, \tag{2.3}$$

where n is the number of electrons in the ion. Identical relations hold for $Y = \sum_i y_i$ and $Z = \sum_i z_i$.

The use of (2.3) enables one to express (2.1) as

$$\alpha = (2e^2 / \bar{E}_1^2) \sum_{\gamma'} E_{\gamma'\gamma} |\langle \gamma | X | \gamma' \rangle|^2 = e^2 \hbar^2 n / 4\pi^2 m \bar{E}_1^2, \tag{2.4}$$

where \bar{E}_1 is a parameter whose magnitude is determined by the equality of the right-hand sides of (2.1) and (2.4). Because the sum rule is identical for all three

coordinates, the polarizability is independent of the direction of the field. Moreover, it may be seen that the expression for α has been reduced to a dependence upon only one unknown parameter, i.e., $\alpha \propto 1/\bar{E}_1^2$. The quantity \bar{E}_1 may be loosely referred to as being a mean excitation energy although this designation is not a precise one since the values of such quantities are dependent upon the sums from which they are obtained.

This fact may be illustrated by obtaining an expression for the polarizability in another way. The sum rule (2.3) may be simplified by taking advantage of the matrix sum rule,

$$\sum_{\gamma' \neq \gamma} |\langle \gamma | X | \gamma' \rangle|^2 = \langle \gamma | X^2 | \gamma \rangle - |\langle \gamma | X | \gamma \rangle|^2, \tag{2.5}$$

to yield the following:

$$\begin{aligned} (8\pi^2 m / \hbar^2) \bar{E}_2^X \langle \gamma | X^2 | \gamma \rangle &= n, \\ (8\pi^2 m / \hbar^2) \bar{E}_2^Y \langle \gamma | Y^2 | \gamma \rangle &= n, \\ (8\pi^2 m / \hbar^2) \bar{E}_2^Z \langle \gamma | Z^2 | \gamma \rangle &= n, \end{aligned} \tag{2.6}$$

where advantage has been made of the fact that $\langle \gamma | X | \gamma \rangle = \langle \gamma | Y | \gamma \rangle = \langle \gamma | Z | \gamma \rangle = 0$, and where \bar{E}_2^X , \bar{E}_2^Y , and \bar{E}_2^Z are parameters whose magnitudes are determined by the equality of the left-hand sides of (2.3) and (2.6).

Equations (2.6) may be simplified further by the use of the principle of spectroscopic stability.⁸ According to this principle, sums of the form $\sum_{n', m'} |\langle nm | A_q | n'm' \rangle|^2$, where m is a space quantization index, are independent of the axis of the quantization so that

$$\begin{aligned} \sum_{n', m', m} |\langle nm | A_x | n'm' \rangle|^2 &= \sum_{n', m', m} |\langle nm | A_y | n'm' \rangle|^2 \\ &= \sum_{n', m', m} |\langle nm | A_z | n'm' \rangle|^2. \end{aligned}$$

In this case, the result is

$$\sum_{\gamma' \neq \gamma} |\langle \gamma | X | \gamma' \rangle|^2 = \sum_{\gamma' \neq \gamma} |\langle \gamma | Y | \gamma' \rangle|^2 = \sum_{\gamma' \neq \gamma} |\langle \gamma | Z | \gamma' \rangle|^2.$$

Consequently, Eqs. (2.6) reduce to

$$(8\pi^2 m / \hbar^2) \bar{E}_2 \left\langle \gamma \left| \begin{Bmatrix} X^2 \\ Y^2 \\ Z^2 \end{Bmatrix} \right| \gamma \right\rangle = n, \tag{2.7}$$

where the \bar{E}_2^q 's have been replaced by \bar{E}_2 . In a similar manner, one may define an \bar{E}_3 given by

$$\bar{E}_3 = 2e^2 \langle \gamma | X^2 | \gamma \rangle / \alpha, \tag{2.8}$$

so that we have as a second expression for α

$$\alpha = 2e^2 nc / \bar{E}_2 \bar{E}_3, \tag{2.9}$$

where $c = \hbar^2 / 8\pi^2 m$. This result is again independent of direction in agreement with (2.4). The quantities \bar{E}_1 , \bar{E}_2 , and \bar{E}_3 , which may be called the mean excitation energies of the first, second, and third kinds, respectively, satisfy the relationship

$$\bar{E}_1^2 = \bar{E}_2 \bar{E}_3. \tag{2.10}$$

⁸ See, for example, J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932).

⁹ W. Thomas, *Naturwissenschaften* **13**, 627 (1925).

¹⁰ W. Kuhn, *Z. Physik* **33**, 408 (1925).

Although they are not equal, one might generally expect them to be of the same order of magnitude. A specific comparison of these quantities is made in the Appendix.

A system of noninteracting free ions is electrically dilute so that the effective and applied fields acting on a given ion are the same. Under these conditions, the polarizability of the system, α_s , is the sum of the ionic polarizabilities, α_i , and is equal to the total polarization divided by the applied field. If

$$\mathbf{X} = \sum_{i=1}^N x_i = \sum_{i=1}^M X_i,$$

where N is the number of electrons in the system and M is the number of ions, then

$$\begin{aligned} \alpha_s &= \sum_{i=1}^M \alpha_i = 2e^2 \sum_{\gamma'} |\langle \gamma | \mathbf{X} | \gamma' \rangle|^2 / E_{\gamma'\gamma} \\ &= 2e^2 \sum_{i=1}^M \langle \gamma | X_i^2 | \gamma \rangle / \bar{E}_{3i} = (2e^2 / \bar{E}_{3s}) \sum_{i=1}^M \langle \gamma | X_i^2 | \gamma \rangle \\ &= 2e^2 c \sum_i (n_i / \bar{E}_{1i}^2) \end{aligned} \quad (2.11)$$

where \bar{E}_{3s} is the mean excitation energy of the third kind for the system. It is evident that

$$\bar{E}_{3s} = 2e^2 \sum_{i=1}^M \langle \gamma | X_i^2 | \gamma \rangle / \sum_{i=1}^M \alpha_i = \sum_{i=1}^M \alpha_i \bar{E}_{3i} / \sum_{i=1}^M \alpha_i. \quad (2.12)$$

Because there is some ambiguity in the value of the mean excitation energy, it is dangerous to attempt to determine polarizabilities by estimating \bar{E}^2 's. However, the value of (2.4) and (2.11) to our approach to the determination of the polarizabilities of ions in crystals lies in calculating \bar{E}_1 's directly from theoretically determined free ion values. Then, given a crystalline environment in which the ions maintain their individuality to a good approximation, and the crystalline interaction is known to the extent that the change in the \bar{E}_1 's from their free ion values may be estimated, values for the ionic polarizabilities may be obtained. The actual mechanics of such an approximate treatment with its application to the alkali halide crystals will now be discussed.

III. TREATMENT OF THE IONIC CRYSTALS IN THE PRODUCT APPROXIMATION

If the ionic picture were completely accurate, the electrons associated with each nucleus would be completely localized in groups usually associated with the electrons in the ions, with no exchange of electrons taking place between groups. This situation cannot exist in the crystalline state, and can only take place if the ionic constituents are separated by large distances so that they are noninteracting. In this case, the total wave function for the system is a product of free ion wave functions. However, the properties of the ionic

crystals, which in many ways resemble those of a lattice of atomic ions, strongly suggest that in an approximate sense, it is possible to distinguish various groups of electrons in these materials. These groups correspond to the ions of the classical model.

The fact that the total energy of the separated ions is very nearly that of the ions merged into crystalline form prompted Moffitt¹¹ to adopt the view that their energy of mutual interaction in the crystal may be taken as a perturbation on the free ion system. He proposed that the N -electron Hamiltonian operator of the system,

$$\mathbf{H} = \frac{e^2}{2} \sum_{i,j=1}^M \frac{Z_i Z_j}{r_{ij}} + \sum_{i=1}^N \left(\frac{\mathbf{p}_i^2}{2m} - e^2 \sum_{j=1}^M \frac{Z_j}{r_{ij}} \right) + \frac{e^2}{2} \sum_{i,j=1}^N \frac{1}{r_{ij}}, \quad (3.1)$$

where Z_i is the i th nuclear charge number and M is the number of nuclear centers in the crystal lattice, could be split up into terms representing "ionic" Hamiltonians and terms representing ionic interaction potentials, and that one could express the crystal wave function as a linear combination of the complete set of zero-order (separated atom) product wave functions corresponding to the usual perturbation theory series expansion. Instead of this approach, however, a simpler but related analysis which distinguishes the electron groups in the ionic crystals will be used here, namely, that an approximate description of the N electron system may be achieved by means of a single generalized antisymmetric product¹² of the group or "ionic" wave functions $\psi_i(n_{i-1}+1 \cdots n_{i-1}+n_i)$ of the sets $\{n_i\}$ of electrons of each ion:

$$\begin{aligned} \Psi(\mathbf{x}_1 \mathbf{x}_2 \cdots \mathbf{x}_n) &= (N! / n_1! n_2! \cdots n_m!)^{-1/2} \\ &\times \sum_p (-1)^p P \psi_1(1 \cdots n_1) \psi_2(n_1+1 \cdots n_1+n_2) \cdots \\ &\times \psi_m(n_{m-1} \cdots n_{m-1}+n_m). \end{aligned} \quad (3.2)$$

In spite of interionic overlap, the generalized orthogonality conditions¹² apply because a linear transformation performed on the linearly independent ψ_i yields a new set of orthogonal functions which leave (3.2) unchanged except for normalization, since an antisymmetric product of functions is invariant under linear transformations of the functions.¹³ Implicit in this statement, of course, is the assumption that ionic functions are

¹¹ W. Moffitt, Proc. Roy. Soc. (London) **A210**, 245 (1951).

¹² R. G. Parr, F. O. Ellison, and P. G. Lykos, J. Chem. Phys. **24**, 1106 (1956).

¹³ The effect of the orthogonality transformation is the following: The set of nonorthogonalized ionic wave functions ψ_i represented by a row vector $\Psi = (\psi_1 \psi_2 \cdots \psi_M)$ may be transformed to an orthogonalized set $\Phi = \sum_j a_{ij} \psi_j$, which may be represented by the row vector $\Phi = \Psi \mathbf{A}$, where \mathbf{A} is a nonsingular $M \times M$ matrix. If one designates the antisymmetrized products built from Ψ and Φ by Ψ and Φ , respectively, then by a well-known theorem $\Phi = \Psi \text{Det}(\mathbf{A})$. Since the a_{ij} are sums of overlap integrals which are constants in the absence of nuclear motion (Born-Oppenheimer approximation), the net effect of the orthogonalization transformation on the antisymmetrized product function is the multiplication of it by the constant factor $\text{Det}(\mathbf{A})$, which amounts to a change in its normalization.

chosen which are capable of being orthogonalized. In the orthogonalized scheme, the crystal constituents under consideration become the electron groups whose probability amplitudes are encompassed in a manner determined by the orthogonalization procedure, rather than the ionic wave functions.

Besides distinguishing the ionic electron groups, a product function has the desirable property of providing a description of physical properties in a way which is physically meaningful for the ionic crystals. This is conveniently demonstrated by the use of the density matrix formalism which has been discussed in detail in a review article by McWeeny.¹⁴

The one- and two-particle density matrices for the product function (3.2) may be expressed in terms of the $\gamma_i^{\{n_i\}}(\mathbf{x}_1'|\mathbf{x}_1)$ and the $\Gamma_i^{\{n_i\}}(\mathbf{x}_1'\mathbf{x}_2'|\mathbf{x}_1\mathbf{x}_2)$, the density matrices for the electron groups in the following way¹⁴:

$$\gamma(\mathbf{x}_1'\mathbf{x}_1) = \sum_{i=1}^M \gamma_i^{\{n_i\}}(\mathbf{x}_1'|\mathbf{x}_1), \quad (3.3)$$

$$\begin{aligned} \Gamma(\mathbf{x}_1'\mathbf{x}_2'|\mathbf{x}_1\mathbf{x}_2) = & \sum_{i=1}^M \Gamma_i^{\{n_i\}}(\mathbf{x}_1'\mathbf{x}_2'|\mathbf{x}_1\mathbf{x}_2) \\ & + \sum'_{i,j=1}^M \gamma_i^{\{n_i\}}(\mathbf{x}_1'|\mathbf{x}_1) \gamma_j^{\{n_j\}}(\mathbf{x}_2'|\mathbf{x}_2) \\ & - \sum_{i,j=1}^M \gamma_i^{\{n_i\}}(\mathbf{x}_1'|\mathbf{x}_2) \gamma_j^{\{n_j\}}(\mathbf{x}_2'|\mathbf{x}_1). \end{aligned} \quad (3.4)$$

It may be seen that the additive separation of the one-particle density matrix (3.3) is consistent with the ionic model since it indicates that the average value for the ground state of a one-particle operator is the sum of the average values for the electron groups. In addition, it is shown in the Appendix that the total electronic energy of the crystalline system, which is the average value of (3.1) evaluated by means of (3.3) and (3.4) may be expressed as a sum of the ionic self-energies and interaction potentials acting upon each ion of the form

$$V_C = V_M + V_X + V_S, \quad (3.5)$$

where V_M is the Madelung potential of the classical ionic theory, V_S is its short-range correction, and V_X is a short-range exchange potential. This result is again consistent with the ionic model and gives a realistic description of the interionic interactions in these materials.

With regard to the polarizability of an ionic crystal, (3.3) and (3.4) yield results which, once again, are in agreement with their empirically determined properties. As in the case of free ions, the ground state is the only one with an appreciable probability of being occupied at ordinary temperatures, so that the static electronic

polarization of the crystal, assuming that the electric field is in the x direction, is given by

$$\mathbf{P} = 2e^2 \mathcal{E}_L \sum_{\gamma'} |\langle \gamma | \mathbf{X} | \gamma' \rangle|^2 / E_{\gamma'\gamma}, \quad (3.6)$$

where \mathcal{E}_L is the effective local field and \mathbf{X} is the sum of the x coordinates of all the electrons in the crystal. In general, the following discussion will deal with materials which have no net electric dipole moments for the ground state, i.e.,

$$\langle \gamma | \mathbf{X} | \gamma \rangle = 0 \quad (3.7)$$

with identical relations for the y and z coordinates. This is a condition which holds for most ionic materials with the exception of ferroelectric or pyroelectric crystals. It is also a less restrictive condition than one requiring the ions to have spherical or inversion symmetry about their nuclear centers. It follows from (3.7) that since

$$\langle \gamma | \mathbf{X} | \gamma \rangle = \sum_{i=1}^M \int \mathbf{x}_i \gamma_i^{\{n_i\}}(\mathbf{x}_1|\mathbf{x}_1) d\mathbf{x}_1 = \sum_{i=1}^M \langle \gamma | X_i | \gamma \rangle,$$

where

$$X_i = \sum_{j=1}^{n_i} x_j,$$

then

$$\sum_{i=1}^M \langle \gamma | X_i | \gamma \rangle = 0, \quad (3.8)$$

so that the sum of the electric dipole moments of the ions must vanish. Making use of this result, the polarization (3.6) may be written

$$\mathbf{P} = (2e^2 \mathcal{E}_L / \bar{E}_{3s}) \langle \gamma | \mathbf{X}^2 | \gamma \rangle, \quad (3.9)$$

where \bar{E}_{3s} is the mean excitation energy of the third kind for the crystalline system.

It is now necessary to evaluate $\langle \gamma | \mathbf{X}^2 | \gamma \rangle$. This quantity may be written

$$\langle \gamma | \mathbf{X}^2 | \gamma \rangle = \sum_{i=1}^N \langle \gamma | x_i^2 | \gamma \rangle + \sum'_{i,j=1}^N \langle \gamma | x_i x_j | \gamma \rangle \quad (3.10)$$

which making use of (3.3) and (3.4) becomes

$$\begin{aligned} \langle \gamma | \mathbf{X}^2 | \gamma \rangle = & \sum_{i=1}^M \int \mathbf{x}_i^2 \gamma_i^{\{n_i\}}(\mathbf{x}_1|\mathbf{x}_1) d\mathbf{x}_1 \\ & + \sum_{i=1}^M \int \mathbf{x}_1 \mathbf{x}_2 \Gamma_i^{\{n_i\}}(\mathbf{x}_1 \mathbf{x}_2 | \mathbf{x}_1 \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \\ & + \sum'_{i,j=1}^M \int \mathbf{x}_1 \mathbf{x}_2 \gamma_i^{\{n_i\}}(\mathbf{x}_1|\mathbf{x}_1) \gamma_j^{\{n_j\}}(\mathbf{x}_2|\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \\ & - \sum'_{i,j=1}^M \int \mathbf{x}_1 \mathbf{x}_2 \gamma_i^{\{n_i\}}(\mathbf{x}_1|\mathbf{x}_2) \gamma_j^{\{n_j\}}(\mathbf{x}_2|\mathbf{x}_1) d\mathbf{x}_2 d\mathbf{x}_1. \end{aligned} \quad (3.11)$$

¹⁴ R. McWeeny, Rev. Mod. Phys. **32**, 335 (1960).

The first two terms of (3.11) comprise $\sum_{i=1}^M \langle \gamma | X_i^2 | \gamma \rangle$, the sum of the average values of the X_i^2 for the ionic groups. The third term is a double sum of terms of the form $\int \mathbf{x}_1 \gamma_i^{(n_i)}(\mathbf{x}_1 | \mathbf{x}_1) d\mathbf{x}_1 \int \mathbf{x}_2 \gamma_j^{(n_j)}(\mathbf{x}_2 | \mathbf{x}_2) d\mathbf{x}_2$ which is a product of the net dipole moments of the i th and j th ionic constituents. Such a sum equals zero for a material having no net dipole moment since in this case the terms are either all zero, corresponding to the situation where all the ionic dipole moments are zero, or can be cancelled pair wise, since for every term, another can be found having the same magnitude but opposite sign because of the inversion symmetry which exists in the crystal as a whole. The final term involves a sum of integral products of the type $\int \mathbf{x}_1 S_{ij}(\mathbf{x}_1) d\mathbf{x}_1 \int \mathbf{x}_2 S_{ij}(\mathbf{x}_2) d\mathbf{x}_2$, where $S_{ij}(\mathbf{x}_1)$ is an overlap integral for the ionic wave functions ψ_i and ψ_j in which the integration is over all coordinates except the only common one, \mathbf{x}_1 . Hence, $\int \mathbf{x}_1 S_{ij}(\mathbf{x}_1) d\mathbf{x}_1$ is analogous to an integral of the type $\int \mathbf{x}_1 \phi_i(\mathbf{x}_1) \phi_j(\mathbf{x}_1) d\mathbf{x}_1$ in one-electron theory. That such a sum of these integral products averages out to zero for a material having no net electric dipole moment may be seen in the following way. Since the crystal as a whole has inversion symmetry, for every positive contribution to an integral for a given ion, there is an

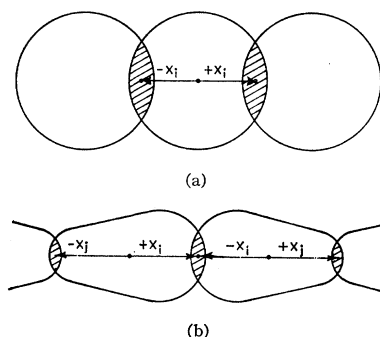


FIG. 1. Illustration of the cancellation of contributions to overlap integrals in crystals possessing inversion symmetry. Case (a) represents ions having inversion symmetry while case (b) represents ions which do not.

equal negative contribution to a similar integral. Figure 1(a) illustrates the case in which the ionic constituents have inversion symmetry and the nearest neighbors surrounding an ion are of the same type. Here it may be seen that points of equal overlap exist with ions of the same type at $+\mathbf{x}_i$ as well as $-\mathbf{x}_i$. For materials where the ions do not have inversion symmetry, the cancellation process involves the consideration of several ions as illustrated in one example in Fig. 1(b).

Making use of this result, (3.9) becomes

$$\mathbf{P} = (2e^2/\bar{E}_{3s}) \sum_i \mathcal{E}_i \langle \gamma | X_i^2 | \gamma \rangle, \quad (3.12)$$

where \mathcal{E}_i is the effective local field acting upon the i th ion. It may be seen that (3.12) completely parallels the result obtained in the discussion of the free ions and summarized in (2.11) and (2.12). Consequently, one may write

$$\mathbf{P} = 2e^2c \sum_i \alpha_i \mathcal{E}_i = 2e^2c \sum_i \mathcal{E}_i (n_i/\bar{E}_{1i}^2). \quad (3.13)$$

In the product approximation, then, the electronic polarization is given by the sum of the polarizations of the ionic constituents, a result which is in accord with experimental evidence for the ionic crystals.

One may conclude from this discussion that this formalism which completely distinguishes groups of electrons in ionic crystals yields results which are physically meaningful. The one serious shortcoming of a description based upon a single configuration product wave function, namely, that it cannot include a description of electron transport effects since all possible partitions of $N = n_1 + n_2 + \dots + n_M$ are not allowed is not a serious one, since these effects are negligibly if not immeasurably small in these materials and certainly do not contribute substantially to the polarizability.

IV. APPLICATION TO THE POLARIZABILITIES OF THE ALKALI HALIDES

The main motivation behind the use of this physical picture in the analysis of the electronic polarizabilities of ionic crystals lies in the attempt to circumvent, using (3.13), the extreme complexity of a direct solution of this problem. The use of (3.13) requires a means of determining both the local field at each ion as well as the \bar{E}_i 's. In the case of the alkali halide crystals, the Lorentz local field correction seems to be well established. Moreover, the close adherence of these materials to the classical ionic model makes possible a rather simple means of estimating the effect which the crystal potential has upon the atomic energy levels. From this, one may estimate the manner in which the \bar{E}_i 's calculated from the Pauling⁴ theoretical values for the free ions by means of (2.4) are changed when the ions are transported to their crystalline environment.

The effect of the crystal environment upon the atomic energy levels may be estimated by a semiclassical procedure which has been used by Seitz.¹⁵ The dominant contribution to the lattice potential (3.5) is the Madelung potential which at a negative ion site in an alkali halide crystal is given by

$$V_M = e\beta A_{\delta_0}/\delta_0, \quad (4.1)$$

where A_{δ_0} is the Madelung constant associated with the characteristic equilibrium separation δ_0 and β is the greatest common factor in the valences of the constituent ions. The potential at a positive ion is the negative of this. Neither the short-range correction to this potential nor the short-range exchange potential have large effects upon the ground state of an ion since the overlap with adjacent ions is not large. Consequently, it is reasonable to estimate that the ground state of a cation is raised with respect to the first ionization continuum by an amount eV_M and the ground state of an anion is lowered by the same amount.

Considering the cations in the crystal for the moment, one would expect the discrete excited states to be raised in a manner similar to the ground state. However, the

¹⁵ F. Seitz, J. Chem. Phys. **6**, 150, 454 (1938).

magnitude of the raising varies since the excited state probability amplitudes are much less localized than that of the ground state and, consequently, overlap adjacent sites to a much greater extent. This means that the short-range potentials begin to become appreciable in magnitude and both diminish the effect of the Madelung potential and, in the one-electron approximation, broaden the levels into quasicontinuous bands. The energy levels are raised less and less because in overlapping the adjacent ions more and more, the wave functions are less and less shielded by the electron clouds from the positive nuclei of the adjacent ions, and also are more strongly influenced by the positive charges of the next-nearest neighbor ions. The magnitude of the broadening is approximately equal to the short-range interaction, and results from the fact that as the wave function becomes less localized, it is subject in the lattice to more of a periodic potential. These considerations apply to all of the discrete and continuous excited states, including those associated with higher degrees of ionization.

The energy level picture for the anions is somewhat more complicated. In the case of the free anion, the first ionization corresponds to the removal of an excess electron, the energy required being the electron affinity of the free atom in the case of a singly charged ion, or of an anion with charge less by one in the case of a multiply charged ion. In the crystal, however, ionization corresponds to removal of the electron to a *distant* cation. von Hippel¹⁶ has shown that to a good approximation, this energy which we will call Δ can be obtained from classical considerations in the case of the alkali halides from a circular process involving the removal from the crystal of a cation to a point infinitely far from the crystal, the similar removal of an anion which is distant from the empty cation site, the transporting of an electron from the anion to the infinitely distant cation, creating in the process two free atoms, and the transporting of these atoms back to their respective lattice sites. The total energy involved in this process is given by

$$\Delta = 2e(V_M - V_R) + E - I + Q_a \quad (4.2)$$

where eV_M and eV_R are the Madelung and repulsive energies, respectively, E is the electron affinity of the halogen atom, I is the ionization potential of the alkali atom, and Q_a is the energy of interaction between the free atoms and the crystal environment.

It is evident that there are excited states which may be thought of as being those of the anion which are lower than this, energetically, speaking. These are the well-known excitation levels, the lowest of which corresponds classically to the transfer of an electron from an anion to a nearest neighbor cation. This state lies above the ground state by an amount $\Delta - e^2/r_0$, where r_0 is the nearest-neighbor separation, since the magnitude of the electrostatic potential at a cation site

is reduced by e/r_0 because of the absence of an electrically charged nearest neighbor. Other states corresponding to the transporting of an electron to more distant cations lie proportionately higher.

Detailed discussions of these levels which exist as quasicontinuous bands in the solid material have been given elsewhere.¹⁵ For the purposes of our discussion, however, it is important to note the relationship which these states have with free ion states. First, it may be seen that they have no real analog in the free anion, since the binding of the excess electrons is accomplished by means of a correlation potential which diminishes too rapidly to allow the existence of any discrete excited states. Consequently, these states merge into the first ionization continuum if the interionic separation is increased to infinity, i.e., the crystal is broken apart into its constituent ions. On the other hand, however, these states are analogous to atomic S , P , etc., functions,¹⁵ so that there is a similarity between the relationship of these states with the first continuum of levels of the anion and the lowest excited discrete states and the first continuum of levels of the cation in the crystal.

In order to estimate the changes in the ionic mean excitation energies in the crystal, one must have, in addition to a knowledge of the relationship between the energy levels in the free ion and those in the crystal, a knowledge of the relative contribution of all the excited states to the polarizability. While the exact contribution of all the various states is not known, in general, a quantitative consideration of the case of the hydrogen atom is useful for the purpose of estimating these various contributions. From the work on the Stark effect in hydrogen of Wentzel, Waller, and Epstein,¹⁷ the polarizability of the ground state is determined⁸ to be 0.663 \AA^3 . In addition, a simple calculation reveals that the contribution of the first excited state is 0.43 \AA^3 , with most of the remaining 0.23 \AA^3 being contributed by the continuum states. The mean excitation energies \bar{E}_1 , \bar{E}_2 , and \bar{E}_3 are equal to $0.47e^2/a_0$, $0.50e^2/a_0$, and $0.44e^2/a_0$, respectively. The fact that the mean excitation energies are all about equal to the ionization energy may be thought of as resulting from a situation in which, neglecting the contribution of the other discrete excited states, the first excited state, which gives about two thirds of the total contribution, lies below the ionization continuum by an amount equal to one quarter of the ionization energy, while the continuum levels, which contribute about one third of the total, may be thought of as balancing this contribution with a mean energy lying above the ionization energy by an amount equal to about half the ionization energy. These results are comparable to those for the hydrogen paramagnetic susceptibility,¹⁸ in which case the continuum contri-

¹⁷ G. Wentzel, Z. Physik **38**, 527 (1926); I. Waller, *ibid.* **38**, 635 (1926); P. S. Epstein, Phys. Rev. **28**, 695 (1926).

¹⁸ L. C. Snyder and R. G. Parr, J. Chem. Phys. **34**, 837 (1961).

¹⁶ A. von Hippel, Z. Physik **101**, 680 (1936).

bution is 43% of the total and the mean excitation energy is $0.67e^2/a_0$, the larger value being due to the somewhat larger contribution of the continuum levels.

With these facts at our disposal, we will proceed in the following somewhat heuristic manner: The change in the character of the ionic energy levels brought about by their crystalline environment will be estimated according to the above discussed procedure and the result for the hydrogen polarizability will be used as a prototype in order to estimate the relative weights to assign the levels in order to estimate the \bar{E}_1 's. The agreement of these results with those obtained empirically will then be taken as a measure of the validity of these assumptions. The cation and anion polarizabilities will now be discussed separately.

Cation Polarizabilities in Crystals

The discrete cation energy levels are raised with respect to the ionization continua above them by the effect of the crystal potential in a manner discussed previously. The energy levels above the first continuum correspond to those resulting from the successive stripping of electrons from the cation. The calculated values of the \bar{E}_1 's for the free ions from the Pauling polarizabilities indicate that, in general, the levels above the first continuum do not contribute substantially to the polarizability since the \bar{E}_1 's do not lie substantially above the first ionization energy. However, the following considerations apply to all the energy levels.

Since, to a first approximation, the ground state is raised with respect to the first continuum by an amount eV_M , one would expect that the continuum contribution to the mean excitation energy would be lessened by that amount. However, the contribution of the continuum is greater, in addition, because of the greater magnitude of the appropriate matrix elements in (2.1). This follows since the raising of the ground state, energetically, results in a greater extension in space of the ground state probability amplitude by an amount which varies roughly as the inverse of the binding energy. In the hydrogen atom, for example, the average value of the radius for a given quantum state, which may be taken as a measure of the extension of the wave function, is given by¹⁹

$$\bar{r}_{nlm} = (n^2 a_0 / Z) \left(1 + \frac{1}{2} \left[1 - \frac{l(l+1)}{n^2} \right] \right) \quad (4.3)$$

an expression which varies very nearly as the inverse of the binding energy of the state under consideration. Since the extension of the ground state is greater, its overlap with the continuum levels increases, thereby increasing the value of the corresponding matrix elements in (2.1).

The excited discrete states are also brought energeti-

cally closer to the ground state since they are raised by amounts somewhat less than eV_M . The lowest excited states, however, are brought closer to the ground state by the smallest amounts since they are energetically raised by the largest amounts. On the other hand, these states experience a considerably greater relative increase in the extension of their probability amplitudes than the ground state because their binding energies are so much smaller and the effect of the Madelung potential amounts to a large fraction of the total. As a result, one would expect the matrix elements in (2.1) associated with these states to diminish in value because the extremely large increase of the extensions of these states results in a much smaller effective overlap with the ground state. The higher discrete states, however, being energetically raised less and less, have the smallest change in their contribution to the polarizability, but are brought nearer to the ground state by an amount closer and closer to eV_M . Since the diminishing of the lower discrete state contributions more or less balances the fact that they are brought closer to the ground state by an amount less than eV_M , and since the continuum levels, which in the crystal probably contribute more than half of the total polarizability, are brought closer to the ground state by an amount eV_M , it seems reasonable to estimate that the mean excitation energy of the cation in the crystal is diminished by eV_M . Therefore, using (2.4), it may be seen that according to the above analysis, the relationship between the free cation polarizability α_p^+ and the value in crystal α_c^+ is given approximately by

$$\alpha_p^+ / \alpha_c^+ = (\bar{E}_p^+ - eV_M)^2 / (\bar{E}_p^+)^2. \quad (4.4)$$

Anion Polarizabilities in Crystals

The anions represent a somewhat different case than that previously described for the cations. First, the existence of the excitation levels provides a contribution to the anion polarizability in the crystal which has no counterpart in the free ion. In addition, unlike the condition which generally exists in the cations, quantum states above the first ionization continuum contribute substantially to the free anion polarizability. The \bar{E}_1 's calculated from the Pauling polarizabilities for the halogen ions usually lie considerably above the second ionization energy, i.e., the first ionization energy for the neutral atom, but somewhat below the third ionization energy. This means that there is a substantial contribution to the polarizability by the levels above the second continuum. The position of the \bar{E}_1 's suggests that the levels of the first continuum as one group, the levels of the second continuum as well as the discrete levels below them as a second group, and all the levels associated with higher degrees of ionization as a third group, contribute comparable amounts to the polarizability, with the levels of the first continuum contributing somewhat less than one-third of the total.

In the crystal, the ground state of the anion lies

¹⁹ L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935).

TABLE I. Pauling polarizabilities and \bar{E}_1 's calculated from them.

Ion	n	α_p (\AA^3)	\bar{E}_p (ev)
Li ⁺	2	0.029	86.2
Na ⁺	10	0.181	77.6
K ⁺	18	0.84	48.3
Rb ⁺	36	1.41	52.6
Cs ⁺	54	2.44	49.1
F ⁻	10	1.05	32.2
Cl ⁻	18	3.69	23.1
Br ⁻	36	4.81	28.4
I ⁻	54	7.16	28.7

below the first continuum by an amount Δ given by (4.2) rather than by an amount E , the electron affinity of the free atom. By an analysis similar to that for the cation and neglecting the excitation levels, the mean excitation energy for the anion is increased by an amount $\Delta - E$. However, the excitation levels exercise a strong diminishing influence upon the mean excitation energy. Considering their atomic character, particularly that of the lowest level, one would expect that, in line with the result for the hydrogen polarizability, these levels contribute an amount somewhat greater than that contributed by the levels of the first continuum or about one quarter of the total value of the anion polarizability in the crystal. Moreover, most of this contribution is from the lowest excitation level which lies $\Delta - e^2/r_0$ above the ground state. From this estimate then, the mean excitation energy of the anion in the crystal is given by

$$\bar{E}_c^- = \frac{1}{4} [(\Delta - e^2/r_0) + 3(\bar{E}_p^- + \Delta - E)] \quad (4.5)$$

so that the relationship between the free anion polarizability α_p^- and its value in the crystal α_c^- is given approximately by

$$\alpha_p^- / \alpha_c^- = \left[\frac{1}{4} \{ (\Delta - e^2/r_0) + 3(\bar{E}_p^- + \Delta - E) \} \right]^2 / (\bar{E}_p^-)^2. \quad (4.6)$$

The alkali halide crystals provide two means of checking the polarizabilities theoretically determined from (4.4) and (4.6) with the empirical data. In addition to the more obvious device of comparing the experimentally determined molar polarizability with

TABLE II. Calculated ionic polarizabilities for the alkali halides in units of \AA^3 . The first and second numbers give the cation and anion polarizabilities, respectively.

	F	Cl	Br	I
Li	0.04 0.69	0.04 2.44	0.04 3.93	0.04 6.38
Na	0.25 0.77	0.23 2.64	0.23 4.19	0.22 6.64
K	1.29 0.84	1.21 2.74	1.18 4.31	1.16 6.74
Rb	2.04 0.87	1.93 2.80	1.90 4.37	1.86 6.87
Cs	3.56 0.90	3.34 2.94	3.32 4.43	3.25 6.96

the sum of the anion and cation polarizabilities calculated from these relations, a comparison between the calculated polarizabilities and those deduced empirically by means of the additivity rule is possible. Since the polarizability of an ion varies with the crystalline environment, the arithmetic average of the calculated ionic polarizabilities will be compared with least square polarizabilities of TKS, which are based upon the additivity rule. The values of the Pauling polarizabilities and the mean excitation energies calculated from them which are necessary to perform the theoretical calculations are listed in Table I.

Table II lists the calculated ionic polarizabilities while Table III shows a comparison of the arithmetic

TABLE III. Comparison of the arithmetic averages (α) of the calculated ionic polarizabilities in the alkali halides and the mean excitation energies determined from them (\bar{E}_1) with the least square polarizabilities for infinite wavelength α_{TKS} and the mean excitation energies \bar{E}_{TKS} determined from them.

Ion	$\langle \alpha \rangle$ (\AA^3)	α_{TKS} (\AA^3)	$\langle \bar{E}_1 \rangle$ (ev)	\bar{E}_{TKS} (ev)
Li ⁺	0.04	a	76.7	a
Na ⁺	0.23	0.255	68.7	65.3
K ⁺	1.21	1.201	40.3	40.4
Rb ⁺	1.93	1.797	45.1	46.6
Cs ⁺	3.37	3.137	41.8	43.3
F ⁻	0.81	0.759	36.8	38.0
Cl ⁻	2.71	2.974	26.9	25.6
Br ⁻	4.25	4.130	30.2	30.7
I ⁻	6.70	6.199	29.7	30.9

* TKS used the Pauling free ion value for Li⁺.

averages of the calculated mean excitation energies and polarizabilities on the one hand, and the least square polarizabilities of TKS and the mean excitation energies calculated from them on the other. The Madelung and repulsive energies necessary to complete these calculations were obtained from the results of Sherman,²⁰ while the electron affinities and ionization potentials used are those quoted by Herzberg.²¹ Following von Hippel,¹⁶ the interaction energy Q_a necessary for the calculation of Δ is arbitrarily set equal to -1 ev for all cases. It may be seen that the average value of the calculated mean excitation energies all lie within 5% of those determined from the least square values of TKS, while the polarizabilities differ by less than 10%. In view of the fact that the Pauling polarizabilities are probably not accurate to better than 10%, the agreement is remarkable. Since the mean excitation energy is the quantity which is estimated, and since the polarizability varies with the inverse square of this quantity, so that the percent difference in the calculated and empirical polarizabilities is twice that occurring in the \bar{E}_1 's, a comparison of the empirical and calculated polarizabilities doubles the percent error in the estimation process. This fact should be kept in mind in

²⁰ J. Sherman, Chem. Rev. **11**, 93 (1932).

²¹ G. Herzberg, *Atomic Spectra and Atomic Structure* (Dover Publications, Inc., New York, 1944).

TABLE IV. Theoretical and experimental molar polarizabilities of the alkali halides in units of \AA^3 . The first number is the sum of the calculated ionic polarizabilities in Table II while the second is the experimental value given by TKS^a for infinite wavelengths. All of these values are for crystals with the NaCl structure.

	F	Cl	Br	I
Li	0.73	2.48	3.97	6.42
	0.909	2.903	4.137	6.225
Na	1.02	2.87	4.42	6.86
	1.162	3.263	4.387	6.263
K	2.13	3.95	5.49	7.90
	2.007	4.172	5.294	7.388
Rb	2.91	4.73	6.27	8.73
	2.528	4.712	5.920	8.092
Cs	4.46	6.28	7.75	10.21
	3.604	6.235	7.328	9.436

^a See reference 2.

comparing the calculated and experimentally determined polarizabilities.

The theoretical and experimental molar polarizabilities displayed in Table IV likewise show good agreement, with a few exceptions. These exceptions lend some insight in the limitations of the simple theory expressed by (4.4) and (4.6). For example, the calculated polarizability of CsF is much too large. A glance at Table II reveals that this is because the calculated polarizability of Cs^+ almost equals the empirical molar polarizability for CsF. The too-large calculated value for the polarizability of Cs^+ in CsF may be attributed to the fact that the size of the Cs^+ ion is significantly greater than that of the F^- ion, as measured by their ionic radii. This is a situation which is contrary to the normal condition in which the cation size is roughly the same or smaller than that of the anion.²² As a result, the Cs^+ ion overlaps the nearest-neighbor F^- ions and the next-nearest-neighbor Cs^+ ions to a much greater extent than is usually the case. One would expect this situation to result in the mean excitation energy of the Cs^+ ion being diminished by an amount less than eV_M so that its polarizability is closer to that of the free ion. The value of the experimental molar polarizability seems to confirm this expectation. Similarly, this situation applies to a lesser extent in RbF.

A more common situation arises when the anion size is significantly larger than that of the cation. This is true in all the lithium halides, and to a lesser degree, in the sodium halides. In this case, several factors complicate the estimation of the ionic polarizabilities. On the one hand, the greater overlapping of the cation sites by the anions results in a lessening of the amount by which the ground states of each are respectively raised and lowered in comparison to the predicted amount eV_M . Since the cation polarizabilities in these cases are small relative to those of the anions, most of the deviation from the predicted value is due to the

deviation in the anion polarizability. The effect of the increased overlapping is to make the quantity Δ smaller than calculated so that the anion polarizability is larger than predicted. This is apparently the case in LiF. On the other hand, when the disparity in sizes of the anion and cation becomes very great, as in the extreme case of LiI where the anions are more than large enough to achieve mutual contact, the anion-cation separation is larger than it would be otherwise, since the anion-anion repulsion does not allow actual contact as measured by the ionic radii between the anion and cation. This factor limits the overlap between the anion and cation and offsets the lessening of Δ according to the above analysis. The agreement of the calculated and empirical polarizabilities of LiI seems to confirm this expectation. The other lithium halides offer intermediate examples between these two extremes. It is apparent, then, that Eqs. (4.4) and (4.6) give their best results in those cases when the ions have approximately the same sizes, although, in general, the deviations are most serious when the cation size is significantly larger than that of the anion.

V. DISCUSSION

The analysis of the previous two sections has attempted to arrive at a quantitative estimate of the electronic polarizabilities of ions in alkali halide crystals through a process of estimating their mean excitation energies. This process requires a knowledge of the free ion polarizabilities as well as a reasonably accurate means of determining the effect of the crystalline interaction on the ionic energy levels. In the last section, it was shown that this process works quite well in the alkali halides and is able to account for most of the main quantitative features of their polarizabilities. It is evident from this result that the additivity rule works in the alkali halides because the crystalline interactions in these materials are qualitatively the same, the small variations in their magnitudes in the various crystals producing changes in the anion and cation polarizabilities which very nearly cancel each other. It is only in the fluorides, where the great disparity in the sizes of the cations in comparison with the fluoride ion as well as with each other cause qualitative changes in the interaction, that the additivity rule breaks down to a significant extent.

While this analysis would not be expected to yield consistently good quantitative results for other ionic crystals, which depart somewhat more from the perfect ionic model, certain qualitative observations can be made. For example, a large class of ionic materials have Madelung energies which are much larger than those of the alkali halides because of the larger valences of the ionic constituents. As a result, the polarizabilities of the ions can be altered drastically from their free ion values in some cases. The relations (4.4) and (4.6) probably represent upper limits to the amount that the

²² For a pictorial comparisons of the sizes of the various ions, the reader is referred to L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1948).

cation and anion polarizabilities are raised and lowered, respectively, since the greater overlapping of the ions which occurs in these crystals in comparison with the alkali halides diminishes the effect of the Madelung potential. In particular, the anion polarizability could vary greatly from such a predicted value for two reasons. First, the greater overlapping in most crystals in comparison with the alkali halides involves, at least in part, an incomplete ionization of the cation which corresponds to a mixing of the excitation levels with the ground state of the anion. This means that these levels lie closer to the ground state than would be measured by the classical analysis of the last section. Second, in materials which have a considerably higher Madelung energy than the alkali halides because of the larger valences of the ionic constituents, the contributions of the groups of energy levels above the first continuum probably differ from those assumed in the previous section and which seem to apply to the alkali halides. Since the ground state of the anion is lowered by an amount which is comparable to or greater than the energetic separation between the first and second continua, the relative contributions of the higher excited states is lessened, and that of the excitation levels and first continuum increased. These factors would both tend to make the anion polarizability larger than that which would be obtained by the analysis of the previous section. The cation polarizabilities are less affected in this way by the Madelung potential because, unlike the situation which exists in the anions, the separation between the first continuum and the higher excited states is usually large compared to eV_M . Although the ionic polarizabilities may differ somewhat from the values which would be predicted by the considerations of the previous section, it is evident

that the larger Madelung potentials of some materials could cause changes in the free ion polarizabilities, particularly those of the cations, by a factor of two or three or more.

From this, one may see the possible origin of some of the large deviations from the additivity rule. In some cases, the amounts of the raising and lowering, respectively, of the cation and anion polarizabilities probably do not cancel, even approximately, in many crystals, particularly if the amounts are large. Moreover, these amounts, themselves, probably vary to a great extent depending upon the quality of the interaction in the crystal.

One may see that these conclusions differ greatly with the usual view regarding the polarizabilities of ions in crystals. First, the additivity rule, itself, is seen in the light of this analysis as an accidental result of the qualitative similarity of the crystalline interactions in various materials which influence the value of the ionic polarizabilities. Moreover, this analysis presents the possibility of large fluctuations in the polarizability of any given ion in different crystalline environments as opposed to the view, implicit in the additivity rule, that the polarizability of a given ion varies little from crystal to crystal. While the accidental validity of the additivity rule has been of great value in considerations involving the polarizabilities of ionic crystals, it is hoped that the conclusions of this work will be of similar value in future considerations of this type.

APPENDIX A. COMPARISON OF THE MEAN EXCITATION ENERGIES

A specific comparison of the mean excitation energies, \bar{E}_1 , \bar{E}_2 , and \bar{E}_3 defined by (2.4), (2.7), and (2.8) is possible since it follows from these equations that

$$c^2/\bar{E}_2^2 = \sum_{\gamma', \gamma''} |\langle \gamma | X | \gamma' \rangle|^2 |\langle \gamma | X | \gamma'' \rangle|^2, \quad (\text{A1})$$

$$c^2/\bar{E}_1^2 = \sum_{\gamma', \gamma''} (E_{\gamma''\gamma} / E_{\gamma'\gamma}) |\langle \gamma | X | \gamma' \rangle|^2 |\langle \gamma | X | \gamma'' \rangle|^2, \quad (\text{A2})$$

$$c^2/\bar{E}_3^2 = \frac{\sum_{\gamma', \gamma'', \gamma''', \gamma^{iv}} (E_{\gamma'''\gamma} E_{\gamma^{iv}\gamma} / E_{\gamma'\gamma} E_{\gamma''\gamma}) |\langle \gamma | X | \gamma' \rangle|^2 |\langle \gamma | X | \gamma'' \rangle|^2 |\langle \gamma | X | \gamma'' \rangle|^2 |\langle \gamma | X | \gamma^{iv} \rangle|^2}{\sum_{\gamma', \gamma''} |\langle \gamma | X | \gamma' \rangle|^2 |\langle \gamma | X | \gamma'' \rangle|^2}. \quad (\text{A3})$$

These quantities are not the same, since $(E_{\gamma''\gamma} / E_{\gamma'\gamma})$ and $(E_{\gamma'''\gamma} E_{\gamma^{iv}\gamma} / E_{\gamma'\gamma} E_{\gamma''\gamma})$ cannot be replaced by unity.

A term by term comparison of (A1) and (A2) reveals that $2|\langle \gamma | X | \gamma' \rangle|^2 |\langle \gamma | X | \gamma'' \rangle|^2$ in (A1) corresponds to $[(E_{\gamma''\gamma} / E_{\gamma'\gamma}) + (E_{\gamma'\gamma} / E_{\gamma''\gamma})] |\langle \gamma | X | \gamma' \rangle|^2 |\langle \gamma | X | \gamma'' \rangle|^2$ in (A2). When the ratio $t = (E_{\gamma''\gamma} / E_{\gamma'\gamma})$ is not much greater than unity then $t+1/t \approx 2$. Consequently, the

majority of the terms in the two series are approximately equal. However, when $t > 2$, then the coefficient $t+1/t$ becomes substantially larger than 2. In an extreme case, one might find a situation in which terms having a $t \geq 10$ give substantial contributions to the series. If these large contributions do not have opposite signs, it is conceivable that \bar{E}_1^2 and \bar{E}_2^2 could differ by a factor of 2 or 3, and since $\bar{E}_3/\bar{E}_2 = (\bar{E}_1/\bar{E}_2)^2$, \bar{E}_2^2

and \bar{E}_3^2 could differ by an order of magnitude. Generally, however, one would expect these quantities to differ by amounts smaller than this.

APPENDIX B. THE INTERIONIC INTERACTION IN THE PRODUCT APPROXIMATION

The total electronic energy equals the average value of the Hamiltonian (3.1), which making use of (3.3) and (3.4) may be expressed as a sum of the kinetic energy E_k , the Coulomb energy E_c , and the exchange energy between ions E_x , where

$$E_k = \frac{1}{2m} \sum_i \int \mathbf{p}_1^2 \gamma_i^{(n_i)}(\mathbf{x}_1' | \mathbf{x}_1) d\mathbf{x}_1, \quad (\text{B1})$$

$$E_c = \frac{e^2}{2} \sum_{i,j}' Z_i Z_j / r_{ij} - e^2 \sum_{i,j} Z_i \int (1/r_{ij}) \gamma_j^{(n_j)}(\mathbf{x}_1 | \mathbf{x}_1) d\mathbf{x}_1 \\ + \frac{e^2}{2} \sum_{i,j}' \int (1/r_{12}) \gamma_i^{(n_i)}(\mathbf{x}_1 | \mathbf{x}_1) \gamma_j^{(n_j)}(\mathbf{x}_2 | \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \\ + \frac{e^2}{2} \sum_i \int (1/r_{12}) \Gamma_i^{(n_i)}(\mathbf{x}_1 \mathbf{x}_2 | \mathbf{x}_1 \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2, \quad (\text{B2})$$

$$E_x = -\frac{e^2}{2} \sum_{i,j}' \int (1/r_{12}) \gamma_i^{(n_i)}(\mathbf{x}_1 | \mathbf{x}_2) \\ \times \gamma_j^{(n_j)}(\mathbf{x}_2 | \mathbf{x}_1) d\mathbf{x}_1 d\mathbf{x}_2. \quad (\text{B3})$$

A form of E_c more in line with the ionic picture may be exhibited by making the following substitution: Let Q_i be designated as the total charge of the electrons associated with the i th lattice site and given by $\int \gamma_i^{(n_i)}(\mathbf{x}_1 | \mathbf{x}_1) d\mathbf{x}_1$; then the Coulomb potential of these electrons at the point j given by $\int (1/r_{ij}) \gamma_i^{(n_i)}(\mathbf{x}_1 | \mathbf{x}_1) d\mathbf{x}_1$ may be set equal to the quantity $Q_i/r_{ij} - V_i(j)$, where Q_i/r_{ij} is the point charge potential and $V_i(j)$ is a short-range correction which accounts for the extension and deformation from spherical symmetry of the charge cloud. Making use of these relations, E_c may be written

$$E_c = \frac{e^2}{2} \sum_{i,j}' (Z_i - Q_i)(Z_j - Q_j) / r_{ij} + \frac{e^2}{2} \sum_{i,j}' (2Z_i - Q_i) V_j(i) \\ - \frac{e^2}{2} \sum_{i,j}' \int \gamma_i^{(n_i)}(\mathbf{x}_1 | \mathbf{x}_1) V_j(\mathbf{x}_1) d\mathbf{x}_1 \\ - e^2 \sum_i Z_i \int (1/r_{1i}) \gamma_i^{(n_i)}(\mathbf{x}_1 | \mathbf{x}_1) d\mathbf{x}_1 \\ + \frac{e^2}{2} \sum_i \int (1/r_{12}) \Gamma_i^{(n_i)}(\mathbf{x}_1 \mathbf{x}_2 | \mathbf{x}_1 \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2. \quad (\text{B4})$$

The first term is the Madelung energy of the classical ionic theory, the next two terms are its short-range

corrections, while the last two terms give the electrostatic self-energy of the ions.

The exchange energy E_x introduces a correlation between electrons of different ions having the same spin by modifying their energy of mutual repulsion. As in one electron theory, the short-range exchange integrals are non-negligible only when the overlap of the ionic probability amplitudes is appreciable. In this case, the even parity of the unperturbed ionic wave functions results in positive definite overlaps, yielding a negative exchange energy which keeps electrons of different ions apart.

It is apparent that (B1), (B3), and (B4) may be thought of as being composed of the sum $\sum_{i=1}^M E_0^i$ of the ionic self-energies, where

$$E_{0i} = \frac{1}{2m} \int \mathbf{p}_1^2 \gamma_i^{(n_i)}(\mathbf{x}_1' | \mathbf{x}_1) d\mathbf{x}_1 \\ - e^2 Z_i \int (1/r_{1i}) \gamma_i^{(n_i)}(\mathbf{x}_1 | \mathbf{x}_1) d\mathbf{x}_1 \\ + \frac{e^2}{2} \int (1/r_{12}) \Gamma_i^{(n_i)}(\mathbf{x}_1 \mathbf{x}_2 | \mathbf{x}_1 \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2, \quad (\text{B5})$$

and the sum $\sum_{i=1}^M V_c^i$, where V_c^i is the effective crystal potential acting upon the i th ion. V_c^i is the sum of the Madelung potential V_M^i , its short-range correction V_S^i , and the short-range exchange potential V_X^i , where

$$V_M^i = \frac{e^2}{2} \sum_{j \neq i} (Z_j - Q_j) / r_{ij}, \quad (\text{B6})$$

$$V_S^i = \frac{e^2}{2} \sum_{j \neq i} (2Z_j - Q_j) V_j(i) \\ - \frac{e^2}{2} \sum_{j \neq i} \int \gamma_j^{(n_j)}(\mathbf{x}_1 | \mathbf{x}_1) V_j(\mathbf{x}_1) d\mathbf{x}_1, \quad (\text{B7})$$

$$V_X^i = -\frac{e^2}{2} \sum_{j \neq i} \int (1/r_{12}) \gamma_i^{(n_i)}(\mathbf{x}_1 | \mathbf{x}_2) \\ \times \gamma_j^{(n_j)}(\mathbf{x}_2 | \mathbf{x}_1) d\mathbf{x}_1 d\mathbf{x}_2. \quad (\text{B8})$$

APPENDIX C. CORRELATION OF THE IONIC SIZES AND THEIR POLARIZABILITIES

If one uses the magnitude of R for a measure of the extension of an ion where $R^2 = \langle \gamma | X^2 | \gamma \rangle + \langle \gamma | Y^2 | \gamma \rangle + \langle \gamma | Z^2 | \gamma \rangle$, then it follows from (2.7) that

$$R^2 = nc / \bar{E}_2. \quad (\text{C1})$$

From (2.4), it may be seen that

$$\alpha / R^4 = (2e^2 / nc) (\bar{E}_2^2 / \bar{E}_1^2), \quad (\text{C2})$$

and the ratios of the polarizabilities of two ions is

given by

$$\frac{\alpha_1}{\alpha_2} = \left(\frac{R_1^4 n_2}{R_2^4 n_1} \right) \left(\frac{\bar{E}_2^2(1)/\bar{E}_1^2(1)}{\bar{E}_2^2(2)/\bar{E}_1^2(2)} \right). \quad (C3)$$

It is evident that if the ratio

$$\frac{\bar{E}_2^2(1)/\bar{E}_1^2(1)}{\bar{E}_2^2(2)/\bar{E}_1^2(2)} \approx 1, \quad (C4)$$

then

$$\frac{\alpha_1}{\alpha_2} \approx \frac{R_1^4 n_2}{R_2^4 n_1}. \quad (C5)$$

One may conclude from (C5) that it is possible to obtain a rough comparison of the relative magnitudes of the polarizabilities of the constituents of a crystal if one has available an estimate of their relative extensions from, for example, a Fourier projection obtained from x-ray data. This technique has applicability even in crystals which are primarily molecular or covalent in nature which, though well represented by the product approximation, have crystalline potentials which are too complicated in nature to make possible an estimate of the \bar{E} 's.

Quadrupole Antishielding Factors of Ions*

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Values of the quadrupole antishielding factor γ_∞ have been calculated for the Mn^{2+} , Fe^{3+} , Ga^{3+} , and Ag^+ ions, using the method of direct solution of the inhomogeneous Schrödinger equation for the perturbed wave functions. For the Fe^{3+} ion, the present value of γ_∞ ($= -9.14$) is appreciably larger in magnitude than that previously obtained by Burns and Wikner, resulting in a decrease of the calculated quadrupole moment of Fe^{57m} as deduced from measurements using ferric compounds. The resulting value of $Q(Fe^{57m})$ is $+0.28 \times 10^{-24} \text{ cm}^2$.

I. INTRODUCTION

VALUES of the quadrupole antishielding factor¹⁻³ have been recently calculated for the following ions: Mn^{2+} , Fe^{3+} , Ga^{3+} , and Ag^+ , using the method of direct solution of the inhomogeneous Schrödinger equation for the perturbed wave functions which has been previously employed by the author.¹⁻³ The unperturbed wave functions used in this work were the Hartree-Fock functions for the four ions considered.⁴⁻⁶

As has been discussed previously,¹⁻³ the contribution $\gamma_\infty(nl \rightarrow l)$ due to the radial modes of excitation of the nl shell is given by

$$\gamma_\infty(nl \rightarrow l) = C_{ll}^{(2)} \int_0^\infty u_0' u_1' r^2 dr, \quad (1)$$

where u_0' is r times the radial unperturbed wave func-

tion, u_1' is r times the radial part of the perturbation of the wave function due to the field of the nuclear quadrupole moment Q ; u_1' is determined by the equation:

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_0 - E_0 \right] u_1'(nl \rightarrow l) = u_0' \left(\frac{1}{r^3} - \left\langle \frac{1}{r^3} \right\rangle_{nl} \right), \quad (2)$$

and by the orthogonality condition:

$$\int_0^\infty u_0' u_1' dr = 0. \quad (3)$$

In Eq. (1), $C_{ll}^{(2)}$ represents the factor which arises from the integration over the angular variables and the summation over the magnetic substates. For a completed p shell, we have $C_{11}^{(2)} = 48/25$, whereas for a completed d shell, $C_{22}^{(2)} = 16/7$. For the cases of Mn^{2+} and Fe^{3+} , where the $3d$ shell is half-filled, we have $C_{22}^{(2)} = 8/7$. The function u_0' is normalized to 1:

$$\int_0^\infty u_0'^2 dr = 1. \quad (4)$$

In Eq. (2), V_0 and E_0 are the unperturbed effective potential and energy eigenvalue, respectively, pertain-

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