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Quantum Theory of the Polarizability of an Idealized Crystal*

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The quantum-mechanical polarizability of an idealized insulating crystal is calculated by the semiclassical method, in which the electromagnetic radiation of frequency small compared with electronic resonance absorption frequencies is treated classically. A generalization of the Lorentz "internal field" effect emerges naturally from the treatment. Correction terms to the Lorentz value for the polarization of a crystal, $n_0[\alpha_a/(1-4\pi n_0\alpha_a/3)]\mathcal{E}$, where α_a is the polarizability of an isolated atom, n_0 the density of atoms, and $\mathcal{E}$ the applied field, arise from three main sources: (1) exchange and overlap effects, (2) higher order terms in the atomic interactions than dipole-dipole terms, and (3) second and higher powers of the small parameter $4\pi n_0\alpha_a/3$. These correction terms, which are shown to be important in real crystals, are briefly discussed, although more must be known about specific wave functions in order to make quantitative calculations. The connection is pointed out between the propagation of excitons and the Lorentz effect.

I. INTRODUCTION

IN actual insulating crystals the forces operating between the crystal constituents range from those involving effectively perfect overlap of valence electron wave functions (as in metals) through those characteristic of valence crystals to the types encountered in ionic and molecular crystals. In the latter the repulsive forces are determined by electronic overlap, but the dominant attractive forces are "long-range" and essentially electrostatic in character. In such crystals, it may happen that even the optical properties are characteristic of "bound" electrons, that is, electrons whose wave functions are quite well characterized by starting from a localized, Heitler-London treatment of the solid (although not necessarily of the constituent atoms of an individual molecule, of course).[1]

In those crystals where this situation obtains, one would infer that the classical conceptions involving bound charged oscillators, found to correspond to the quantum theory of atomic optical properties, should have some significance for the discussion of their optical spectra. As opposed to conditions in a dilute gas, where the classical oscillators have already been found to give results equivalent to quantum theory, the major difference will now be that the electromagnetic oscillators involved are in each other's "near," or quasi-static zone, i.e., their separation is much less than a wavelength.

A treatment familiar to most physicists is the calculation of the "local field" acting on an ion, first given by Lorentz.[2] In this now conventional treatment, a sphere large relative to atomic dimensions, centered on the ion in question, is considered as one boundary of a continuously polarized medium, and if the material inside of this sphere is isotropically or cubically distributed, one can show that no force is exerted by this material on the ion. Thus the remaining forces can be ascribed to the external field, to the charges on the surface of the surrounding sphere, and to any external surfaces. The contribution of the surface charge on the sphere to the field at the ion can easily be shown to be $4\pi\mathbf{P}/3$, where $\mathbf{P}$ is the polarization of the medium. This in turn leads to the formula (applying to a crystal of identical atomic oscillators) for the polarization of the crystal,

$$\mathbf{P}=n_0\left(\frac{\alpha_a}{1-4\pi n_0\alpha_a/3}\right)\mathcal{E}, \tag{1a}$$

or to the polarizability per atom *within the crystal*,

$$\alpha=\frac{\alpha_a}{1-4\pi n_0\alpha_a/3}. \tag{1b}$$

Either of these relations is equivalent to the Lorentz-Lorenz equation,

$$(\kappa-1)/(\kappa+2)=4\pi n_0\alpha_a/3. \tag{1c}$$

Here n_0 = density of atoms. $\mathbf{P}$, $\mathcal{E}$ = polarization, field strength (including "depolarization"), α_a = polarizability of an isolated atom, and κ = optical dielectric constant.

It is perhaps worth while to emphasize that the classical electron theory of dielectrics does not rest solely on the electrostatic treatment of Lorentz. Ewald[3] discussed the problem of the propagation of electromagnetic waves in an infinite idealized crystal consisting of bound oscillators, near each of which the field takes on the character of the quasi-static dipole field. The requirement that the form of the solutions be consistent

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* A preliminary report of this work was given at the Chicago meeting of the American Physical Society, October, 1951 [Phys. Rev. **85**, 723 (1952)].

[1] In this connection we may cite the recent work of D. L. Dexter [Phys. Rev. **83**, 435, 1044 (1951)] on the wave functions of excitons in NaCl, which shows that an atomic picture of the optical excitation is a good approximation in obtaining oscillator strengths, a procedure more sensitive to the goodness of wave functions than is the calculation of energies alone.

[2] See, for example, M. Abraham and R. Becker, *Theorie der Elektrizitat* (Teubner, Leipzig, 1933), Vol. 2, pp. 120–123.

[3] P. Ewald, dissertation, Munich, 1912; Ann. Physik **49**, 1 (1916). An exposition is also to be found in M. Born, *Optik* (Verlag Julius Springer, Berlin, 1933), p. 327.

with the macroscopic interpretation of Maxwell's equations for refracting media is just sufficient to give the same result for the polarizability per crystal atom as written in Eq. (1b).

Proceeding along similar lines, Van Vleck[4] and Huang[5] have discussed the quantum-mechanical problem of a crystalline array of coupled harmonic oscillators. These authors also came to the conclusion that the polarization is exactly that given by the Lorentz theory.

In treating real crystals, Herzfeld and Wolf[6] have shown that the dispersion of the alkali halides can be understood on the basis of a formula which represents a generalization of Eq. (1) to the case where the oscillator strengths need not be unity, and where all of the principal resonant frequencies of these crystals are empirically taken into account. Further, Shockley[7] has shown that one can fit the values of the optical refractive index of the alkali halides by assuming each ion to have a definite polarizability and using a generalization of Eq. (1) to the case where two types of oscillators are present.

The most painstaking survey of experimental data on optical refraction is that of Eykman,[8] who, including liquids as well as solids, found that the best fit of data for a given substance as a function of temperature and pressure was represented by

$$\frac{\kappa-1}{\kappa^{\frac{1}{2}}+0.4}\frac{1}{n_0}=\text{constant.} \tag{2}$$

In addition to the fact that no general quantum theory of crystalline refraction which connects with the classical treatment seems to have been given, this subject has somewhat more than academic interest. The interpretation of absorption data requires some assumption about the internal field acting on a polarizable entity in a crystal. Thus, especially to those who study the optical properties of ionic and molecular crystals, it is of great interest to be able to compare the oscillator strengths derived from theoretical estimates or measurements in the gaseous state with those for condensed systems. A discussion referring to this point has been given by Mulliken.[9] In such comparisons, one would like to separate, where possible, the effects of essential changes in the electronic wave functions (e.g., those demanded by change of symmetry or strong overlapping in the condensed system) from those effects which are the quantum-mechanical analog of the "local field."

It is also a point of some current interest to relate the variation of refractive index with density and temperature to existing theories of dispersion, since these theories[10] proceed on specific (classical) assumptions about the nature of the forces between ions. A quantum mechanical theory of the local field may cast light on the type of wave functions and hence the behavior of forces which correspond to the actual electron distribution in crystals.

A consideration of the work mentioned above has led the authors to attempt a quantum theory of the dispersion of an idealized insulating crystal on the basis of the usual semiclassical account of the electromagnetic effects.

Use is made of the work of Heller and Marcus,[11] who have worked out the energy spectrum of single excitation waves in a model crystal, pointing out that the interaction among oscillators is a long-range principally dipole-dipole effect ($\sim 1/r^3$), and thus that excitons may be propagated in a crystal with negligible overlap of the significant electronic wave functions. Using the same model, we shall show in the present paper that the "local field" effects emerge in a natural way as a consequence of this same dipole-dipole interaction, and also shall indicate the higher order correction terms required in actual insulating crystals.

A conceptual difference exists between the early, classical work and that reported here, in that the present authors do not introduce an "effective," or "local" field. In extensions of the early work the polarizability of each oscillator was considered to remain unchanged by the presence of neighbors, but the induced dipole fields of the neighbors, in the presence of an applied field, was taken to reinforce the applied field in such a way that the product $n_0\alpha_a\mathcal{E}_{\text{eff}}$ had the value given in Eq. (1a). As we shall see, however, the presence of neighbors does modify the wave functions (and hence polarizability) of each oscillator, *even in the absence of an applied field*. Consequently, we prefer to include the interactions among the oscillators in the calculation of the wave functions, and, having once included these interactions, we need not subsequently introduce an effective field to take them into account. The products $\alpha_a\mathcal{E}_{\text{eff}}$ and $\alpha\mathcal{E}$, if computed correctly, should, of course, agree, and from the standpoint of the calculation of the dielectric constant both methods are equivalent. In other calculations, however, it must be borne in mind that the field is "effective" only in the above limited sense, and that if all interactions are included in the Hamiltonian of the system, the proper value of the electric field is not $\mathcal{E}_{\text{eff}}$ but $\mathcal{E}$.

The method used here is the calculation of the electric

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[4] J. H. Van Vleck, J. Chem. Phys. **5**, 320, 556 (1937).

[5] K. Huang, Proc. Cambridge Phil. Soc. **45**, 452 (1949).

[6] K. Herzfeld and K. L. Wolf, Ann. Physik **76**, 71, 567 (1925).

[7] W. Shockley, Phys. Rev. **70**, 105 (1946).

[8] J. F. Eykman, *Recherches Refractometriques* (Natuurkundige Verhandelingen Hollandsche Maatschappij Wetenschappen; edited by A. F. Holleman, printed in French by De Erven Loosjes, Haarlem, 1919).

[9] R. S. Mulliken and C. A. Rieke, Repts. Progr. in Phys. **8**, 231 (1941).

[10] H. Mueller, Phys. Rev. **47**, 947 (1935). E. Burstein and P. Smith, Phys. Rev. **74**, 229 (1948). D. A. A. S. Narayana Rao, Phys. Rev. **82**, 118 (1951).

[11] W. R. Heller and A. Marcus, Phys. Rev. **84**, 809 (1951). This work was stimulated by the remark of Professor F. Seitz that the electromagnetic interaction of oscillators might in certain cases be an important mode of energy propagation in insulating solids.

moment of the effectively infinite model crystal in the presence of electromagnetic radiation of wavelength large relative to the lattice spacing, but not infinitely large. (This procedure avoids the introduction of surface effects aside from those implicit in the use of the "depolarized" field strength.) The next section deals with this calculation, and in the final section we discuss the significance of the results for some actual crystals.

II. CALCULATION OF POLARIZABILITY

The model with which we shall work, because of its simplicity, is essentially that treated by Frenkel,[12] Peierls,[13] Slater and Shockley,[14] Seitz,[15] and Heller and Marcus.[11] According to this model, we consider a simple cubic crystal of effectively infinite size, on the lattice sites of which are arranged identical one electron atoms. For convenience in carrying out the calculation and to demonstrate briefly and without nonessential complications the main effect of the virtual dipole-dipole interaction, we shall impose the following limitations and approximations in our model: There is no overlapping of the ground-state atomic functions[16] (although there may be overlapping of excited state atomic functions with neighboring ground or excited functions); it should be remarked that the nonoverlap condition is not equivalent to a statement that exchange effects may be ignored, and we shall include exchange terms, at least formally, throughout the calculation. All spin effects are ignored. Inasmuch as cubic symmetry does not remove the degeneracy for p states,[17] we shall allow our excited state p functions to be triply degenerate. Thermal and zero-point vibrations are neglected throughout; errors resulting from this approximation should be important only near frequencies of absorption bands, with which frequencies this calculation is not concerned. In this connection it should be stated that the electric field, in whose presence we shall calculate the dipole moment of the crystal, is assumed to oscillate with a frequency small compared with that corresponding to the first electronic absorption band in the crystal, but large compared with nuclear vibration frequencies ($\sim 10^{13}$ sec^{-1}). That is, we are interested only in the electronic polarizability, and shall ignore any nuclear motion in the presence of the field. A related condition is that we consider only electric fields of wavelength large compared to the lattice constant, but not infinite; by treating only finite wavelengths we eliminate the necessity for considering effects arising from the surface of the crystal. A further assumption we shall make is that the Lorentz correction $4\pi n_0\alpha_a/3$ is small in comparison with unity, and our results will only be accurate to the first power of this parameter.

With these limitations, the Hamiltonian of the system in the absence of a field may be written

$$H=\sum_{i=1}^{N} H_i+\tfrac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}{}'\frac{e^2}{r_{ij}}-\sum_{i=1}^{N}\sum_{J=1}^{N}{}'\frac{e^2}{r_{iJ}}+\tfrac{1}{2}\sum_{I=1}^{N}\sum_{J=1}^{N}{}'\frac{e^2}{r_{IJ}}, \tag{3}$$

where H_i is the atomic Hamiltonian; the lower case indices refer to electrons and the upper case indices refer to nuclear coordinates. N is the number of atoms in the crystal. The form of the eigenfunctions of this Hamiltonian is well known from the band theory of solids, and from the work of Frenkel, Peierls, and others on the theory of excitation waves. (See, for example, reference 15 for a discussion of the energy states of this system.) The ground state, for example, is an antisymmetrized product of ground-state atomic functions [Eq. (5)] plus a mixture of higher atomic states induced by the interactions among the atoms. These interactions may result from an overlapping of the electric (dipole) fields of the constituent atoms, and from exchange, which involves the overlapping of the atomic wave functions. Heller and Marcus[11] have concluded that in some crystals where the atomic wave functions are not greatly extended spatially, the overlapping of the dipole fields is the predominant interaction, and this situation is assumed to obtain in the present discussion. Equation (4) is the normalized ground-state eigenfunction of the above Hamiltonian, and includes the admixture of higher excited states in the summation,

$$\Phi_0=\Psi^0+(8\pi n_0/3)P_2(\cos\varphi)[j_0(\rho)-j_2(\rho)]$$
$$\times\sum_{n_1}\sum_{n_2}\sum_{\mathbf{k}}\frac{(\mu_{n_1}\mu_{n_2}+W_{n_1n_2})}{\epsilon_{n_1}+\epsilon_{n_2}-2\epsilon_0}\Psi^{n_1n_2}(\mathbf{k},-\mathbf{k}), \tag{4}$$

where

$$\Psi^0=(N!)^{-\frac{1}{2}}\begin{vmatrix}\psi_1{}^0(\mathbf{r}_1) & \cdots & \psi_1{}^0(\mathbf{r}_N)\\ \cdot & & \cdot\\ \cdot & & \cdot\\ \psi_N{}^0(\mathbf{r}_1) & \cdots & \psi_N{}^0(\mathbf{r}_N)\end{vmatrix}, \tag{5}$$

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[12] J. Frenkel, Phys. Rev. **37**, 17, 1276 (1931); Physik. Z. Sowjetunion **9**, 158 (1936).

[13] R. Peierls, Ann. Physik **13**, 905 (1932).

[14] J. C. Slater and W. Shockley, Phys. Rev. **50**, 705 (1936).

[15] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 414.

[16] Since the initial preparation of this manuscript (which was withdrawn from publication following the discovery of a mathematical error) work has been reported by Krishnan and Roy which has an important bearing on this topic [K. S. Krishnan and S. K. Roy, Proc. Roy. Soc. (London) **A207**, 447 (1951); Phil. Mag. **44**, 19 (1953)]. These writers conclude from comparison of theory with observed reststrahlen frequencies that overlapping of the atomic wave functions greatly reduces the polarization correction associated with the electronic modes in the alkali halides. If this conclusion is correct, the present work is not applicable even qualitatively to the alkali halides.

[17] H. Bethe, Ann. Physik **3**, 143 (1929).

and

$\Psi^{n_1n_2}(\mathbf{k}_1, \mathbf{k}_2)$ is a "double exciton" wave function,

$$\Psi^{n_1n_2}(\mathbf{k}_1, \mathbf{k}_2)=N^{-1}(N!)^{-\frac{1}{2}}(1+\delta_{\mathbf{k}_1,\,\mathbf{k}_2}\delta_{n_1,\,n_2})\sum\sum_{L\neq M}$$

$$\times e^{2\pi i(\mathbf{k}_1\cdot\mathbf{r}_L+\mathbf{k}_2\cdot\mathbf{r}_M)}\begin{vmatrix} \psi_1{}^0(1) & \cdots & \psi_1{}^0(N) \\ \vdots & & \vdots \\ \psi_L{}^{n_1}(1) & \cdots & \psi_L{}^{n_1}(N) \\ \vdots & & \vdots \\ \psi_M{}^{n_2}(1) & \cdots & \psi_M{}^{n_2}(N) \\ \vdots & & \vdots \\ \psi_N{}^0(1) & \cdots & \psi_N{}^0(N) \end{vmatrix}, \quad (6)$$

corresponding to the presence of two excited atoms simultaneously. Such a term corresponds to the presence of excited states in two atoms coupled by van der Waals' and exchange interactions, and is induced by the second term in the Hamiltonian [Eq. (3)]. The lower case psi's, $\psi_J{}^i$, refer to the ith excited eigenfunctions of the atomic Hamiltonian of energy ϵ_i. $P_2(\cos\varphi)$ is the second Legendre polynomial, and φ is the angle between the propagation vector of the exciton, $\mathbf{k}$, and the transition moment $\boldsymbol{\mu}_n$ of magnitude $\mu_n=\int\psi^{n*}ex\psi^0 d\tau$ chosen to lie along the x-axis. Since we shall be interested only in excitons created by electromagnetic radiation (rather than by fast particles), the only values of $\mathbf{k}$ and $\boldsymbol{\mu}$ that enter will be mutually orthogonal, so that $P_2(\cos\varphi)$ may be replaced by $-\frac{1}{2}$. The Bessel functions[18] j_0 and j_2 are functions of $\rho\equiv2\pi ka(3/4\pi)^{\frac{1}{3}}$, where a is the lattice spacing, and for all values of $\mathbf{k}$ that will be of interest here, ρ is of the order 10^{-3} so that j_0-j_2 may be replaced by unity. The quantities $W_{n_1n_2}$ arise from exchange, and will subsequently be assumed small in comparison with $\mu_{n_1}\mu_{n_2}$. The indices n_1 and n_2 refer to p functions since we assume ψ^0 to be an s function. The indices L and M refer to the Lth and Mth atoms in the lattice. The energy associated with the eigenfunction Φ_0 is equal to[11]

$$E_0=N\epsilon_0-\tfrac{1}{2}\sum_{I=1}^{N}\sum_{J=1}^{N}{}'\int\psi_I{}^{0*}(1)\psi_J{}^{0*}(2)\frac{e^2}{r_{12}}$$

$$\times\psi_I{}^0(2)\psi_J{}^0(1)d\tau_{12}, \quad (7)$$

plus terms in a^{-5}, a^{-6} and so forth. According to our assumption that $4\pi n_0\alpha_a/3$ is small, these terms are negligible. The first term in Eq. (7) is the energy of N isolated atoms in their ground state, and the second is an exchange energy.

The excited state wave functions of the crystal are given by

$$\Phi_n(\mathbf{k})=\Psi^n(\mathbf{k})+(4\pi n_0/3)\sum_{j\neq n}\frac{(\mu_n\mu_j+V_{nj})}{\epsilon_j-\epsilon_n}\Psi^j(\mathbf{k}), \quad (8)$$

where

$$\Psi^n(\mathbf{k})=(NN!)^{-\frac{1}{2}}\sum_L e^{2\pi i\mathbf{k}\cdot\mathbf{r}_L}\begin{vmatrix} \psi_1{}^0(1) & \cdots & \psi_1{}^0(N) \\ \vdots & & \vdots \\ \psi_L{}^n(1) & \cdots & \psi_L{}^n(N) \\ \vdots & & \vdots \\ \psi_N{}^0(1) & \cdots & \psi_N{}^0(N) \end{vmatrix}, \quad (9)$$

are typical (single) exciton wave functions of energy,[11]

$$E_n(\mathbf{k})=E_0+(\epsilon_n-\epsilon_0)-(4\pi n_0/3)\mu_n{}^2+U_n. \quad (10)$$

V and U are sums of exchange terms similar to those in Eqs. (4) and (7), respectively. The characteristic form[15] of Eq. (9) is a result of the periodicity of the lattice, and the amount of admixture in Eq. (8) is again determined by the strength of the interactions among the atoms.

Note that the wave functions given by Eqs. (4) and (8) are different from the corresponding wave functions[11,15] which are given by just the first terms of Eqs. (4) and (8), i.e., by Eqs. (5) and (9). The first terms by themselves do not diagonalize the Hamiltonian to the first power in $4\pi n_0\alpha_a/3$, and have, therefore, been improved. The energies given in reference 11 are changed only in the second order of $4\pi n_0\alpha_a/3$ by the inclusion of other terms in the wave functions. Equation (8) should likewise contain sums of triple exciton (p) states and sums of double excition (dd, ds, ss) states, but these terms only contribute to the polarizability in the second order of $4\pi n_0\alpha_a/3$ and have been omitted.

We shall use time-dependent perturbation theory to calculate the expectation value of the dipole moment of one of the electrons of the crystal in the presence of an electromagnetic field. The change in the Hamiltonian due to the field is

$$H'=\sum_{i=1}^{N}\left(\frac{-e\hbar}{2\pi m\nu}\right)\boldsymbol{\nabla}_i\cdot\boldsymbol{\mathcal{E}}_0(e^{2\pi i(\mathbf{u}\cdot\mathbf{r}-\nu t)}-e^{-2\pi i(\mathbf{u}\cdot\mathbf{r}-\nu t)}), \quad (11)$$

where the electric field is

$$\boldsymbol{\mathcal{E}}_0[\exp\{2\pi i(\mathbf{u}\cdot\mathbf{r}-\nu t)\}+\exp\{-2\pi i(\mathbf{u}\cdot\mathbf{r}-\nu t)\}].$$

We shall take $\boldsymbol{\mathcal{E}}_0$ in the direction of the x-axis and $\mathbf{u}$ along the z-axis. The perturbed wave function is then

$$\Phi=\Phi_0 e^{-iE_0t/\hbar}+\sum_{n\neq0}\sum_{\mathbf{k}}a_{\mathbf{k},\,n}(t)e^{-iE_nt/\hbar}\Phi_n(\mathbf{k}), \quad (12)$$

where

$$a_{\mathbf{k},\,n}(t)=$$

$$-\boldsymbol{\mathcal{E}}_0\left\{\frac{\mathbf{b}^+(\mathbf{k},n)[1-\exp\{-it(E_0-E_n(\mathbf{k})+h\nu)/\hbar\}]}{E_0-E_n(\mathbf{k})+h\nu}\right.$$

$$\left.\frac{-\mathbf{b}^-(\mathbf{k},n)[1-\exp\{-it(E_0-E_n(\mathbf{k})-h\nu)/\hbar\}]}{E_0-E_n(\mathbf{k})-h\nu}\right\}, \quad (13)$$

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[18] P. M. Morse, *Vibration and Sound* (McGraw-Hill Book Company, Inc., New York, 1948), second edition, p. 416.

and

$$\mathbf{b}^{+}(\mathbf{k}, n)=\frac{-e\hbar}{2\pi m\nu}\int\Phi_n^*(\mathbf{k})(\textstyle\sum_i \nabla_i e^{2\pi i\mathbf{u}\cdot\mathbf{r}_i})\Phi_0 d\tau; \quad (14)$$

$\mathbf{b}^{-}(\mathbf{k}, n)$ is the same as Eq. (14) except for the sign of $\mathbf{u}$. Evaluating Eq. (14), we find

$$\boldsymbol{\varepsilon}_0\cdot\mathbf{b}^{+}(\mathbf{k}, n)=\frac{\mathcal{E}_0 N^{\frac{1}{2}}}{2\pi\hbar\nu}\delta_{\mathbf{k},\mathbf{u}}\mu_n(\epsilon_n-\epsilon_0)$$

$$\times\left\{1-\frac{4\pi n_0}{3}\sum_i\frac{\mu_j^2(\epsilon_j-\epsilon_0)}{(\epsilon_j+\epsilon_n-2\epsilon_0)(\epsilon_n-\epsilon_0)}\right.$$

$$\left.+\frac{4\pi n_0}{3}\sum_{j\neq n}\frac{\mu_j^2(\epsilon_j-\epsilon_0)}{(\epsilon_j-\epsilon_n)(\epsilon_n-\epsilon_0)}\right\}. \quad (15)$$

The expectation value of the dipole moment of the ith electron is

$$\mathbf{P}_i=\int\Phi^* e\mathbf{r}_i\Phi d\tau,$$

which, upon substitution of Eqs. (12), (13), and (15) becomes

$$\mathbf{P}_i=\boldsymbol{\varepsilon}(\mathbf{r}_i)\left\{2\sum_n\frac{\mu_n^2(\epsilon_n-\epsilon_0)}{(E_n-E_0)^2-(2\pi\hbar\nu)^2}\right.$$

$$\times\left[1-\frac{4\pi n_0}{3}\sum_i\frac{\mu_j^2(\epsilon_j-\epsilon_0)}{(\epsilon_j+\epsilon_n-2\epsilon_0)(\epsilon_n-\epsilon_0)}\right.$$

$$\left.+\frac{4\pi n_0}{3}\sum_{j\neq n}\frac{\mu_j^2}{\epsilon_j-\epsilon_n}\frac{\epsilon_j-\epsilon_0}{\epsilon_n-\epsilon_0}\right]$$

$$\times\left[1+\frac{4\pi n_0}{3}\sum_i\frac{\mu_j^2}{\epsilon_j+\epsilon_n-2\epsilon_0}\right.$$

$$\left.\left.+\frac{4\pi n_0}{3}\sum_{j\neq n}\frac{\mu_j^2}{\epsilon_j-\epsilon_n}\right]\right\}. \quad (16)$$

In obtaining this expression we have for the usual reasons dropped all time-dependent terms except those oscillating with frequency $\pm\nu$. We have likewise dropped all exchange terms from Eqs. (15) and (16) for the sake of brevity.

Far from resonance, where $(2\pi\hbar\nu)\ll(E_n-E_0)$, we find upon substituting Eq. (10) in Eq. (16),

$$\alpha=2\sum_n\frac{\mu_n^2}{\epsilon_n-\epsilon_0}\left(1+\frac{8\pi n_0}{3}\sum_i\frac{\mu_j^2}{\epsilon_j-\epsilon_0}\right)+J, \quad (17)$$

where we have made use of the fact that the sum,

$$\sum_{n\neq j}\sum\left\{\frac{\mu_n^2\mu_j^2[\epsilon_j^2+\epsilon_n^2-2\epsilon_0(\epsilon_n+\epsilon_j)+2\epsilon_0^2]}{(\epsilon_j-\epsilon_0)(\epsilon_n-\epsilon_0)(\epsilon_n+\epsilon_j-2\epsilon_0)}\right\}\frac{1}{\epsilon_j-\epsilon_n},$$

is identically equal to 0 because of term by term cancellation. (The cancellation can easily be seen from the the fact that if n and j are interchanged, the quantity is curly brackets remains the same, whereas the last factor changes sign. Thus the term with $j=1$ and $n=2$ is canceled by the term with $j=2$ and $n=1$, and so forth.) Since for an isolated atom the polarizability is given by

$$\alpha_a=2\sum_n\frac{\mu_n^2}{\epsilon_n-\epsilon_0}, \quad (18)$$

Eq. (17) becomes

$$\alpha=\frac{\alpha_a}{1-4\pi n_0\alpha_a/3}+J'. \quad (19)$$

With the exception of J', therefore, Eq. (19) is the same as the classical expression Eq. (1b). In Eqs. (17) and (19) J and J' are quantities included formally to suggest the influence of terms involving exchange, overlap, dipole-quadrupole, quadrupole-quadrupole and higher multipole interactions, and second-order terms in $4\pi n_0\alpha_a/3$. There is a very large number of such terms, and in practice it seems hopeless to attempt their evaluation, both because of their number and complexity, and because of insufficient knowledge of wave functions in any specific case.

III. CONCLUSIONS

Equation (19) now shows in what sense the use of the Lorentz local field is justified in actual crystals. In the limit of low atomic densities, the local field correction is given by the classical formula. It is also possible to discuss the relevance of the results for actual crystalline media.

First, we may ask how well the condition is satisfied in some actual crystals that the local field correction, while not negligible, is not too large, inasmuch as we have treated it as a small quantity as compared to unity. An idea may be given by the example of an alkali halide, where the refraction may be thought of as attributable largely to the lattice of halide ions. Then $4\pi n_0\alpha_a/3$ is of the order of 0.2 in the case of KCl if we take n_0 as the atomic density of halide ions (1.6×10^{22} cm^{-3}) and α_a as their polarizability ($\sim3.3\times10^{-24}$ cm^3).

The exchange terms are likewise small in alkali halides, being of the order of or less than (A/R) $\times\exp-2R/A$, where A is the damping length of the excited state wave function and R is the distance between nearest halide ions; these terms amount to perhaps 1/10 of the Lorentz term.[11]

The dipole-quadrupole terms mentioned above arise from higher expansions of the interaction terms e^2/r_{ij}, and vary as $(q/a\mu)^2$ times the Lorentz term, where q is a quadrupole moment. These terms also represent important corrections to the Lorentz term in actual crystals, and are perhaps of the order of 1/10 the

Lorentz term. Of this same magnitude also are the terms involving the square of the Lorentz term.[19]

As a caution, it should be pointed out that the present treatment may be applicable in a quantitative way only to certain molecular crystals in which the refracting electrons are relatively well confined to particular molecules, and thus do not have strong mutual overlapping of their wave functions. Just this condition may be satisfied, however, in crystals of some large organic dye molecules which are of great practical interest.

Finally, mention should be made of an important physical restriction not hitherto discussed. This is the fact that lattice vibrations have been left out of account. While these have only a very secondary effect on refractive phenomena, it would be necessary to discuss such effects should a treatment be attempted in analogy to that of Peierls,[13] dealing with the absorption of light. Even in discussing refractive effects, the lattice vibrations may need to be brought in when treating the optical properties of thin films, if the film thickness is much less than a wavelength; under these circumstances the energy spectrum of the single exciton levels, of primary importance in the present calculation, will be changed because of the long range of dipole-dipole forces, and the incoherence of the wave function, introduced by the collisions of excitons with the lattice vibrations, will be an essential factor.

This work was begun while the writers were members of the Physics Department of the University of Illinois. We welcome the opportunity to express our appreciation to members of the department, and particularly to F. Seitz, for the cooperation and hospitality extended to us at that time.

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[19] In view of the statements in reference 16, it is possible that the corrections to the Lorentz term are in fact larger than estimated here, for the alkali halides.

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Adiabatic Demagnetization of Chromium Methylamine Alum*

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Adiabatic demagnetization experiments have been performed on a specimen of methylamine chromic alum, $CH_3NH_3 \cdot Cr(SO_4)_2 \cdot 12H_2O$, comprising a spherical mass of small crystals. Using fields up to 23 000 oersteds and starting temperatures of the order of 1.15°K, the "free-spin" entropy of $R \log_e 4$ could be reduced to $0.26R$, and the magnetic susceptibility *versus* entropy relation has been obtained over this range of entropy. The susceptibility was measured at 210 cps with an ac mutual inductance bridge. For temperatures above 0.1°K very good agreement is obtained between these results and the Hebb-Purcell theoretical curve with a value of 0.275° (0.19 cm^{-1}) for the crystalline field splitting of the ground level of the Cr^{+++} ion. In the neighborhood of entropy $R \log_e 2$ the susceptibility begins to increase rapidly and goes through a maximum at $S=0.53R$. As in the case of other paramagnetic alums previously investigated, ac losses occur in the region of maximum susceptibility (the loss component also showing a maximum), and ballistic measurements show hysteresis effects occurring on the low entropy side of the susceptibility maximum.

SINCE the beginning of adiabatic demagnetization experiments many investigations have been made with chromium potassium alum.[1–6] This salt proved to have several properties especially suitable for measurements in the region of temperature below 1°K. It is chemically more stable than iron ammonium alum. In the region between 1°K and 0.1°K its magnetic behavior is in rather good agreement with theoretical predictions.[1,5] The temperatures obtained with initial fields of the order of 20 kilo-oersteds are very low (a few thousandths of a degree Kelvin) and these temperatures can easily be determined with some precision by means of caloric measurements with the help of ac heating.[3]

Recently, however, some disadvantages of the salt were noticed. The Stark splitting of the fourfold-degenerate ground level of the Cr^{+++} ion caused by the crystalline electric field varied considerably for different samples [values between 0.24° and 0.27° were found for the parameter, δ/k, where δ is the energy separation of the two spin doublets[6]]. Small but systematic deviations from the theoretical formulas occur in the neighborhood of 0.2°K. The flat part of the entropy *versus* temperature curve, which is expected to occur at $S=R \log_e 2$, was found at a much lower entropy value, namely, $S=0.4R$. And, finally, the measurements of the lowest temperatures made at Leiden gave results widely different from those found at Oxford.

An explanation for the deviations from the theoretical predictions in the neighborhood of 0.2°K was given by Bleaney.[5] From his microwave experiments it followed

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