

## Theory of Dielectric Constants of LiF†

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(Received January 8, 1960)

The static and high-frequency dielectric constants and the effective charge of LiF are calculated on the basis of a simplified model in which the polarizability of the positive ion is neglected and that of the negative ion is attributed entirely to perturbations in the outermost subshell ( $2p$ ) of electrons. The present calculation differs from the variational treatment of Yamashita mainly in the inclusion of perturbed wave functions for the  $2p$  electrons which are orthogonal to the core-electron wave functions. Also, different methods are employed in evaluating portions of the energy of the crystal in a field and in deducing the effective charge ratio  $e^*/e$  from the calculated energy. It is found that the use of trial wave functions which preserve the orthogonality within individual ions is of prime importance, and leads to results in generally better agreement with observation than the previously used nonorthogonal functions.

## I. INTRODUCTION

It has been pointed out by Brown<sup>1</sup> that the complete theory of dielectrics involves the simultaneous consideration of quantum theory, statistical mechanics, and many-body electrostatic interactions. Any one of these factors alone gives considerable difficulty; a treatment including any two of them is at present the best one can hope to pursue with some success. In the case of ionic crystals, it is usual to neglect temperature effects (the dielectric constants change only by several hundredths percent per degree<sup>2</sup>), and proceed to an approximate theory which takes account of one or both of the other complicating factors in a crystal at absolute zero. Although the theory of dielectric constants of ionic crystals has received much attention from this point of view, no completely satisfactory treatment has yet been given.

The simple classical theory considers only one of the complicating factors, the many-body interactions. The furthest advance of this approach is represented by the well-known Szigeti equation,<sup>3</sup> which relates the high-frequency dielectric constant  $\epsilon_\infty$ , the static dielectric constant  $\epsilon_0$ , and the rest-strahlen frequency  $\nu_t$ . For a lattice of singly-charged ions of reduced mass  $M$ , this important relation may be written

$$\epsilon_0 - \epsilon_\infty = \left( \frac{\epsilon_\infty + 2}{3} \right)^2 \frac{N(e^*)^2}{\pi \nu_t M}, \quad (1)$$

where the quantity  $e^*$  appears in place of the net ionic charge  $e$ . In the classical theory, the magnitude of  $e^*$  is determined empirically from known values  $\epsilon_0$ ,  $\epsilon_\infty$ , and

$\nu_t$ , in accordance with this equation; no independent determination of  $e^*$  is possible on strictly classical grounds. The ratio  $e^*/e$  is less than unity for all alkali halides of the NaCl structure. When  $e^*$  is interpreted as the "effective charge" that is displaced with the center of mass of an ion, it becomes clear that the simple classical theory fails in its inability to treat quantitatively the electronic redistributions that accompany relative displacements of neighboring ions.

The failure of the classical theory necessitates introduction of the second complicating factor—quantum theory. Recently, Dick and Overhauser<sup>4</sup> treated the alkali halides semiclassically, using a "spring" model for the ions and obtaining the interactions of nearest neighbors by extrapolation of the quantum-mechanical results for the interaction energy of two helium atoms to other closed-shell configurations. While the method presents considerable improvement over the simple classical theory, in that it provides explicit description of the ionic deformations and also incorporates quantum effects connected with the overlapping of electron clouds, several factors limit its effectiveness: A number of broad assumptions and some rather rough approximations must be made in deriving the constants for the model ions, in characterizing the near-neighbor interactions and in taking account of various polarization mechanisms. Yet, only the ratio  $e^*/e$  (and the compressibility, which does not enter the present discussion) have been evaluated, and not the dielectric constants themselves.

Because of these difficulties, it appears that an approach based entirely on quantum-theoretical methods is required to place the theory on a firm foundation. That this is a difficult task probably accounts in large measure for the dearth of work along these lines. The only quantum-mechanical treatment of dielectric con-

† Based on a thesis submitted to the Graduate Council of Temple University (by E. R. L.) in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

<sup>1</sup> W. F. Brown, Jr., *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. XVII, p. 20.

<sup>2</sup> A. Eucken and A. Büchner, *Z. physik. Chem.* **27**, 321 (1934).

<sup>3</sup> B. Szigeti, *Trans. Faraday Soc.* **45**, 155 (1945).

<sup>4</sup> B. G. Dick, Jr., and A. W. Overhauser, *Phys. Rev.* **112**, 90 (1958).

stants to date is the variational calculation for LiF and MgO by Yamashita.<sup>5</sup> He describes the distortion of the ions in the presence of an applied field by assuming a simple form for changes of the electronic wave functions. Several points in this treatment are open to question, the most important being that the wave functions employed do not fulfill the tacitly assumed condition of orthogonality among the atomic orbitals associated with a given ion. It is well known that such a situation often leads to large errors in the calculated energy of a system. While Yamashita's results suggest that his calculation is not seriously in error, it is of considerable interest to know the extent to which the orthogonality of the wave functions influences the calculation. The present paper is intended primarily to elucidate this aspect of the theory.

A new calculation for LiF, following the general lines of Yamashita's variational method, is presented. The energy of the crystal in an applied field has been completely re-evaluated, rather than amended to take account of the nonorthogonality of the Yamashita wave functions. Different methods, believed to give a truer accounting of the nearest-neighbor interactions, are employed to obtain the energy, and several energy contributions neglected in the earlier treatment have been included. The energy calculation, which is of central importance, is described in Sec. II. Then, in Sec. III, the dielectric constants and the effective charge are deduced from the resulting energy expression.

## II. ENERGY CHANGE IN AN ELECTRIC FIELD

We consider the LiF crystal a lattice of  $F^-$  and  $Li^+$  ions. In the absence of an externally applied field, the ions are all spherically symmetric, centered at the normal lattice sites. The electrons are described by atomic orbitals (AO) of the central field type: for the  $Li^+$  1s and  $F^-$  1s, 2s orbitals we used the analytical functions of Löwdin,<sup>6</sup> which closely approximate the Hartree free-ion functions; for the  $F^-$  2p orbitals we employed the radial function given by Yamashita.<sup>7</sup> All of these radial wave functions may be expressed as

TABLE I. Radial wave functions for  $F^-$  and  $Li^+$ .  
 $P_{nl}(r) = r \sum_k A_k \exp(-\alpha_k r) + r^2 \sum_k B_k \exp(-\beta_k r)$ .

AO		$k=1$	$k=2$	$k=1$	$k=2$	$k=3$
$Li^+(1s)$	$\alpha_k$	2.4346	4.4250			
	$A_k$	6.6641	2.5618			
$F^-(1s)$	$\alpha_k$	8.1890	12.187			
	$A_k$	40.285	9.5770			
$F^-(2s)$	$\alpha_k$	7.1485		$\beta_k$	1.6465	2.7178
	$A_k$	11.755		$B_k$	-1.3054	-8.7816
$F^-(2p)$				$\beta_k$	3.05	1.25
				$B_k$	11.07	1.05

<sup>5</sup> J. Yamashita, Progr. Theoret. Phys. (Kyoto) 8, 280 (1952).

<sup>6</sup> P. O. Löwdin, Phys. Rev. 90, 120 (1953).

<sup>7</sup> J. Yamashita, J. Phys. Soc. Japan 7, 284 (1952).

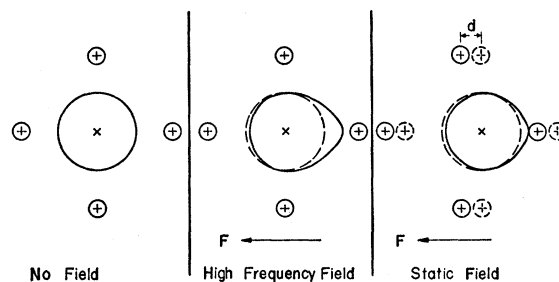


FIG. 1. Polarization of crystal (schematic).

sums of exponentials in the form

$$P_{nl}(r) = r \sum_k A_k e^{-\alpha_k r} + r^2 \sum_k B_k e^{-\beta_k r}. \quad (2)$$

The constants  $A_k$ ,  $\alpha_k$ , etc., are given in Table I.

When a field is applied to the crystal, the electron distributions about the nuclei are altered and the ions have induced dipole moments. We neglect the distortion of  $Li^+$  ions, in view of the fact that their polarizability is 30 to 40 times smaller than that of the larger  $F^-$  ions.<sup>8,9</sup> In a high-frequency (optical) field, the entire polarization of the crystal then results from the  $F^-$ -ion distortion dipole moments; in a static (or low-frequency) field, relative displacement of the positive- and negative-ion lattices gives rise to an additional polarization component. We can consider that the negative ions remain fixed in position while all the positive ions are displaced a distance  $d$  in the direction of the field, as illustrated schematically in Fig. 1. The distortion of the  $F^-$  ion in a static field is expected to be smaller than the corresponding distortion in a high-frequency field, because the displacement of the positive- and negative-ion centers towards each other reduces the space available for distortion. This results in an effective charge that is less than unity.

The polarizability of the  $F^-$  ion is assumed to arise entirely from alterations of the 2p orbitals, which are given (without spin) by the trial functions

$$\psi_n = Y_n - u_{1s} \langle 1s | Y_n \rangle - u_{2s} \langle 2s | Y_n \rangle, \quad (3)$$

where  $u_{1s}$  and  $u_{2s}$  are the  $F^-$  1s, 2s orbitals, respectively, and

$$\langle 1s | Y_n \rangle \equiv \int u_{1s} Y_n d\tau; \quad \langle 2s | Y_n \rangle \equiv \int u_{2s} Y_n d\tau.$$

The functions  $Y_n$  are, in turn, given by

$$\begin{aligned} Y_1 &= \psi_1^0 (1 + \lambda r \cos \theta) = [P_{2p}(r)/r] \cos \theta (1 + \lambda r \cos \theta), \\ Y_2 &= \psi_2^0 (1 + \lambda r \cos \theta) \\ &= [P_{2p}(r)/r] \sin \theta \cos \phi (1 + \lambda r \cos \theta), \end{aligned} \quad (4)$$

$Y_3 = \psi_3^0 (1 + \lambda r \cos \theta) = [P_{2p}(r)/r] \sin \theta \sin \phi (1 + \lambda r \cos \theta)$ , where the  $\psi_n^0$  are the  $F^-$  2p orbitals in the normal

<sup>8</sup> L. Pauling, Proc. Roy. Soc. (London) A114, 181 (1927).

<sup>9</sup> J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. 92, 890 (1953).

crystal (no field) and  $\lambda$  is a variational parameter; the polar ( $\theta$ ) axis is antiparallel to the applied field. The  $Y_n$  are the variational wave functions employed by Yamashita. While they are orthogonal to each other, one of them,  $Y_1$ , is not orthogonal to  $u_{1s}$  or  $u_{2s}$ . The function  $\psi_1$  [ $n=1$ , Eq. (3)], constructed from  $Y_1$  according to well-known procedures,<sup>10</sup> restores the orthogonality within the  $F^-$  ion. It is to be noted that  $Y_2$  and  $Y_3$  are orthogonal to  $u_{1s}$  and  $u_{2s}$ , so that  $\psi_2=Y_2$  and  $\psi_3=Y_3$ . In what follows, the function  $Y_n$  will be termed the "nonorthogonal wave function," and the  $\psi_n$  the "orthogonal wave function."

The Hamiltonian of a crystal in an applied field may be written

$$H=H_0+V, \quad (5)$$

where  $H_0$  is the Hamiltonian in absence of a field and  $V$  is the operator for potential energy due to the field. If the field is uniform over the crystal and acts in the  $x$  direction,

$$V=-eF(\sum_{\alpha} Z_{\alpha} x_{\alpha}-\sum_i x_i), \quad (6)$$

where  $x_{\alpha}$  designates the  $x$  coordinate of the nucleus  $\alpha$ , and  $x_i$  that of the  $i$ th electron. Since all the wave functions are AO centered on the ionic nuclei, it is meaningful to separate  $H_0$  as

$$H_0=H_{se}+H_{coh},$$

$$H_{se} \equiv \sum_{\alpha} \sum_i^{\alpha} \left( -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Z_{\alpha} e^2}{r_{i\alpha}} + \frac{e^2}{2} \sum_{j \neq i}^{\alpha} \frac{1}{r_{ij}} \right), \quad (7)$$

$$H_{coh} \equiv \sum_{\alpha} \left[ \sum_{\beta} \frac{Z_{\alpha} Z_{\beta} e^2}{r_{\alpha\beta}} + e^2 \sum_i^{\alpha'} \left( -\frac{Z_{\alpha}}{r_{i\alpha}} + \frac{1}{2} \sum_j^{\alpha} \frac{1}{r_{ij}} \right) \right], \quad (8)$$

where  $\sum_i^{\alpha}$  denotes summation over only those electrons which occupy AO associated with the nucleus  $\alpha$ , and  $\sum_i^{\alpha'}$  indicates summation over all electrons except those occupying AO associated with nucleus  $\alpha$ . Then  $H_{se}$  [Eq. (7)] contains only operators associated with interactions within individual ions, and leads to the self-energy of the ions;  $H_{coh}$  [Eq. (8)] contains all the interactions between different ions, and leads to the cohesive energy of the crystal; similarly,  $V$  [Eq. (6)] gives the interaction of the lattice with the field—the "field energy." The energy per ion pair resulting from application of the field can be conveniently discussed in terms of these three contributions.

### (1) The Field Energy

The total crystal energy arising from the partial Hamiltonian  $V$  [Eq. (6)] is

$$E_F = -F \sum_{\alpha} \left[ e(Z_{\alpha} - n_{\alpha}) x_{\alpha} - e \sum_i^{\alpha} \int \psi_i^* x_i \psi_i d\tau \right], \quad (9)$$

where  $n_{\alpha}$  is the number of electrons associated with the nucleus  $\alpha$ ,  $Z_{\alpha}$  is the atomic number of the nucleus, and  $\psi$  is the total crystal wave function (a Slater determinant of the one-electron wave function in the presence of a field). Since all the ions are singly charged, and the positive- and negative-ion lattices are displaced relatively by a distance  $d$  from their normal positions, the first term in brackets [ ] of (9) gives rise to an average displacement dipole moment  $ed$  per ion pair. Identifying the second term in brackets as the dipole moment  $e\bar{x}(\alpha)$  of the electronic charge of ion  $\alpha$ , the field energy per ion pair becomes

$$E_F = -F[ed + e\bar{x}(F^-) + e\bar{x}(\text{Li}^+)]. \quad (10)$$

This is just the (classical) energy of the dipole per ion pair in the field  $F$ .

Neglecting the small contribution due to the overlapping of neighboring ions, we may write

$$\begin{aligned} \bar{x}(\alpha) &= \sum_i^{\alpha} \int \psi_i^*(-x_i) \psi_i d\tau = \sum_i^{\alpha} \int \psi_i^*(r_i \cos\theta_i) \psi_i d\tau \\ &\simeq \sum_j^{\alpha} \int \psi_j^*(\bar{r})(r \cos\theta) \psi_j(\bar{r}) d\tau, \end{aligned} \quad (11)$$

where the  $\psi_j$  are now the one-electron wave functions. The  $\text{Li}^+$  AO are spherically symmetric  $1s$  functions, so that  $\bar{x}(\text{Li}^+)=0$ . Similarly, the  $F^-$   $1s$ ,  $2s$  AO make no contribution to the ionic dipole moment; the whole of  $\bar{x}(F^-)$  arises from the perturbations of the  $2p$  orbitals in the applied field. The numerical values of  $\bar{x}(F^-)$  calculated from (11) for the AO (3) and (4) are shown in the first line of Table II. The present result for the nonorthogonal wave function differs from that given by Yamashita because of different normalization criteria: We normalized the  $2p$  AO over all space; Yamashita has normalized in a sphere of radius equal to the interionic distance.

### (2) Self-Energy of the Ions

Although the partial Hamiltonian  $H_{se}$  (7) is independent of the external field, the self-energy of the ions changes because the wave functions are altered in the presence of a field. Again neglecting overlap, it is evident that the change in self-energy of a particular ion depends only on the changes in the AO associated with it and not on its position in the lattice. The change in self-energy of an ion pair is then just that of a single  $F^-$  ion, and is independent of the displacement parameter  $d$ . From the statement of  $H_{se}$  it can be seen that the change in self-energy of an  $F^-$  ion consists of three contributions: the changes in kinetic energy of the  $2p$  electrons, the altered Coulomb attractions between the nucleus and the  $2p$  electrons, and the altered Coulomb and exchange energy among the electrons. Yamashita included the kinetic energy, but neglected the intra-

<sup>10</sup> See, e.g., L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, New York, 1949), p. 171.

TABLE II. Contributions to energy per ion pair due to field.

Source of contribution	Nonorthogonal wave function			Orthogonal wave function			Yamashita		
Field energy	$-dF$	$-8.82\lambda F$		$-dF$	$-7.19\lambda F$		$-dF$	$-7.60\lambda F$	
Self-energy of ions	$\times d^2$	$\times \lambda d$	$\times \lambda^2$	$\times d^2$	$\times \lambda d$	$\times \lambda^2$	$\times d^2$	$\times \lambda d$	$\times \lambda^2$
Kinetic			3.00			5.08			3.00
Coulomb			1.60			0.97			
Exchange			-0.67			-0.24			
Cohesive energy									
Electrostatic	-0.0189	-0.333	-1.47	-0.0189	-0.271	-0.98	-0.019	-0.294	-1.11
Exchange	-0.0482	-0.306	-0.16	-0.0482	-0.289	-0.15	}	0.0278	0.251
Overlap	0.0752	0.768	0.42	0.0752	0.724	0.37			

ionic interactions. All of these contributions to the ionic self-energy were considered in the present treatment.

The calculated values of the separate contributions to the change in self-energy of an  $F^-$  ion are given in Table II, to second order in the variational parameter  $\lambda$ . These were obtained by straightforward procedures. For the evaluation of the electronic kinetic energy, we used an expression derived by Kirkwood<sup>11</sup> in an investigation of the polarizabilities of rare gases. The electron-nucleus Coulomb contributions, which are one-center integrals, were obtained by simple integration. The electron-electron interactions (Coulomb and exchange) are two-center integrals, which were evaluated analytically by expanding the operator  $1/r_{12}$  in spherical harmonics.<sup>12</sup>

### (3) Cohesive Energy

The cohesive energy contributions to the change of energy per ion pair were calculated on the basis of the well-known expression of Löwdin<sup>13</sup> for the cohesive energy of an ionic crystal. According to this formulation, the cohesive energy itself may be considered as the sum of three contributions: the electrostatic energy  $E_E$ , the exchange energy  $E_X$  and the overlap energy  $E_S$ :

$$E_{\text{coh}} = E_E + E_X + E_S,$$

$$\begin{aligned}
 E_E &= e^2 \sum_{\alpha} \left[ \frac{1}{2} \sum_{\beta'} (Z_{\alpha} Z_{\beta'} / r_{\alpha\beta'}) + \sum_{i,j} S_{ij} (i|H^i|i) \right. \\
 &\quad \left. + \frac{1}{2} \sum_{i,j} S_{ij} (ij|G|ij) \right], \\
 E_X &= -\frac{1}{2} e^2 \sum_{\alpha} \sum_{i,j} S_{ij} (ij|G|ji), \\
 E_S &= -e^2 \sum_{\alpha} \sum_{i,j} S_{ij} \{ S_{ij} [(j|H^{j'}|i) \\
 &\quad + \sum_{m,n} (jm|G|im) - (jj|G|ji) \\
 &\quad + S_{ij} S_{ji} [(i|H^{i'}|j) + \sum_{m,n} (im|G|jm) \\
 &\quad - \frac{1}{2} (ij|G|ij)] \}.
 \end{aligned} \quad (12)$$

In these equations  $S_{ij}$  is the overlap integral,

$$S_{ij} \equiv \int \psi_i^*(1) \psi_j(1) d\tau(1), \quad (13)$$

and the quantities in parentheses denote matrix ele-

ments of the one-electron wave functions, which may be identified as

$$\begin{aligned}
 (i|H^{i'}|j) &\equiv \int \psi_i^*(1) \left[ -\sum_{\beta \neq \alpha} Z_{\beta} / r_{1\beta} \right] \psi_j(1) d\tau(1) \\
 &\equiv \sum_{\beta \neq \alpha} (i|H^{\beta}|j), \quad (14) \\
 (ij|G|mn) &\equiv \int \frac{\psi_i^*(1) \psi_j^*(2) \psi_m(1) \psi_n(2)}{r_{12}} d\tau_{12}.
 \end{aligned}$$

The electrostatic energy is just the total of the Coulomb interactions between the ions; in the normal crystal these interactions produce the Madelung energy. The corrections to the Madelung energy brought about by the distortion of the  $F^-$   $2p$  orbitals in an applied field can be expressed as lattice sums involving the multipole moments of the  $F^-$  charge cloud. However, these sums may be readily shown to be equivalent to the energy obtained from assumption of the Lorentz field factor  $(4\pi/3)P$ . If  $\mu$  is the dipole moment of an ion pair and  $a$  the interionic distance, the electrostatic part of the cohesive energy per ion pair is then [see Eq. (10)]:

$$E_E = -\frac{1}{2} \frac{4\pi}{3} P \mu = -\frac{1}{2} \frac{4\pi}{3} \frac{[ed + e\bar{x}(F^-)]^2}{2a^3}. \quad (15)$$

The numerical values of this contribution are given in Table II. Again, the differences between our results for the nonorthogonal wave function and the corresponding terms from Yamashita's paper are due to the difference in normalization procedures.

### (4) Treatment of Exchange and Overlap

Evaluation of the changes of  $E_X$  and  $E_S$  resulting from application of a field presents the most formidable problem in the energy calculation, since both  $E_X$  and  $E_S$  depend entirely on products of AO centered on different nuclei. We have treated this problem by approximation techniques which closely parallel the rigorous mathematical treatment. Considering only nearest neighbor overlap, and writing the perturbed  $F^-$   $2p$  orbitals as  $\psi_i = \psi_i^0 + \lambda \phi_i$ , each of the overlap

<sup>11</sup> J. G. Kirkwood, *Physik. Z.* **33**, 57 (1932).

<sup>12</sup> See, e.g., D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, New York, 1957), p. 46.

<sup>13</sup> P. O. Löwdin, *Arkiv Mat. Astron. Fysik* **35A**, No. 30 (1948).

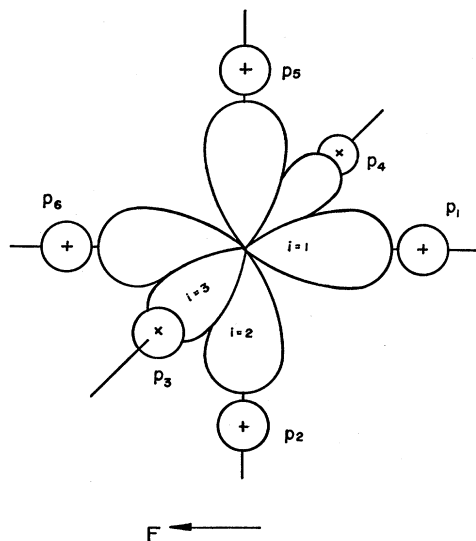


FIG. 2. A negative ion and its positive neighbors, showing the symmetry of the negative-ion orbitals (schematic).

integrals has the form

$$S_{i\gamma} = \int \psi_i(r) \psi_\gamma(r) d\tau = \int \psi_i^0 \psi_\gamma d\tau + \lambda \int \phi_i \psi_\gamma d\tau$$

$$= \int \rho_{i\gamma}^0 d\tau + \lambda \int \rho_{i\gamma}' d\tau, \quad (16)$$

where  $\psi_\gamma$  is the  $1s$  AO centered on one of the  $\text{Li}^+$  neighbors ( $p_\gamma$ ). The total overlap integral  $S_{i\gamma}$  essentially represents a charge, which we will designate as the "overlap charge"; the integrands  $\rho_{i\gamma}^0$  and  $\rho_{i\gamma}'$  are then charge densities—the "overlap-charge densities." All of the terms in  $E_X$  and  $E_S$  may be considered as electrostatic interactions involving the overlap charge distributions. For example, the exchange integral

$E_X(i\gamma)$

$$= \int \psi_i^*(1) \psi_\gamma^*(2) (1/r_{12}) \psi_\gamma(1) \psi_i(2) d\tau_{12}$$

$$= \int \frac{[\rho_{i\gamma}^0(1) + \lambda \rho_{i\gamma}'(1)] [\rho_{i\gamma}^0(2) + \lambda \rho_{i\gamma}'(2)]}{r_{12}} d\tau_{12} \quad (17)$$

may be interpreted as the electrostatic interaction energy of two similar charge distributions of density  $(\rho_{i\gamma}^0 + \lambda \rho_{i\gamma}')$ .

In order to carry through the approximate treatment of the exchange and overlap on this basis, it is necessary to investigate the spatial distribution of the overlap charge densities and their variation with relative position of the neighboring ions. Figure 2 is a schematic representation of a reference negative ion and its six nearest neighbors, showing the symmetry of the unper-

turbed negative-ion AO ( $i=1, 2, 3$ ). The interactions corresponding to  $(i\gamma)=(11), (16)$  are the most important for the field direction shown in the diagram. The  $(22)$ -type interactions are about two orders of magnitude smaller; the four equivalent sets of these interactions  $[(i\gamma)=(22), (25), (33), (34)]$  influence the results by only a few percent. All other interactions are zero or negligibly small.

Figure 3 shows  $\rho_{11}^0$  and  $\rho_{11}'$  as functions of distance along the line joining the Li and F nuclei, for the normal internuclear distance of the LiF crystal ( $a=3.81$  atomic units). On the opposite side of the Li nucleus, along this line, the overlap charge densities decrease more rapidly with distance from the Li nucleus, since in this region both  $\psi_{\text{Li}}$  and  $\psi_1$  are decaying exponentials. Along any direction in the plane perpendicular to this line, the dependence of  $\rho_{11}^0$  and  $\rho_{11}'$  on distance from the Li nucleus is determined mainly by the  $\text{Li}^+$ -ion wave function. The behavior along all three directions is shown in Fig. 4. To determine the effect of relative displacement of positive and negative ions on the overlap charges, it is necessary only to note the exponential character of the overlap charge distributions (see Fig. 3). Since both the  $\text{Li}^+$  and  $\text{F}^-$  AO are almost

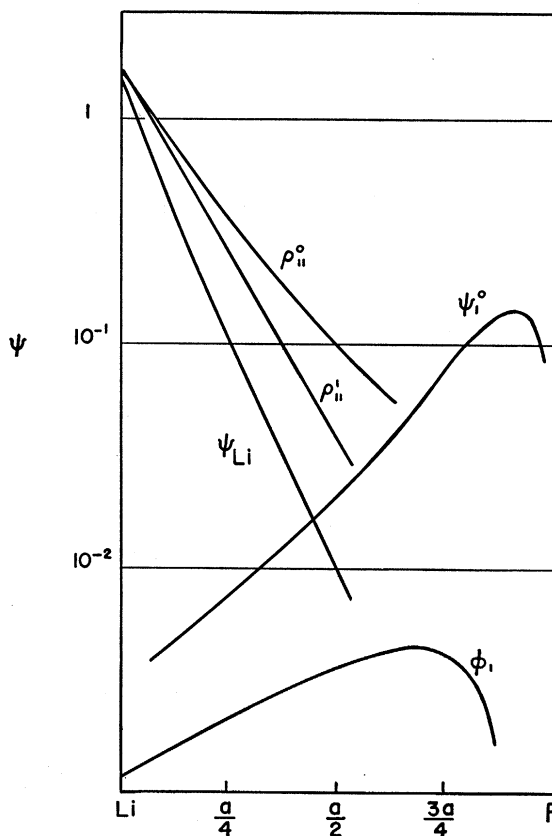


FIG. 3. Wave functions and overlap-charge densities as functions of distance along line joining Li and F nuclei. The ordinates are in arbitrary units.

pure exponentials in the vicinity of the Li nucleus, the total overlap charge  $S_{i\gamma}$  must vary with small displacement of the nuclei in much the same way  $\rho_{i\gamma}$  varies with distance from the Li nucleus. Accordingly, we have assumed  $S_{i\gamma}$  (and  $\rho_{i\gamma}$ ) to vary exponentially with relative displacement of the positive and negative ion:

$$\begin{aligned}\rho_{11}^0(d) &= e^{\alpha_0 d} \rho_{11}^0(0); & \rho_{11}'(d) &= e^{\alpha_1 d} \rho_{11}'(0), \\ \rho_{16}^0(d) &= e^{-\alpha_0 d} \rho_{16}^0(0); & \rho_{16}'(d) &= e^{-\alpha_1 d} \rho_{16}'(0),\end{aligned}\quad (18)$$

the constants  $\alpha_0$  and  $\alpha_1$  being given by the reciprocals of the distances (Fig. 4) in which  $\rho_{11}^0(x)$  and  $\rho_{11}'(x)$ , respectively, decay to  $1/e$  of their values at the Li nucleus. The  $S_{i\gamma}$  themselves were evaluated, for the case where the nuclei are at the normal interionic distance, by expanding the  $\text{Li}^+$  1s function in spherical harmonics about the nucleus of the neighboring  $\text{F}^-$  ion and then integrating the product  $\psi_i \psi_\gamma$ . Because of the orthogonal properties of the spherical harmonics, only a few terms of the integrated expansion are nonzero.

The most important terms in the overlap energy of the crystal are those which reduce to the form

$$E_S(1) \equiv S_{i\gamma}(\gamma | H^{r\gamma} | i) \text{ and } E_S(2) \equiv S_{i\gamma}(\gamma\gamma | G | i\gamma), \quad (19)$$

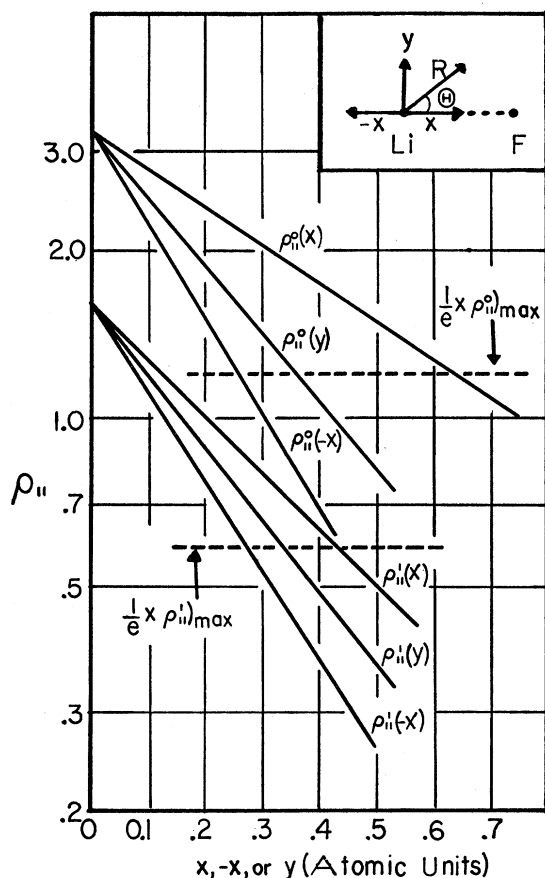


FIG. 4. Directional dependence of  $\rho_{11}^0$  and  $\rho_{11}'$ . The ordinate is in arbitrary units.

which represent the interaction of the overlap charges with the positive ion on which the overlap is localized. These terms, together with the exchange energy, which we have already characterized [Eq. (17)] as interactions among the overlap charges, constitute the major contribution of overlap to the crystal energy. To evaluate this contribution, we represented the overlap-charge densities as decaying exponentials of ellipsoidal symmetry, centered on the Li nucleus:

$$\begin{aligned}\rho_{11}^0 &\propto \exp[-R(\alpha_0^2 \cos^2 \Theta + \beta_0^2 \sin^2 \Theta)^{1/2}] & 0 < \Theta < \pi/2 \\ \rho_{11}^0 &\propto \exp[-R(\gamma_0^2 \cos^2 \Theta + \beta_0^2 \sin^2 \Theta)^{1/2}] & \pi/2 < \Theta < \pi, \\ \rho_{11}' &\propto \exp[-R(\alpha_1^2 \cos^2 \Theta + \beta_1^2 \sin^2 \Theta)^{1/2}] & 0 < \Theta < \pi/2 \\ \rho_{11}' &\propto \exp[-R(\gamma_1^2 \cos^2 \Theta + \beta_1^2 \sin^2 \Theta)^{1/2}] & \pi/2 < \Theta < \pi.\end{aligned}\quad (20)$$

This representation is in consonance with both the symmetry discussed above and the exponential behavior illustrated in Fig. 4. The constants  $\alpha_0$ ,  $\beta_0$ , and  $\gamma_0$  were taken as the reciprocals of the distances (Fig. 4) along  $x$ ,  $y$ , and  $-x$ , respectively, in which  $\rho_{11}^0$  decays to  $1/e$  of its initial value at the Li nucleus;  $\alpha_1$ ,  $\beta_1$ , and  $\gamma_1$  were similarly obtained for  $\rho_{11}'$ . The total charge contained in the distributions was normalized to the value of the overlap integral  $S_{11}$ , in accordance with (16). With these charge distributions, the terms (19) and the exchange integrals were readily obtained by standard techniques.

We have also calculated the exchange energy (for the case  $d=0$ ) by expanding both the  $\text{Li}^+$ -ion wave function and the operator  $1/r_{12}$  in spherical harmonics about the negative-ion nucleus, and then computing each exchange term as a series of one-center integrals. Although the series converged rather slowly, we obtained the series limits by approximation estimated to yield the exchange energy with an accuracy of about 10%. [The exchange, however, is only a small part of the total energy (see Table II), so a 10% error here is equivalent to an error of only  $\sim 1\%$  in the over-all energy calculation.] The exchange energy calculated by this method was in good agreement with the corresponding result obtained with the ellipsoidally-symmetric overlap-charge distributions (20).

The remaining terms in the overlap energy, i.e., those which are not of the type (19), may all be characterized as electrostatic interactions between the overlap charges and charges not associated with the positive ion on which the overlap is localized. For the evaluation of these terms, we have considered the total overlap integral  $S_{i\gamma}$  to be a point charge at the center of the positive ion. This representation accords well with the indications in Fig. 4 that the overlap is appreciable only in a small region near the Li nucleus. Dick and Overhauser have also used the point charge assumption in connection with their "exchange charge" ( $= 4 \sum_i S_{i\gamma}^2$ ). Figures 3 and 4 show clearly why their "extreme" case, in which the exchange charge is

situated at the center of the positive ion, gave somewhat better results than the normal case, where the exchange charge is located at points of tangency of Zachariasen spheres.

Numerical values of the exchange and overlap energy contributions, computed by the methods described in this section, are given in Table II.

### III. DETERMINATION OF DIELECTRIC CONSTANTS AND EFFECTIVE CHARGE

The sum of the separate contributions of Table II represents the total energy per ion pair resulting from application of a field to the LiF crystal. To second order in the distortion parameter  $\lambda$  and the displacement parameter  $d$ , this energy can be written in the generalized form,

$$\Delta E = -Fd - AF\lambda + B\lambda^2 + B_0d^2 + C\lambda^2. \quad (21)$$

Minimizing the energy with respect to both  $\lambda$  and  $d$ , we obtain for the case of a static or low-frequency field ( $d \neq 0$ )

$$\lambda_0 = \frac{\begin{vmatrix} AF & C \\ F & 2B_0 \end{vmatrix}}{\begin{vmatrix} 2B & C \\ C & 2B_0 \end{vmatrix}}, \quad d = \frac{\begin{vmatrix} 2B & AF \\ C & F \end{vmatrix}}{\begin{vmatrix} 2B & C \\ C & 2B_0 \end{vmatrix}}, \quad (22)$$

$$\Delta E_0 = -\frac{1}{2} \left[ \frac{2(B + A^2B_0 - AC)}{4B_0B - C^2} \right] F^2; \quad (23)$$

and for a high-frequency field ( $d=0$ )

$$\lambda_\infty = AF/2B, \quad (24)$$

$$\Delta E_\infty = -\frac{1}{2} [A^2/2B] F^2. \quad (25)$$

Now, from elementary considerations, the energy in a polarized dielectric is  $-\frac{1}{2}\chi F^2$ , where  $\chi$  is the (macroscopic) susceptibility: Accordingly, we can identify the quantities in brackets [ ] in (23) and (25) as the static and high-frequency susceptibility per ion pair, respectively. The corresponding dielectric constants are obtained from the relation

$$\epsilon - 1 = 4\pi N\chi, \quad (26)$$

where  $N$  is the number of ion pairs per unit volume.

The effective charge ratio  $e^*/e$  can also be determined simply from the coefficients of the energy expression (21). Following the treatment of Szigeti, the total polarization of a crystal in a static (or low-frequency) field may be written as the sum of the high-frequency (optical) polarization and an infrared component

$$P_0 = P_{\text{ir}} + P_\infty. \quad (27)$$

The infrared polarization contains the effects of both the displacement of the ions as a whole and the electronic redistributions which accompany displacement

of the ions. The effective charge  $e^*$  is defined (for  $Z=1$ ) by

$$P_{\text{ir}} = P_0 - P_\infty \equiv Ne^*d. \quad (28)$$

From the previous discussion [see Eq. (10) ff.], the dipole moment per ion pair in a static field is  $(ed + eA\lambda_0)$ , and in a high-frequency field it is  $eA\lambda_\infty$ . Then, from (27) and (28)

$$e^*/e = 1 - A(\lambda_\infty - \lambda_0)/d. \quad (29)$$

By substituting for the quantities  $\lambda_\infty$ ,  $\lambda_0$ , and  $d$  from (22) and (24),  $e^*/e$  may be expressed completely in terms of the coefficients of the energy expression; this yields the surprisingly simple result

$$e^*/e = 1 - AC/2B. \quad (30)$$

### IV. RESULTS AND DISCUSSION

The coefficients for the energy equation (21) are obtained by summing the several contributions of Table II. The resultant values are given in Table III, together with the dielectric constants and effective charge ratio deduced from them. Results obtained with both the "orthogonal" and "nonorthogonal" wave functions are included to illustrate the effect of the orthogonalization; Yamashita's results for LiF are also listed for comparison. Significant differences between the energy coefficients for the orthogonal and nonorthogonal cases are evident; this is particularly so for the coefficients  $A$  and  $B$ , about which more will be said presently.

The results for our nonorthogonal case and Yamashita's calculation are directly comparable, since the same wave functions were employed for both. Although considerably different methods were employed for the energy calculation—particularly in the nearest neighbor interactions—the results agree fairly well on the whole. The difference in sign of the coefficient  $C$  is, however, quite significant. Referring to Eq. (30), it is seen that the negative value of  $C$  causes  $e^*/e$  to deviate in the wrong direction from unity. In this connection it should be noted that Yamashita derived the value 0.76 for  $e^*/e$ , rather than 1.06 (Table III), as we have calculated for his data from (30). The difficulty lies in the derivation of  $e^*/e$ : Yamashita used the relation

$$P_\infty/N = \alpha_\infty [F + (4\pi/3)P_0], \quad (31)$$

where  $\alpha_\infty$  is the high-frequency polarizability per ion

TABLE III. Numerical results.

	$A$	$B$	$B_0$	$C$	$\epsilon_0$	$\epsilon_\infty$	$e^*/e$
Nonorthog wave function	8.82	2.72	0.0081	0.129	8.0	2.63	0.79
Orthog. wave function	7.19	5.05	0.0081	0.164	8.1	1.59	0.88
Yamashita	7.60	2.69	0.0088	-0.043	10.1	2.33	1.06 <sup>a</sup>
Observed					9.3	1.92	0.87 <sup>b</sup>

<sup>a</sup> From Eq. (30). See text.

<sup>b</sup> Equation (1) (Szigeti).

pair. Since  $\alpha_\infty$  may be applied only to the high-frequency polarization component,  $P_\infty$  rather than  $P_0$  should appear on the right of (31).

There is little difference between the static dielectric constants obtained with the orthogonal and non-orthogonal wave functions. This is a consequence of the fact that the term  $B_0 d^2$ , which is not affected by the orthogonalization of the wave function, is dominant in the energy expression. Despite its importance, this is a difficult term to evaluate accurately, for (see Table II) it is the sum of positive and negative contributions of nearly the same magnitude; its numerical value is a small remainder, close to the limits of the approximations used in the cohesive energy calculation.

The calculated high-frequency dielectric constant and the effective charge, on the other hand, are greatly affected by the orthogonalization of the wave function. The coefficients  $A$  and  $B$  completely determine  $\epsilon_\infty$  [see Eq. (25)] and, since  $C$  is not greatly affected by orthogonalization, are also of prime importance in fixing the value of  $e^*/e$ . While  $B\lambda^2$  is the composite result of a number of different energy contributions, its value, in all three sets of data given in Tables II and III, is very close to the altered kinetic energy of the electrons alone. The total energy change in a high-frequency field then essentially contains just two contributions: the kinetic energy of the electrons and the interaction of the negative-ion distortion moment with the macroscopic field. Thus the key to the theory of the dielectric constant—at high frequency, at least—appears to be the choice of orthogonal wave functions that produce an ionic dipole moment and altered electronic kinetic energy which are in proper balance.

From this discussion, it is concluded that the use of wave functions which preserve the orthogonality within individual ions is very important in the quantum theory of dielectric constants. In this connection, one further aspect of the present results is worthy of note.

According to the variation principle, no wave function, used in conjunction with the correct Hamiltonian, can lead to an energy that is lower than the true energy of a system. This is equivalent to the requirement that the dielectric constant deduced from a complete variational calculation cannot exceed the observed value. The values 2.63 and 2.33, listed for  $\epsilon_\infty$  in Table III, violate this requirement. The apparent contradiction arises from the fact that nonorthogonal wave functions were used in the calculations, but were treated in the same way as orthogonal wave functions; the energy terms thereby neglected would presumably remove the difficulty. Since the  $\epsilon_\infty$  obtained with the orthogonal wave function is somewhat lower than the observed value, while that obtained with the nonorthogonal wave function is considerably higher, the implication is that the orthogonal wave function employed here overcompensates in some way for the errors inherent in the use of the nonorthogonal wave function. Better choice of the orthogonal trial function could lead to results which are better in agreement with experiment, even with the simple model employed in this paper. A negative-ion wave function that is not so much peaked in the direction of the nearest neighbor may be indicated.

Finally, it should be mentioned that the method employed in this paper is not generally applicable to all ionic crystals because the positive-ion polarizability is neglected and the entire negative-ion polarizability is attributed to the outermost subshell of electrons. However, the results obtained indicate that an idealized model such as this can be applied with reasonable success to other ionic solids in which the positive-ion polarizability is small compared with that of the negative ion. It is also hoped that the broad features of the present work will be useful in considerations of more complicated systems, where these conditions are not well met.