PHYSICAL REVIEW VOLUME 112, NUMBER 5 DECEMBER 1, 1958

# Theory of the Contribution of Excitons to the Complex Dielectric Constant of Crystals*†

J. J. HOPFIELD‡
*Physics Department, Cornell University, Ithaca, New York*

(Received July 16, 1958)

It is shown that the ordinary semiclassical theory of the absorption of light by exciton states is not completely satisfactory (in contrast to the case of absorption due to interband transitions). A more complete theory is developed. It is shown that excitons are approximate bosons, and, in interaction with the electromagnetic field, the exciton field plays the role of the classical polarization field. The eigenstates of the system of crystal and radiation field are mixtures of photons and excitons. The ordinary one-quantum optical lifetime of an excitation is infinite. Absorption occurs only when "three-body" processes are introduced. The theory includes "local field" effects, leading to the Lorentz local field correction when it is applicable. A Smakula equation for the oscillator strength in terms of the integrated absorption constant is derived.

## I. INTRODUCTION

THE lowest energy excited states of insulating crystals are usually states of an electron in the conduction band bound to a hole in the valence band. These bound states, called excitons, were first introduced by Frenkel[1] in 1931. The existence of such nonconducting excited states has been tentatively verified in both extremes of exciton models, the Frenkel (tight-bonding) model and the Wannier (weak-bonding) model, by means of optical absorption experiments in the visible and near ultraviolet regions.[2]

The usual method of calculating the optical properties due to exciton states is by use of the semiclassical theory of radiation. This method is satisfactory for the calculation of the dielectric constant in frequency regions of no absorption. The use of this method to treat optical absorption by exciton states raises difficulties perculiar to sets of energy states for which there is but one crystal state having a given wave number $k$ in a finite energy interval. The problem of the description of the fundamental absorption process is the subject of Sec. II. This problem was the motivation for the investigation of the exciton-photon system.

The purpose of the present work is to formulate the problem of the optical properties of excitons in a more rigorous manner than the semiclassical theory through the use of a quantum-electrodynamical formalism and to present a more complete view of the absorption process. The theory, as developed here, is applicable only to crystals exhibiting optical isotropy. The frequency region considered is limited to frequencies for which the wavelength of light is much greater than a lattice constant.[3]

In Sec. III the quantum theory of a classical dielectric is developed. This problem reduces to the interaction of the radiation field with a second boson field, the polarization field. Some possible generalizations of the classical dielectric theory are briefly discussed. Section IV is devoted to constructing an approximate exciton Hamiltonian and to finding the interaction between excitons and photons for this approximate Hamiltonian. It is shown that excitons are approximate bosons and, in interactions with the electromagnetic field, play the role of the quantized polarization field of Sec. III.

In Sec. V the interactions which cause true absorption in crystals are introduced. These interactions result in finite lifetimes for the mixed eigenstates constructed in Sec. IV, and can be treated in terms of a complex dielectric constant. The final section is a summary of the theory, with emphasis on the application to experiments.

## II. PROBLEMS IN THE TREATMENT OF THE OPTICAL PROPERTIES OF EXCITONS

The general theory of the interaction of radiation with insulating crystals is well known.[4] In order to show why the theory as it exists is not complete, the nature of the fundamental absorption process for exciton states will be discussed in detail. The usual description of the absorption process will be shown to be unsound. The inappropriateness of the usual description was the incentive for developing a more complete theory of the optical properties of exciton states.

Unessential complications in the discussion can be avoided by choosing a very simple model of an insulating crystal. The model used here is a simple cubic array of

---

* Based on a Ph.D. thesis submitted to Cornell University.

† A summary of this work was given at the March meeting of the American Physical Society [J. J. Hopfield, Bull. Am. Phys. Soc. Ser. II, 3, 125 (1958)].

‡ Present address: Bell Telephone Laboratories, Murray Hill, New Jersey.

[1] J. Frenkel, Phys. Rev. **37**, 17 (1931).

[2] For experimental evidence of tight-binding excitons, see L. Apker and E. Taft, Phys. Rev. **79**, 964 (1950); **81**, 698 (1951); **87**, 814 (1951). For experimental work on weak-binding excitons, see Gross, Zakharchenya, and Reinov, Doklady Akad. Nauk S.S.S.R. **92**, 265 (1953); **97**, 57, 221 (1954). J. H. Apfel and L. N. Hadley, Phys. Rev. **100**, 1689 (1955).

[3] The general mathematical approach is the same as that of U. Fano, Phys. Rev. **103**, 1202 (1956).

[4] For a brief review of the semiclassical theory and further references, see F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), pp. 647 ff.

nonoverlapping identical atoms.[5] For simplicity, the atoms are assumed to have $S$-type ground states $\psi_0$ and three (degenerate) $P$-type excited states $\psi_p$. The atomic positions are denoted by $\mathbf{L}$. The zero-order ground state of the crystal is a state with every atom in its ground state (i.e., $\Psi_0=\prod_{\mathbf{L}}\psi_{0,\mathbf{L}}$). The elementary excitations of this crystal are states in which one atom at $\mathbf{L}$ is excited and all other atoms are in their ground states. Interactions between the atoms prevent these elementary excitations from being suitable zero-order excited state wave functions. Instead, the zero-order excited state wave functions of this model are linear combinations of the elementary excitations chosen so that the resultant wave functions have translational symmetry. The zero-order excited state (exciton) wave functions are

$$\Psi_{\mathbf{k},p}=\frac{1}{\sqrt{N}}\sum_{\mathbf{L}}\exp(i\mathbf{k}\cdot\mathbf{L})\psi_{p,\mathbf{L}}\prod_{\mathbf{L}'\neq\mathbf{L}}\psi_{0,\mathbf{L}'}, \tag{1}$$

where $N$ is the total number of atoms in the crystal, and $\mathbf{k}$ is an allowed wave vector in the first Brillouin zone. The lattice points are understood to be fixed in space.

The simplest calculation which can be made having anything to do with optical absorption is the calculation of the optical lifetime of an exciton state. The matrix element for the transition to the crystal ground state with emission of a photon of wave vector $\mathbf{k}'$ is given by the atomic matrix element for this process times the factor

$$\frac{1}{\sqrt{N}}\sum_{\mathbf{L}}\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{L}]. \tag{2}$$

If the box in which the radiation field is given periodic boundary conditions is the same size as the crystal, then the factor (2) is zero unless $\mathbf{k}-\mathbf{k}'=2\pi\mathbf{G}$, where $\mathbf{G}$ is a vector of the reciprocal lattice. (This is the well-known wave-vector conservation rule.)

The excitons of interest in the optical properties of solids are those for which $|\mathbf{k}|$ is in the optical wave-vector region. It is these excitons which are coupled to photons having about the same energy as the excitons. Umklapp processes ($\mathbf{G}\neq 0$) couple excitons having optical-region wave vectors with photons of x-ray energy and can be neglected in transition calculations.[6] For optical cases, the wave-number conservation rule is $\mathbf{k}=\mathbf{k}'$. Each exciton $\mathbf{k}$ is coupled to only one radiation mode for radiative single-photon emission. Since transitions, in the framework of second-order perturbation theory, occur only when there is a density of final states to which the initial state is coupled (and the coupling matrix element must not change rapidly over this set of final states), no real transitions take place in the exciton system, contrary to the usual view. Instead, energy oscillates back and forth between the exciton and the photon.[7] This mutual exchange of energy can be described by constructing new eigenstates of the complete Hamiltonian (crystal plus radiation field plus interaction) as is done in Sec. IV.

This lack of one-quantum radiative decay of exciton states is, of course, related to the use of the same periodic boundary conditions for the radiation field as for the crystal. A finite crystal in an infinitely large box containing the radiation field has a finite lifetime for one-photon exciton decay. The ordinary transition probability argument cannot be used to compute the decay behavior,[8] but a calculation based on general damping theory could be made. The form of the optical lifetime of excitons for large crystals is clear on physical grounds. For large crystals, the energy of excitation is shared between excitons and internal photons. Decay takes place when these photons leak out of the crystal. The rate at which the energy leaks out of the crystal is proportional to the energy density in the crystal, some propagation velocity, and the area of the crystal. The decay rate must then be proportional to $N^{-\frac{1}{3}}$ (the surface to volume ratio) and vanishes for large crystals.

With an understanding of the infinite optical lifetime for one-quantum decay for large crystals, a discussion of the fundamental absorption process for exciton states is possible. For an isolated atom, the absorption of light should be treated as a problem of resonance fluorescence. The simplest such process is the two-step process

$$\begin{aligned}&\text{photon } \mathbf{k}+\text{atom in ground state}\\ &\rightarrow \text{no photon}+\text{atom in excited state}\\ &\rightarrow \text{photon } \mathbf{k}'+\text{atom in ground state.}\end{aligned}$$

The photon $\mathbf{k}'$ can be emitted in virtually any direction, so this process represents the scattering of a photon out of the initial state.

For absorption of light by exciton states, the resonance fluorescence process does not represent a scattering process (neglecting surface scattering). The wave-number conservation rule restrains the intermediate-state exciton and the final-state photon to the same wave vector as the incident photon. Again, there is no density of final states to which to make

---

[5] Similar atomic models have been treated in detail by W. R. Heller and A. Marcus, Phys. Rev. 84, 809 (1951), and also in Peierls' early work on the absorption of light by solids: R. Peierls, Ann. Physik 13, 905 (1932).

[6] The results obtained are not correct when the wavelength of light having the same energy as the exciton is less than or equal to a lattice constant. In this case, umklapp processes dominate. This is the reason why there is no conflict between the results obtained and the intuitive idea that in the limit of large lattice constants, an exciton must decay with the same radiative lifetime as an isolated atom.

[7] This phenomenon can be understood from the point of view of the elementary excitations. If two atoms, one of them in an excited state, are separated by a distance small compared to a wavelength, energy transfer by the transfer of a virtual photon is an important process. The use of exciton states avoids the problem of keeping track of phase memory as energy is transported from one atom to another.

[8] For large but finite crystals, the matrix element is not a slowly varying function of energy.

transitions. Energy is again shared between the exciton state and the photon just as it was in the calculation of exciton radiative decay. Thus the fundamental absorption process should not be considered as

$$\text{photon} \longrightarrow \text{exciton},$$

but rather as

$$\text{photon} \longrightarrow \text{exciton (intermediate state)}$$
$$\longrightarrow \text{final energy-absorbing states.}$$

In passing through a crystal, a beam of photons gives up a net amount of energy to the crystal. This energy absorbed by the crystal is not stored in the exciton states (i.e., those exciton states directly coupled to the photon beam). Instead, the energy is stored in those crystal states which, through their coupling with the excitons, cause finite exciton lifetimes. From the point of view of perturbation theory, the so-called "direct" optical absorption processes must in reality be second-order processes. This difference in point of view makes a new attack on the exciton-photon interaction problem seem desirable. It is the exciton-to-energy sink coupling rather than the exciton-to-photon coupling which causes true optical absorption. Sections III and IV are devoted to the diagonalization of the exciton-photon interaction. This approach makes it possible to treat the second-order absorption process by calculating the lifetime due to other interactions of the eigenstates of the exciton-photon system.

The semiclassical theory of the optical properties determines the constitutive relations between $\mathbf{P}$ and $\mathbf{E}$ and between $\mathbf{J}$ and $\mathbf{E}$ for use in Maxwell's equations. This can be done by dividing the crystal into sub-blocks small compared to the wavelength of the incident radiation but large compared to the lattice constant. The constitutive relations are then found for these small blocks and used as point relations in Maxwell's equations. This procedure is not really satisfactory because the wave number conservation rule is lost. The procedure, if properly used, works for absorption processes whose absorption cross sections do not depend on the volume of the sub-block (e.g., photon-exciton processes which also involve phonons). The method is not satisfactory for the treatment of fluorescence processes, for it leads in this case to a dependence of the radiative widths on the dimensions of the sub-blocks used.

A better method of treatment is to use the Fourier decomposition of the radiation and polarization fields. Pekar[9] has recently used this method to treat the dielectric tensors of insulators when no absorption is present. This method should be readily extensible to include the case of absorption by computing in addition the relation between $\mathbf{J}_{\mathbf{k}}$ and the perturbing electromagnetic field (although to the author's knowledge such an extension has not been made in the treatment of excitons). Such an extension must be based on smearing out the exciton states over a finite energy interval. Otherwise there are no real transitions, and $\mathbf{J}_{\mathbf{k}}$ cannot be computed (unless higher order processes are directly taken into account).

The interaction between the radiation field and a crystal for interband electronic transitions is quite different from the exciton-photon interaction just described. In the treatment of interband coupling with photons, there are $N$ electron-hole pair states having a given total wave number $\mathbf{k}$. These $N$ states form an energy continuum (in the limit of large $N$), and absorption transitions can be described in terms of ordinary time-dependent perturbation theory. For a tight-binding model of a crystal, the matrix element coupling the crystal ground state plus one photon with wave number $\mathbf{k}$ to a particular electron-hole pair state of total wave number $\mathbf{k}$ is the order of the atomic matrix element for this transition. Thus, whereas the interaction matrix element is proportional to $V^{-\frac{1}{2}}$ for interband transitions, and $N$ electron-hole pairs interact with each photon, the interaction matrix element is proportional to $(N/V)^{\frac{1}{2}}$ for exciton states, and but one (or a small number in the case of several exciton bands) exciton state is coupled to each photon state.

If the semiclassical theory is used to describe the optical properties of interband transitions, no difficulty is encountered, because real transitions can be computed. In order to justify the use of the semiclassical theory, the tacit assumption must be made that the electrons and holes created in an absorption process are scattered by the lattice and eventually return to the thermal equilibrium distribution. To treat this electron scattering as independent of the electromagnetic interaction is probably justifiable, because each electron-hole pair is very weakly coupled to the electromagnetic field. The qualitative difference between the result of an application of the semiclassical theory to absorption due to interband transitions and absorption due to excitons can be summed up briefly as follows. For the case of interband transitions, energy band structure and the weak electromagnetic field coupling with electron-hole pairs permit the use of semiclassical theory. The gross features of the absorption are independent of the coupling to the lattice. For the case of absorption due to exciton states, the form of the coupling between excitons and the electromagnetic field does not permit the direct application of the semiclassical method. The exciton-lattice collision mechanism is completely responsible for the shape of the absorption line. (The integrated absorption is, however, essentially independent of the absorption mechanism.)

The calculation of the optical properties of exciton states when absorption occurs cannot be carried out by the usual methods without an artificial broadening of the exciton states. Assigning to the exciton lines an energy shape function in order to compute the optical

---

[9] S. I. Pekar, J. Exptl. Theoret. Phys. U.S.S.R. **33**, 1022 (1957) [translation: Soviet Phys. JETP **6**, 785 (1958)]; J. Phys. Chem. Solids **5**, 11 (1958).

properties is not a really satisfactory procedure. There are technical difficulties[10] involved in the shape-function approach. More important, the semiclassical approach treats excitons as independent entities, whereas in reality an exciton which interacts with the radiation field does not exist as an independent entity. Such excitons are always accompanied by a photon component. The separation of the exciton from its photon component as is done in the semiclassical method produces a misleading interpretation of the absorption process.

In the following sections, a field-theoretic (rather than a semiclassical) method is developed for treating the mixed state of excitons and photons. The fundamental absorption process in the interpretation to be developed is the scattering of the mixed states. A complex dielectric constant will be derived from the properties of these states.

## III. QUANTUM THEORY OF A CLASSICAL DIELECTRIC

The classical theory of light propagating in a simple isotropic dielectric with dispersion can be characterized by the frequency dependence of the dielectric constant $\epsilon(\omega)$. Since the exciton contribution to the complex dielectric constant can be most easily understood through comparison to a classical dielectric, it is useful to begin by developing the quantized form of a classical dielectric. The role of boundary conditions and deviations from simple classical behavior are briefly discussed.

The Lagrangian density for an infinite classical dielectric in interaction with the electromagnetic field may be taken to be

$$\mathcal{L}=\frac{1}{8\pi}\left(\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t}+\nabla\varphi\right)^2-\frac{1}{8\pi}(\nabla\times\mathbf{A})^2+\frac{1}{2\omega_0^2\beta}\left(\frac{\partial \mathbf{P}}{\partial t}\right)^2 -\frac{1}{2\beta}(\mathbf{P})^2+\varphi(\nabla\cdot\mathbf{P})+\frac{1}{c}\mathbf{A}\cdot\frac{\partial \mathbf{P}}{\partial t}. \tag{3}$$

This is the Lagrangian density for an oscillating polarization density **P** with a restoring force, as can be seen by comparing (3) with the Lagrangian for a moving charged particle. The equations of motion for the field variables of (3), in conjunction with the usual definitions of **B**, **E**, and **D**, are equivalent to the usual Maxwell's equations plus the constitutive equation

$$\frac{1}{\omega_0^2}\frac{\partial^2\mathbf{P}}{\partial t^2}+\mathbf{P}=\beta\mathbf{E}. \tag{4}$$

If the equations of motion are solved for solutions periodic in time, with angular frequency $\omega$, the dielectric dispersion law determined by (4) is simply

$$\epsilon=1+\frac{4\pi\beta}{1-\omega^2/\omega_0^2}. \tag{5}$$

Equation (3) is thus a suitable Lagrangian density for a classical dielectric.

In order to quantize the fields, the Coulomb gauge ($\nabla\cdot\mathbf{A}=0$) and Born-von Kármán periodic boundary conditions in a rectangular parallelepiped box of volume $V$ are used to expand **A**, **P**, and $\varphi$ in plane waves. The Lagrangian and Hamiltonian of the system can then be expressed in terms of the Fourier components of the fields and their conjugate momenta. The longitudinal modes are not of interest for radiation problems, and can be omitted.

The resultant Hamiltonian represents a system of coupled harmonic oscillators. It is, of course, possible to find the normal modes of these oscillators before quantizing the system. This will not be done, because the Hamiltonian of the coupled oscillators is the analog of the exciton-phonton Hamiltonian of Sec. IV. We therefore quantize the coupled system. The Hamiltonian for the system is

$$\begin{aligned}H=\sum_{\mathbf{k},\lambda_\perp}\Bigg(&\hbar c|\mathbf{k}|(a_{\mathbf{k},\lambda}{}^*a_{\mathbf{k},\lambda}+\tfrac{1}{2})+\hbar\omega_0(b_{\mathbf{k},\lambda}{}^*b_{\mathbf{k},\lambda}+\tfrac{1}{2})\\&+\frac{i\hbar\omega_0^2(4\pi\beta)^{\frac{1}{2}}}{2(c|\mathbf{k}|\omega_0)^{\frac{1}{2}}}\times[(a_{\mathbf{k}\lambda}{}^*b_{\mathbf{k}\lambda}-a_{\mathbf{k}\lambda}b_{\mathbf{k}\lambda}{}^*)\\&+(a_{-\mathbf{k}\lambda}b_{\mathbf{k}\lambda}-a_{-\mathbf{k}\lambda}{}^*b_{\mathbf{k}\lambda}{}^*)]+\pi\beta\omega_0^2\frac{\hbar}{c|\mathbf{k}|}\\&\times[a_{\mathbf{k}\lambda}a_{\mathbf{k}\lambda}{}^*+a_{\mathbf{k}\lambda}{}^*a_{\mathbf{k}\lambda}+a_{\mathbf{k}\lambda}{}^*a_{-\mathbf{k}\lambda}{}^*+a_{-\mathbf{k}\lambda}a_{\mathbf{k}\lambda}]\Bigg),\end{aligned} \tag{6}$$

where the $a$'s and $b$'s are those combinations of coordinate and momentum which, when quantum-mechanical commutation rules are applied, are boson creation and destruction operators. $a_{\mathbf{k}\lambda}{}^*$ is the Hermitian conjugate operator to $a_{\mathbf{k}\lambda}$, etc., and

$$\begin{aligned}&[a_{\mathbf{k}\lambda},a_{\mathbf{k}'\lambda'}]=[a_{\mathbf{k}\lambda},b_{\mathbf{k}'\lambda'}]=[a_{\mathbf{k}\lambda},b_{\mathbf{k}'\lambda'}{}^*]=[b_{\mathbf{k}\lambda},b_{\mathbf{k}'\lambda'}]=0,\\&[a_{\mathbf{k}\lambda},a_{\mathbf{k}'\lambda'}{}^*]=[b_{\mathbf{k}\lambda},b_{\mathbf{k}'\lambda'}{}^*]=\delta_{\mathbf{k}\mathbf{k}'}\delta_{\lambda\lambda'}.\end{aligned} \tag{7}$$

The operators $a_{\mathbf{k}\lambda}{}^*$ are exactly the photon creation operators of the usual Maxwell field while the $b_{\mathbf{k}\lambda}{}^*$ are creation operators for the polarization field. The polarization field "particles" analogous to photons will be called "polaritons." (Excitons will be shown to be one kind of polariton in Sec. IV. Optical phonons are another example of polaritons.) The sum is taken over all **k** space and over polarizations perpendicular to **k**.

---

[10] The chief objection to the shape-function approach is that phase averages are taken at the wrong point in the calculation. Matrix elements between initial and intermediate states are squared and summed, whereas in a second-order process it is actuallly the compound matrix elements to the final states which should be squared and summed. This can give rise to a dependence of calculated results on the method of describing the intermediate states.

The field operators are given in terms of $a$'s and $b$'s by

$$\mathbf{A}=\left(\frac{2\pi c\hbar}{V|\mathbf{k}|}\right)^{\frac{1}{2}}\sum_{\mathbf{k},\lambda_\perp}\boldsymbol{\varepsilon}_\lambda(a_{\mathbf{k}\lambda}e^{i\mathbf{k}\cdot\mathbf{r}}+a_{\mathbf{k}\lambda}{}^*e^{-i\mathbf{k}\cdot\mathbf{r}}),$$
$$\mathbf{P}=\left(\frac{\hbar\omega_0\beta}{2V}\right)^{\frac{1}{2}}\sum_{\mathbf{k},\lambda_\perp}\boldsymbol{\varepsilon}_\lambda(b_{\mathbf{k}\lambda}e^{i\mathbf{k}\cdot\mathbf{r}}+b_{\mathbf{k}\lambda}{}^*e^{-i\mathbf{k}\cdot\mathbf{r}}). \qquad (8)$$

The normal modes of the Hamiltonian will be expressed in terms of a new set of creation and annihilation operators. It is sufficient to work with a single wave number $\mathbf{k}$ and polarization $\lambda$, since $H$ is invariant under translation and different polarizations are not coupled. Define

$$\alpha_\mathbf{k}=wa_\mathbf{k}+xb_\mathbf{k}+ya_{-\mathbf{k}}{}^*+zb_{-\mathbf{k}}{}^*. \qquad (9)$$

If $\alpha_\mathbf{k}$ is to be a normal-mode annihilation operator, then

$$[\alpha_\mathbf{k},H]=E_\mathbf{k}\alpha_\mathbf{k}. \qquad (10)$$

Using definition (9) and Eqs. (6) and (7), the eigenvalue problem (10) may be written in matrix form,

$$\begin{bmatrix} \hbar c|k|+2D & -iC & -2D & -iC \\ +iC & \hbar\omega_0 & -iC & 0 \\ +2D & -iC & -\hbar c|\mathbf{k}|-2D & -iC \\ +iC & 0 & +iC & -\hbar\omega_0 \end{bmatrix}\begin{bmatrix} w \\ x \\ y \\ z \end{bmatrix}=E\begin{bmatrix} w \\ x \\ y \\ z \end{bmatrix}, \qquad (11)$$

where

$$C=\frac{\hbar\omega_0{}^2(\pi\beta)^{\frac{1}{2}}}{(c|\mathbf{k}|\omega_0)^{\frac{1}{2}}},\quad D=\pi\beta\omega_0{}^2\frac{\hbar}{c|\mathbf{k}|}.$$

In units of $\hbar=c=1$, the eigenvalues of (11) are determined by the equation

$$\epsilon\equiv\frac{\mathbf{k}^2}{E^2}=1+\frac{4\pi\beta}{1-E^2/\omega_0{}^2}. \qquad (12)$$

(In the present units, $n\equiv$index of refraction$=|\mathbf{k}|/E$, and $\epsilon=n^2=\mathbf{k}^2/E^2$.) The same relation exists between frequency and wave number for the quantum-mechanical normal modes as for the classical ones.

If the Hamiltonian in the uncoupled system is to be that of uncoupled harmonic oscillators, the new oscillator operators will have the usual commutator relations

$$[\alpha_{\mathbf{k}i},\alpha_{\mathbf{k}'j}]=[\alpha_{\mathbf{k}i}{}^*,\alpha_{\mathbf{k}'j}{}^*]=0,$$
$$[\alpha_{\mathbf{k}i},\alpha_{\mathbf{k}'j}{}^*]=\delta_{\mathbf{k}\mathbf{k}'}\delta_{ij}. \qquad (13)$$

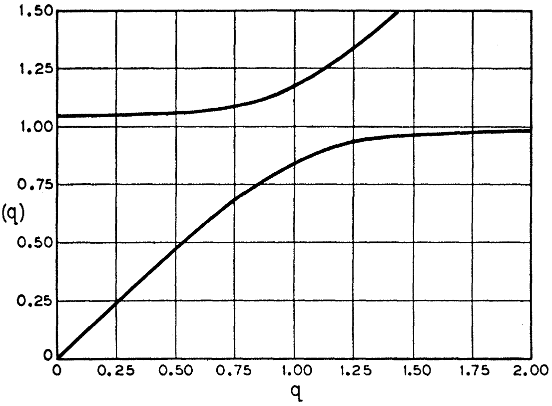

FIG. 1. $E(k)$ for $4\pi\beta=0.1$. Units of $\hbar=c=1$, and $\mathcal{E}=E/\omega_0$, $q=k/\omega_0$.

There are two normal modes for a given wave vector. The second subscript labels these modes. Let $C$ be the four-by-four matrix between the coupled and uncoupled systems of oscillators:

$$\begin{bmatrix} \alpha_{\mathbf{k}1} \\ \alpha_{\mathbf{k}2} \\ \alpha_{-\mathbf{k}1}{}^* \\ \alpha_{-\mathbf{k}2}{}^* \end{bmatrix}=\begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} \\ C_{21} & C_{22} & C_{23} & C_{24} \\ C_{31} & C_{32} & C_{33} & C_{34} \\ C_{41} & C_{42} & C_{43} & C_{44} \end{bmatrix}\begin{bmatrix} a_\mathbf{k} \\ b_\mathbf{k} \\ a_{-\mathbf{k}}{}^* \\ b_{-\mathbf{k}}{}^* \end{bmatrix}. \qquad (14)$$

The combination of the commutation rules for the $\alpha$ representation and for the $a$, $b$ representation yield relations between the $c_{ij}$, which are sufficient to show that

$$C^{-1}=\begin{bmatrix} C_{11}{}^* & C_{21}{}^* & -C_{31}{}^* & -C_{41}{}^* \\ C_{12}{}^* & C_{22}{}^* & -C_{32}{}^* & -C_{42}{}^* \\ -C_{13}{}^* & -C_{23}{}^* & C_{33}{}^* & C_{43}{}^* \\ -C_{14}{}^* & -C_{24}{}^* & C_{34}{}^* & C_{44}{}^* \end{bmatrix}. \qquad (15)$$

A plot of $E(\mathbf{k})$ and some useful combinations of $c_{ij}(\mathbf{k})$ are given in Figs. 1 and 2 for the particular case

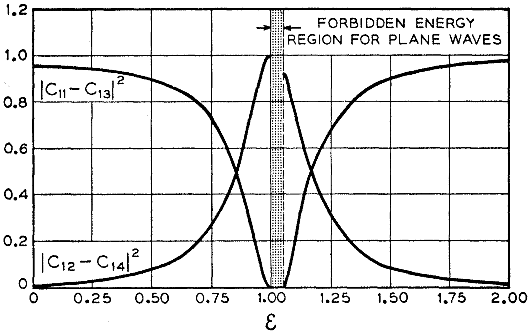

FIG. 2. $|c_{11}-c_{13}|^2$ and $|c_{12}-c_{14}|^2$ as functions of energy. Units $\hbar=c=1$, $4\pi\beta=0.1$, and $\mathcal{E}=E/\omega_0$.

$4\pi\beta=0.1$. The transformation[11] $C$ is given in detail in (16).

$$\begin{aligned}
C_{11}&=\left(1-\frac{E_1}{\omega_0}\right)\left(\frac{|\mathbf{k}|}{\omega_0}+\frac{E_1}{\omega_0}\right)\left(1+\frac{E_1}{\omega_0}\right)\Bigg/\left\{2\left[\frac{\big||\mathbf{k}|E_1\big|}{\omega_0^2}\right]^{\frac{1}{2}}\left[\left(1-\frac{E_1^2}{\omega_0^2}\right)^2+4\pi\beta\right]^{\frac{1}{2}}\right\},\\
C_{12}&=-i(\pi\beta)^{\frac{1}{2}}\left(1+\frac{E_1}{\omega_0}\right)\Bigg/\left\{\left[\frac{|E_1|}{\omega_0}\right]^{\frac{1}{2}}\left[\left(1-\frac{E_1^2}{\omega_0^2}\right)^2+4\pi\beta\right]^{\frac{1}{2}}\right\},\\
C_{13}&=-\left(1-\frac{E_1}{\omega_0}\right)\left(\frac{|\mathbf{k}|}{\omega_0}-\frac{E_1}{\omega_0}\right)\left(1+\frac{E_1}{\omega_0}\right)\Bigg/\left\{2\left[\frac{\big||\mathbf{k}|E_1\big|}{\omega_0^2}\right]^{\frac{1}{2}}\left[\left(1-\frac{E_1^2}{\omega_0^2}\right)^2+4\pi\beta\right]^{\frac{1}{2}}\right\},\\
C_{14}&=-i(\pi\beta)^{\frac{1}{2}}\left(1-\frac{E_1}{\omega_0}\right)\Bigg/\left\{\left[\frac{|E_1|}{\omega_0}\right]^{\frac{1}{2}}\left[\left(1-\frac{E_1^2}{\omega_0^2}\right)^2+4\pi\beta\right]^{\frac{1}{2}}\right\}.
\end{aligned}\tag{16}$$

The quantities $C_{j1}$, $C_{j2}$, $C_{j3}$, $C_{j4}$ may be obtained from the above expressions by replacing $E_1$ by $E_j$ and multiplying by $(i)^j$. Here $E_1$ is the smaller positive root of Eq. (12), $E_2$ the larger positive root, and $E_3=-E_1$, $E_4=-E_2$. The arbitrary constants in $C$ have been so chosen that for $|\mathbf{k}|<\omega_0$ and $\beta_i\rightarrow 0$, $a_\mathbf{k}=\alpha_{\mathbf{k}1}$, $b_\mathbf{k}=\alpha_{\mathbf{k}2}$, $a_{-\mathbf{k}}^*=\alpha_{-\mathbf{k}1}^*$, $b_{-\mathbf{k}}^*=\alpha_{-\mathbf{k}2}^*$.

The ground state in the $\alpha$, or uncoupled, system can now be written in terms of the wave functions for the unperturbed system. The conditions

$$\alpha_{\mathbf{k}1}\psi_{\text{ground}}^{\alpha}=\alpha_{\mathbf{k}2}\psi_{\text{ground}}^{\alpha}=\alpha_{-\mathbf{k}1}\psi_{\text{ground}}^{\alpha}=\alpha_{-\mathbf{k}2}\psi_{\text{ground}}^{\alpha}=0$$

generate recursion relations for the expansion coefficients of the new ground-state wave functions in the photon-polariton occupation-number representation. The result is free of the infrared divergence which would occur if ordinary perturbation theory were used to find the ground-state wave function.

Although it will prove advantageous to work in the $\alpha$ system with "clothed" photons and polaritons, nevertheless for the problems to be worked out it is not necessary to calculate the "clothed" wave functions in terms of the original basis. The operator transformation $C$ is sufficient to calculate the most useful observables.

It is of interest to ask to what extent such a quantum-mechanical dielectric may be treated as a classical system when interactions of the dielectric with a subsystem which is coupled to electromagnetic radiation are considered. In treating radiative problems in a nondispersive dielectric, one may simply start from the Lagrangian (3) with $\mathbf{P}=0$ and multiply the first term by $\epsilon$, the dielectric constant. By using the transformation (14), it can be directly shown that outside the region of strong dispersion, the vector potential operator involves only one set of normal-mode operators. In the low-frequency region, the electrodynamics is equivalent to that obtained in the simple nondispersive treatment outlined above. In the high-frequency region, ordinary vacuum electrodynamics results. In the dispersive region, both sets of normal modes are important, and no simplification of this more complicated electrodynamics is possible.

It is not necessary to treat the case of a finite dielectric medium in detail. One can show that the analytic extension of the quantum-mechanical dispersion relation of an infinite medium to include all frequencies, in conjunction with the classical boundary conditions, describes properly a dielectric of finite extent. It is sufficient, then, to compute the dielectric constant only for infinite geometry.

So far we have considered the usual classical model of a dielectric. There are only a few modifications which can be made to this model in the realm of linear isotropic dielectric theory.[12] In the classical model the polarization $\mathbf{P}(\mathbf{r})$ depends only on the electric field $\mathbf{E}$ at the point $\mathbf{r}$. A generalization of this dependence would allow $\mathbf{P}(\mathbf{r},t)$ to depend on $\mathfrak{F}\mathbf{E}(\mathbf{r}',t')$, where $\mathfrak{F}$ is a linear operator.[13] Another generalization which might be made would be to replace the classical restoring force proportional to $\mathbf{P}$ in the equation of motion of $\mathbf{P}$ by a more general linear restoring force. Both of these modifications will be present to some extent in a real physical dielectric.[14]

A more general restoring force allows a dependence of the polarization frequency on wave number, and is equivalent to using a finite effective mass for excitons. Estimates based on parameters suitable to the alkali halides indicate that the finite-mass effects are small, although they technically introduce a second mode for any given frequency (compare with Fig. 1) and an

---

[11] $C$ is not unitary; the "Hamiltonian" matrix of (11) is not Hermitian. This does not imply that the wave-function transformation represented by $C$ is not unitary. $C$ is not a wave-function transformation but rather defines a particular linear combination of operators. The matrix of (11) is not the Hamiltonian, but rather defines a useful commutator relation. It can, however, easily be shown (by making use of the fact that $C$ has an inverse) that the transformation on Hilbert space from the representation in which the number operators $a^*_\mathbf{k}a_\mathbf{k}$, $b_\mathbf{k}^*,b_\mathbf{k}$, etc. are diagonal to the representation in which the number operators $\alpha_\mathbf{k}^*\alpha_\mathbf{k}$ are diagonal is a unitary transformation.

[12] One trivial modification which will not be discussed now is the addition of more polarization fields.

[13] There are restrictions on the form of $\mathfrak{F}$ if there is to exist a causal relation between $\mathbf{E}$ and $\mathbf{P}$.

[14] Pekar (reference 9) has derived these effects from the semiclassical theory of radiation in the case of no damping (no true absorption). The existence of these effects will be mentioned, but neglected, in the present treatment of absorption.

additional boundary condition at the surface of the crystal. Since the inclusion of such effects would complicate the mathematics, while at the same time should lead to no appreciable physical effects, they will be ignored in the theory to follow.

## IV. INTERACTION OF PHOTONS WITH EXCITONS

An exciton band in an insulating or semiconducting crystal is thought of as a band of nonconducting excited electronic states of the entire crystal. There are two extreme sets of basis functions for describing electronic wave functions in crystals: the Heitler-London scheme of localized atomic wave functions and the Hund-Mulliken-Bloch scheme of electrons spread throughout the entire crystal. Corresponding to these extremes are two models of excitons: the Frenkel or tight-binding exciton and the Wannier or weak-binding exciton. A useful approximate exciton Hamiltonian and the interaction of photons with excitons can be derived for simplified cases of both models.

It will be shown that excitons are approximate bosons (to the same degree that spin waves are bosons) for the tight-binding model. The proof of the validity of the derived Hamiltonian for the weak-binding model will be omitted here.[15] Terms which can cause absorption will be dropped from the approximate Hamiltonian until Sec. V where they will be treated as a perturbation. The approximate exciton-photon Hamiltonian derived (for one exciton band) will be exactly the same as the photon-polariton Hamiltonian (6) of Sec. III.

The extreme tight-binding crystal that is treated here consists of a cubic array of identical atoms separated by distances large enough that the overlap of wave functions of nearest-neighbor atoms can be neglected. If the lattice sites of the atoms are $\mathbf{L}$ and the atomic number of the atoms is $Z$, then the Hamiltonian for the electrons in the absence of radiation is, in dipole approximation,

$$H=\sum_{\mathbf{L}}^{N}\left[\sum_{i=1}^{Z}\frac{\mathbf{p}_{i\mathrm{L}}^2}{2m}-\frac{Ze^2}{|\mathbf{x}_{i\mathrm{L}}|}+\tfrac{1}{2}\sum_{j\neq i}\frac{e^2}{|\mathbf{x}_{i\mathrm{L}}-\mathbf{x}_{j\mathrm{L}}|}\right]+\sum\sum_{\mathbf{L}\neq\mathbf{L}'}^{N}\frac{\mathbf{X}_{\mathrm{L}}\cdot\mathbf{X}_{\mathrm{L}'}}{|\mathbf{L}-\mathbf{L}'|^3}-\frac{3[\mathbf{X}_{\mathrm{L}}\cdot(\mathbf{L}-\mathbf{L}')][\mathbf{X}_{\mathrm{L}}\cdot(\mathbf{L}-\mathbf{L}')}{(\mathbf{L}-\mathbf{L}')^5},\qquad(17)$$

where $\mathbf{X}_{\mathrm{L}}=\sum_{i=1}^{Z}\mathbf{x}_{i\mathrm{L}}$, and $N$ is the number of atoms in the crystal.

A suitable set of $(-1)$th order wave functions for describing the electronic state of the crystal is $\Psi=\prod_{\mathrm{L}}\psi_{\mathrm{L}t}$, where $\psi_{\mathrm{L}t}$ is the wave function of atomic state $t$ on atom $\mathbf{L}$, having atomic energy eigenvalue $E_t$. The ground-state wave function is $\psi_0\equiv\prod_{\mathrm{L}}\psi_{\mathrm{L}0}$. All energies will be considered to be measured from $NE_0$.

The zero-order lowest-energy excited states of the crystal should not be taken as $\Psi_t=\psi_{\mathrm{L}t}\prod_{\mathrm{L}'\neq\mathrm{L}}\psi_{\mathrm{L}'0}$, for there are matrix elements of the dipole interaction of such states between degenerate states having the same excitation on different atoms. If instead the states

$$\Psi_{\mathbf{k}t}=\frac{1}{\sqrt{N}}\sum_{\mathbf{L}}\psi_{\mathrm{L}t}\exp[(i\mathbf{k}\cdot\mathbf{L})]\prod_{\mathbf{L}'\neq\mathbf{L}}\psi_{\mathrm{L}'0}$$

are used, where $\mathbf{k}$ is an allowed wave vector of the first Brillouin zone and periodic boundary conditions are applied in a volume $V$ with number of atoms $N$, the $\Psi_{\mathbf{k}t}$ are orthonormal wave functions for which matrix elements of $H$ between states $t\mathbf{k}$ and $t\mathbf{k}'$ vanish. For these states, $\langle H\rangle$ can be shown[5] to have the form given by (18) for $|\mathbf{k}|V^{\frac{1}{3}}\gg1$,

$$\langle H\rangle_{\mathbf{k}t}=E_t+\frac{N}{V}\frac{8\pi}{3}|\mathbf{X}_{0t}|^2P_2(\cos\theta)\times[j_0(|\mathbf{k}|r)+j_2(|\mathbf{k}|r)],\qquad(18)$$

where $\theta$ is the angle between $\mathbf{k}$ and $\langle\psi_0|\mathbf{X}|\psi_t\rangle$, and $|\mathbf{X}_{0t}|^2\equiv\langle\psi_0|\mathbf{X}|\psi_t\rangle\cdot\langle\psi_t|\mathbf{X}|\psi_0\rangle$.

It is convenient to define a set of operators $d_{\mathrm{L}t}$ and $d_{\mathrm{L}t}^*$ (for $t\neq0$) which operate on the wave function and obey the following rules[16]:

$$\begin{aligned}d_{\mathrm{L}t}\psi_{\mathrm{L}'t'}&=\psi_{\mathrm{L}0}\delta_{\mathrm{LL}'}\delta_{tt'},\\ d_{\mathrm{L}t}^*\psi_{\mathrm{L}'t'}&=\psi_{\mathrm{L}t}\delta_{\mathrm{LL}'}\delta_{t'0},\\ d_{\mathrm{L}t}d_{\mathrm{L}'t'}-d_{\mathrm{L}'t'}d_{\mathrm{L}t}&=0.\end{aligned}\qquad(19)$$

Operator $d_{\mathrm{L}t}^*$ acts only on the wave function of atom $\mathbf{L}$, raising the atom to state $t$ if the atom was previously in state $\psi_0$, and giving a zero result otherwise. Operator $d_{\mathrm{L}t}$ acts only on the wave function of atom $\mathbf{L}$ and yields zero unless the atom was in state $t$, in which case $d_{\mathrm{L}t}$ produces the ground state function. Particularly useful linear combinations of the raising and lowering operators are

$$\begin{aligned}b_{t\mathbf{k}}^*&=\frac{1}{\sqrt{N}}\sum_{\mathbf{L}}\exp(i\mathbf{k}\cdot\mathbf{L})d_{\mathrm{L}t}^*;\\ b_{t\mathbf{k}}&=\frac{1}{\sqrt{N}}\sum_{\mathbf{L}}\exp(-i\mathbf{k}\cdot\mathbf{L})d_{\mathrm{L}t}.\end{aligned}\qquad(20)$$

In terms of these operators, $\psi_{\mathbf{k}t}=b_{t\mathbf{k}}^*\Psi_0$; $\Psi_0=b_{t\mathbf{k}}\psi_{\mathbf{k}t}$. The Hamiltonian (17) can be exactly expressed in terms of the operators $d_{\mathrm{L}t}$. The operator $\mathbf{X}_{\mathrm{L}}$ can be written as

$$(\mathbf{X}_{\mathrm{L}})_{\mathrm{operator}}=\sum_t\langle0|\mathbf{X}_{\mathrm{L}}|t\rangle d_{\mathrm{L}t}+\sum_t\langle t|\mathbf{X}_{\mathrm{L}}|0\rangle d_{\mathrm{L}t}^*+\sum_{t\neq t'}\sum\langle t|\mathbf{X}_{\mathrm{L}}|t'\rangle d_{\mathrm{L}t}^*d_{\mathrm{L}t'}.\qquad(21)$$

---

[15] See J. J. Hopfield, Ph.D. thesis, Cornell University (unpublished).

[16] That $d_{\mathrm{L}t}$ and $d_{\mathrm{L}'t'}$ should commute (rather than anticommute) can easily be shown if the atomic wave functions are written in terms of one-particle functions. Then $d_{\mathrm{L}t}$ involves the product of one electron creation operator and one electron destruction operator. Since individual electron creation and destruction operators (referring to different states) anticommute, pairs of such operators (referring to different states) commute.

The atomic part of the Hamiltonian is

$$\sum_{\mathbf{L}} H_{\mathbf{L}} = \sum_{t,\mathbf{L}} E_t d_{\mathbf{L}t}{}^* d_{\mathbf{L}t} = \sum_{\mathbf{k},t} E_t b_{t\mathbf{k}}{}^* b_{t\mathbf{k}}. \tag{22}$$

The complete Hamiltonian will not be written out, but instead only the terms of $X_{\mathbf{L}}X_{\mathbf{L}'}$ which involve the least number of operators will be retained in an approximate Hamiltonian. The physical interpretation of the omitted terms will be given after the formalism developed for the approximate Hamiltonian is completed. Then the reasons why the dropping of higher powers of operators can often be justified will be more readily apparent. The approximate Hamiltonian, for small ($|\mathbf{k}|r \ll 1$) but nonzero $\mathbf{k}$, is

$$H = \sum_{\mathbf{k},t} E_t b_{t\mathbf{k}}{}^* b_{t\mathbf{k}} + \frac{4\pi}{3}\frac{Ne^2}{V}\sum_{\mathbf{k},t,t'} \times\left[\frac{3(\mathbf{k}\cdot\mathbf{X}_t)(\mathbf{k}\cdot\mathbf{X}_{t'})}{k^2} - \mathbf{X}_t\cdot\mathbf{X}_{t'}\right] \times[b_{t\mathbf{k}}{}^* b_{t'-\mathbf{k}}{}^* + b_{t\mathbf{k}} b_{t'-\mathbf{k}} + b_{t\mathbf{k}} b_{t'\mathbf{k}}{}^* + b_{t\mathbf{k}}{}^* b_{t'\mathbf{k}}], \tag{23}$$

where we have, for convenience, assumed that the matrix elements $\mathbf{X}_t \equiv \langle 0|\mathbf{X}|t\rangle$ are real.

The commutator of $b_{t\mathbf{k}}$ and $b_{t'\mathbf{k}'}{}^*$ is given by

$$[b_{t\mathbf{k}}, b_{t'\mathbf{k}'}{}^*] = \frac{1}{N}\sum_{\mathbf{L}} \exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{L}] \times[d_{\mathbf{L}t} d_{\mathbf{L}t'}{}^* - d_{\mathbf{L}t'}{}^* d_{\mathbf{L}t}], \tag{24}$$

$$[b_{t'\mathbf{k}'}{}^*, b_{t\mathbf{k}}{}^*] = 0.$$

The number operator for the state $\mathbf{L}t$ is $d_{\mathbf{L}t}{}^* d_{\mathbf{L}t}$; $d_{\mathbf{L}t} d_{\mathbf{L}t}{}^*$ is a number operator for the ground state $\mathbf{L}0$ (there are many number operators for the ground state). If matrix elements for the commutator are considered only for states of the crystal in which the total number of excited atoms is at most $M$, then the number of nonzero matrix elements of $d_{\mathbf{L}t}{}^* d_{\mathbf{L}t}$ is less than $M$ while the number of atoms in the state zero is greater than $N-M$. Thus for the states of excitation less than $M$, and $t=t'$, $[b_{t\mathbf{k}}, b_{t\mathbf{k}'}{}^*] = \delta_{\mathbf{k}\mathbf{k}'}$ to order $M/N$, where $N$ is the total number of atoms in the crystal. Similarly for $t \neq t'$, $d_{\mathbf{L}t}{}^* d_{\mathbf{L}t'}$ has a nonzero value for the order of $M$ atoms, zero for the rest, while $d_{\mathbf{L}t} d_{\mathbf{L}t'}{}^*$ is zero for $t \neq t'$. To order $M/N$,

$$[b_{t\mathbf{k}}, b_{t'\mathbf{k}'}{}^*] = \delta_{\mathbf{k}\mathbf{k}'}\delta_{tt'}. \tag{25}$$

In the approximation (25), the Hamiltonian (23) represents a set of coupled harmonic oscillators. The Hamiltonian (23) can in principle be diagonalized by a unitary transformation of the type used in Sec. III and can be expressed in terms of a new set of uncoupled harmonic oscillators.

It is now possible to give a physical interpretation of $b_{t\mathbf{k}}$ and $b_{t\mathbf{k}}{}^*$. The operator $b_{t\mathbf{k}}{}^*$ is so constructed that acting on the ground state it produces an exciton of wave-number $\mathbf{k}$ and atomic state $t$. The operator $b_{t'\mathbf{k}'}{}^*$ applied to the exciton state $t,\mathbf{k}$ produces a crystalline state in which *two* atoms are excited. (This may be verified by direct recourse to the definitions of $b_{t'\mathbf{k}'}{}^*$ and $b_{t\mathbf{k}}$.) Such double excitations are correctly generated by the $b_{t\mathbf{k}}{}^*$ but for one detail. There are $N$ atoms in the crystal and only $N(N-1)$ pairs of atoms taken in either order. Using boson operators produces an error in the normalization of the double-excitation wave functions of $1/N$. The zero-order wave functions for multiple-wave functions can then be represented by boson operators in a manner analogous to spin waves in a lattice,[17] with the same restriction to states with numbers of excited atoms much less than $N$.

The terms which were omitted from the model Hamiltonian (23) have two physical interpretations. Firstly, the $b_{t\mathbf{k}}{}^*$ produces multiple excitations in which the excited atoms are not spatially correlated. Correlated multiple excitations could be constructed which would have different energies from the uncorrelated multiple excitations. Since the correlation energy of $M$ dipoles vanishes as the dipoles are separated, the number of correlated states of appreciably different energy from the uncorrelated states should again be of order $M/N$. Secondly, the dipole interaction of single excitations depends on the presence or possibility of other excitations. These effects have atomic analogies. If an atom in its ground state is placed in an electric field, not only the states which are coupled to the ground state by the perturbation are mixed in with the ground-state wave function, but all accessible states are mixed in through higher-order perturbations. If a gas of atoms contains some atoms in an excited state, its dielectric constant will be different from that of a gas of atoms all in their ground states. Both of these atomic effects are omitted in the linearization of the model.

The perturbation Hamiltonian for the interaction of an atom with the radiation field (in dipole approximation) can be written as

$$\begin{aligned} H_{\text{atom}}' = {} & \frac{ie}{m}\sum_{t'\neq 0,\, t\neq 0,\, t'\neq t}\ \sum_{\mathbf{k},\lambda}\left(\frac{2\pi\hbar c}{V|\mathbf{k}|}\right)^{\frac{1}{2}} \\ & \times \omega_{t't} d_{\mathbf{L}t'}{}^* d_{\mathbf{L}t}\langle t'|\mathbf{X}|t\rangle\cdot\boldsymbol{\varepsilon}_{\mathbf{k}\lambda} \\ & \times[a_{\mathbf{k}\lambda}{}^*\exp(-i\mathbf{k}\cdot\mathbf{L}) + a_{\mathbf{k}\lambda}\exp(i\mathbf{k}\cdot\mathbf{L})] \\ & + \frac{ie}{m}\sum_{t,\mathbf{k},\lambda}\left(\frac{2\pi\hbar c}{V|\mathbf{k}|}\right)^{\frac{1}{2}}\omega_{0t} \\ & \times[\langle 0|\mathbf{X}|t\rangle d_{\mathbf{L}t} - \langle t|\mathbf{X}|0\rangle d_{\mathbf{L}t}{}^*]\cdot\boldsymbol{\varepsilon}\mathbf{k}_{\lambda} \\ & \times[a_{\mathbf{k}\lambda}{}^*\exp(-i\mathbf{k}\cdot\mathbf{L}) + a_{\mathbf{k}\lambda}\exp(i\mathbf{k}\cdot\mathbf{L})] \\ & + \frac{e^2}{2m}\sum_{\mathbf{k},\lambda}\frac{2\pi\hbar c}{V|\mathbf{k}|}Z \\ & \times[a_{\mathbf{k}\lambda}{}^* a_{-\mathbf{k}\lambda}{}^* + a_{\mathbf{k}\lambda}a_{-\mathbf{k}\lambda} + a_{\mathbf{k}\lambda}{}^* a_{\mathbf{k}\lambda} + a_{\mathbf{k}\lambda}a_{\mathbf{k}\lambda}{}^*]. \end{aligned} \tag{26}$$

---

[17] For a discussion of the conversion to boson operators for the spin wave case, see F. J. Dyson, Phys. Rev. **102**, 1217 (1956).

The first term of this perturbation Hamiltonian couples the different excited states of the atom to each other, but does not couple any excited states to the ground state. The effect of this term will be omitted from the radiative interaction Hamiltonian and will be treated as a perturbation on the last two terms. The model radiation Hamiltonian will be expressed in terms of the exciton and photon creation and annihilation operators. Umklapp processes will be omitted for the usual reasons. It is assumed that the ground state of the atoms under consideration is an $S$ state (all electrons being considered). There will then exist matrix elements of $\mathbf{X}$ from the ground state only to $P$ states. The three degenerate $P$ states may be always so arranged that the state created by $b_{\mathbf{k}t}{}^*$ has matrix elements of $\mathbf{X}$ for a single atom only in directions perpendicular or parallel to $\mathbf{k}$. Such an arrangement divides the excitons into two categories: transverse excitons with $\langle 0|\mathbf{X}|t\rangle$ perpendicular to $\mathbf{k}$ and longitudinal excitons with $\langle 0|\mathbf{X}|t\rangle$ parallel to $\mathbf{k}$. There is no interaction between the longitudinal excitons and photons since $\boldsymbol{\varepsilon}_{\mathbf{k}\lambda}\cdot\langle 0|\mathbf{X}|t\rangle=0$ for longitudinal excitons of wave number $\mathbf{k}$. Similarly there is no interaction between any of the three exciton modes in the Hamiltonian (23). For consideration of optical interactions, the longitudinal excitons can be omitted. In (23) and (26) only $P$-states have interactions with each other or with the radiation field, so all other exciton states will be omitted from the final Hamiltonian. The transverse $P$-states will be labeled by a principal quantum number $n$ and a polarization $\lambda$. By utilizing the atomic $f$-sum rule,[18] we obtain the exciton photon interaction in the form

$$
\begin{aligned}
H' = \sum_t \Bigg( \sum_{\mathbf{k},\lambda} \Bigg[ & i\left(\frac{2\pi\hbar c}{V|\mathbf{k}|}\right)^{\frac{1}{2}} \left(\frac{e\omega_{0t}}{c}\right) \langle 0|\mathbf{X}|t\rangle \\
& \times (b_{\mathbf{k}\lambda t}a_{\mathbf{k}\lambda}{}^* - b_{\mathbf{k}\lambda t}{}^* a_{\mathbf{k}\lambda} + b_{\mathbf{k}\lambda t}a_{-\mathbf{k}\lambda} - b_{\mathbf{k}\lambda t}{}^* a_{-\mathbf{k}\lambda}{}^*) \\
& + \frac{2\pi e^2 N}{c|\mathbf{k}|V}\omega_{0t}|\langle 0|\mathbf{X}|t\rangle|^2 \\
& \times (a_{\mathbf{k}\lambda}{}^* a_{\mathbf{k}\lambda} + a_{\mathbf{k}\lambda}a_{\mathbf{k}\lambda}{}^* + a_{\mathbf{k}\lambda}{}^* a_{-\mathbf{k}\lambda}{}^* + a_{\mathbf{k}\lambda}a_{-\mathbf{k}\lambda}) \Bigg] \Bigg). \qquad (27)
\end{aligned}
$$

This is the approximate exciton-photon interaction Hamiltonian of the tight-binding excitons.

The total model Hamiltonian for the excitons and photons which interact is

$$H = H_{\text{exciton}} + H_{\text{photon}} + H_{\text{exciton-photon}} + H_{\text{exciton-exciton}},$$

where

$$
\begin{aligned}
H_{\text{photon}} &= \sum_{\mathbf{k},\lambda} \hbar c|\mathbf{k}|(a_{\mathbf{k}\lambda}{}^* a_{\mathbf{k}\lambda}), \\
H_{\text{exciton}} &= \sum_{\mathbf{k},t,\lambda} E_t(b_{t,\mathbf{k},\lambda}{}^* b_{t,\mathbf{k},\lambda}), \\
H_{\text{exciton-exciton}} &= -\frac{2\pi}{3}\frac{Ne^2}{V} \sum_{t',t,\mathbf{k},\lambda} (\mathbf{X}_t\cdot\mathbf{X}_{t'}b_{t\mathbf{k}\lambda}{}^* b_{t',-\mathbf{k}\lambda}{}^* \\
&\quad + \mathbf{X}_t{}^*\cdot\mathbf{X}_{t'}{}^* b_{t\mathbf{k}\lambda}b_{t',-\mathbf{k}\lambda} + \mathbf{X}_t{}^*\cdot\mathbf{X}_{t'}b_{t\mathbf{k}\lambda}b_{t'\mathbf{k}\lambda}{}^* \\
&\quad + \mathbf{X}_t\cdot\mathbf{X}_{t'}{}^* b_{t\mathbf{k}\lambda}{}^* b_{t\mathbf{k}\lambda}) \\
&\quad (\mathbf{X}_t \equiv \langle 0|\mathbf{X}|t\rangle), \qquad (28)
\end{aligned}
$$

and $H_{\text{exciton-photon}}$ is given by (27).

A comparison of (27) with (6) shows that each exciton type $t$ interacts with radiation exactly as the quantized polarization field interacts with radiation. In the absence of interaction between the excitons, the system of excitons in interaction with radiation in the model under consideration can be represented as a quantized set of classical polarization fields, one for each exciton band which interacts with radiation. Thus excitons are a physical example of the general polaritons of Sec. III.

The dipole interaction term of the exciton Hamiltonian is the quantum-mechanical expression of the classical "local field" correction to the polarizability of a density of atoms. For the case of only one exciton mode (transverse) with dipole matrix element $|X|$ and atomic energy level $E$, the relation between the energy and wave number can be determined by using the diagonalization method of Sec. III. Direct application of the diagonalization procedure yields the secular equation

$$\frac{\mathbf{k}^2}{\omega^2} = 1 + \frac{8\pi(N/V)e^2|X|^2E}{E^2 - (8\pi/3)(N/V)e^2|X|^2E - \omega^2}. \qquad (29)$$

It is seen that the dipole coupling has two effects: it reduces the frequency of the excitons from that of the free atom and it increases the oscillator strength. Since $2e^2|X|^2E/(E^2-\omega^2)$ is the polarizability of a free atom, (29) can be rewritten in the more familiar Lorenz-Lorentz form

$$\epsilon = \frac{\mathbf{k}^2}{\omega^2} = 1 + \frac{4\pi(N/V)\alpha}{1-(4\pi/3)\alpha(N/V)}, \quad \text{or} \quad \frac{\epsilon-1}{\epsilon+2} = \frac{4\pi}{3}\alpha\frac{N}{V}. \qquad (30)$$

The energy of the coupled excitons is

$$E_{\text{coupled}} = E\left(1 - \frac{8\pi}{3}\frac{N}{V}e^2\frac{|X|^2}{E}\right)^{\frac{1}{2}}.$$

The expansion of the square root to first order yields $E-(4\pi/3)(Ne^2/V)|X|^2$, which agrees with the expression obtained by Dexter[19] from perturbation theory.

---

[18] The $f$-sum rule was used by Neamtan in his perturbation treatment of the dielectric properties (neglecting absorption) of a dilute gas to divide the $A^2$ term into contributions from the individual dispersion oscillators. See S. M. Neamtan, Phys. Rev. **92**, 1362 (1953); **94**, 327 (1954).

[19] D. L. Dexter, Phys. Rev. **101**, 52 (1956).

If the radiation field is omitted from the problem, and the coupled exciton problem is solved, the shift in zero-point energy corresponds to the van der Waals forces.

There are two points of view which can be adopted for treating the "local field" effects in the extreme tight-binding model. The semiclassical treatment assigns to each atom in the crystal a polarizability. The dielectric constant of the crystal is then computed by taking into account the dipole interactions between different polarized atoms. In the quantum-mechanical treatment, there are terms in the crystal Hamiltonian representing pairs of atoms. This interaction makes the crystal wave functions and energy levels different from the wave functions and energy levels of a collection of noninteracting atoms. Since the dipole interactions of the various atoms have, in this view, been properly taken into account in the quantum mechanics, it is not necessary to specifically include "local field" effects in the electrodynamics of the crystal.

The quantum-mechanical point of view is used throughout the present work. It is simpler to work in terms of an assumed set of entire crystal eigenfunctions than to work directly with the atomic wave functions. In addition, interpretation is easier on an entire-crystal basis. An example is the occurrence of the $4\pi/3$ catastrophe of the semiclassical theory at a finite frequency $\omega$ not the same as any atomic transition frequency. This occurrence is easily understood in the quantum-mechanical description in terms of the difference between the energy levels of an atom and the crystal energy levels. Finally, the "Lorentz local field correction" is only a first approximation to the exact result which would be obtained by using the exact Hamiltonian.[20] A formalism written in terms of whole-crystal states (in which it is assumed that the entire crystal Hamiltonian has been diagonalized) can be valid whether or not the semiclassical local field correction is an adequate description of interactions between atoms.

For the theory of absorption it will be assumed that the exciton-exciton interaction Hamiltonian has been unscrambled so that the exciton creation and annihilation operators for different bands are no longer coupled. The Hamiltonian for either the weak- or the tight-binding model will be taken to be

$$H_{\text{exciton}}+H_{\text{photon}}+H_{\text{exciton-photon}}$$

plus a perturbing term which will induce transitions. The exciton energies and oscillator strengths which belong in this Hamiltonian can in principle be obtained from the diagonalization of the exciton-exciton interaction.

In the absence of absorption, the role of exciton states in dielectric phenomena is clear from the comparison of the Hamiltonian derived here and the generalization of Sec. III to include more polarization modes. The exciton states simply represent the quantized form of the classical polarization field. The eigenstates (normal modes) of the total Hamiltonian represent those combinations of polarization waves and electromagnetic waves which propagate in an ideal classical dielectric medium.

## V. COMPLEX DIELECTRIC CONSTANT

Absorption, from the point of view of the present paper, is due to terms which have been left out of the approximate Hamiltonian. In Sec. IV, the "many-body" interactions of excitons with all other energy modes of the crystal were omitted. The simplest of these interactions are the three-body interactions (in an "unclothed" notation):

$$\text{exciton} \leftrightarrow \text{exciton}'+\text{photon}, \tag{a}$$

$$\text{exciton} \leftrightarrow 2 \text{ photons}, \tag{b}$$

$$\text{exciton} \leftrightarrow \text{exciton}'+\text{phonon}, \tag{c}$$

$$\text{exciton} \leftrightarrow 2 \text{ phonons}, \tag{d}$$

$$\text{exciton} \leftrightarrow \text{phonon}+\text{photon}, \tag{e}$$

and their variations.[21] The fact that fluorescence is not usually observed in pure materials implies that (a), (b), and (e) are probably not the dominant decay processes. The possibility of a sizeable energy shift in the exciton states due to interaction (c), the exciton polaron problem, is not expected to invalidate the general results of this paper. The author sees no reason why the qualitative conclusions to be derived would be altered in form by the use of excitons clothed in phonons, although the physical parameters would in any particular instance, of course, be altered by the inclusion of lattice polarization effects.

Order of magnitude estimates of the transition probabilities of different possible processes leading to exciton decay also indicate that process (c) should be the dominant decay process. The scattering lifetime for process (c) should be of the same order as free carrier scattering lifetimes for carriers having the

---

[20] There is a simple classical analogy which points out why the Lorentz-Lorenz equation is a linear approximation. Classically, there is a large and rapidly varying field near an atom in an $S$-state due to the instantaneous value of its dipole moment. Thus an atom in a crystal feels the applied field, the mean interaction field of all induced dipoles, and a large, randomly varying field having an average value of zero. If the polarization of the atom is given by $\mathbf{P}=\alpha\mathbf{E}+\delta\mathbf{E}E^2$ (there will be no $E^2$ term for spherically symmetric atoms), then the time-averaged polarization $\mathbf{P}$ in the presence of an applied field $\mathbf{E}_a$ (small) and a large fluctuating field $E_0(t)$ will be approximately $\mathbf{P}=[\alpha+\delta'[\bar{E}_0(t)]^2\mathbf{E}_a$ where $\delta'$ can be computed from $\delta$ and the details of the large, rapidly varying field. The observed polarization is proportional to $\mathbf{E}_a$, but the observed polarizability is not $\alpha$. This effect is not included in classical local field formulas.

[21] If the phonons are coupled to the electromagnetic field, a second type of process is possible. The mixed states of photon and phonon (for which the formalism of Sec. III is also applicable) can decay into exciton states. This gives rise to a kind of indirect absorption process.

same kinetic energy as the exciton, and thus be about $10^{-10}$ to $10^{-14}$ second. All the other processes are much slower. Process (e), for instance, has a lifetime greater than (but of the same order as) $\alpha^{-1}T_0$, where $\alpha$ is the exciton-lattice coupling constant, and $T_0$ is the lifetime of decay of a localized exciton for photon decay neglecting the resonant sharing of energy. $T_0$ thus lies between $10^{-4}$ and $10^{-8}$ second, depending upon the exciton oscillator strength, whole $\alpha$ for most excitons will be of the same order as $\alpha$ for free carriers, lying between 0.1 and 5. Processes (a), (b), and (d) are also slow relative to (c).

Any of these three-body interactions which produce transitions represent a sink from the optical point of view, for a three-body transition is a method of transferring energy from a mode of wave vector **k** into modes of wave vectors not equal to **k**. From a physical point of view this represents a scattering, whereas two-body interactions which conserve wave number do not in general cause a process which can be viewed as scattering or an "absorption" because the restriction of wave-vector conservation usually prohibits real transitions. On the other hand, any of the three-body processes listed have an energy continuum of final states of the same wave number as the initial exciton state, producing the possibility of real transitions if the exciton energy overlaps this continuum.

Observed exciton absorption lines are virtually always broad compared to atomic line widths and the widths are strongly temperature dependent. An inference which may be drawn from this fact is that the exciton-lattice interaction is dominant in exciton decay processes. It would then seem to be the exciton part of the clothed exciton which causes clothed excitons to scatter and produces the effect of optical absorption.

In order to represent the coherent propagation of the primary beam, it is sufficient to take into account the attenuation of the primary beam, without calculating explicitly the final history of the scattered waves. We follow the treatment of the complex dielectric constant given by Fano[22] to derive a complex dielectric constant which expresses the effects of higher-order couplings. We therefore assume that each of the normal modes of the approximate exciton-photon Hamiltonian is coupled weakly to a continuum of states through the three-body (and higher-order) processes described. This coupling is assumed to be weak (the transition probability for decay is much less than the reciprocal of the normal-mode frequency). It must be further assumed that the matrix elements and density of final states for normal-mode decay are slowly varying functions. Neglecting the energy shift due to the "dissipative" interaction, Fano shows that a suitable complex dielectric constant is

$$\epsilon(\omega)=1+\sum_j \frac{4\pi\beta_j}{1-(\omega^2/\omega_j^2)+i\gamma_j\omega}, \tag{31}$$

where $\gamma_j$ is the transition probability for decay of the $j$th normal mode, and $\beta_j$ is the polarizability of the $j$th mode.

The $\gamma_j$ can in turn be expressed in terms of bare exciton lifetimes if the decay process is sufficiently simple. For example, if the exciton → exciton′+phonon process is assumed to be the decay-causing interaction, and the exciton′ is assumed not to interact with radiation, then the relation between $\gamma_j$ and the decay lifetime for a bare exciton is determined by writing the exciton → exciton′+phonon interaction in terms of the normal mode operators. In the simple case of only one exciton band, the transformation is described by Eq. (16). In the simple one-band case, $|C_{12}|^2\approx 1$ for $E\approx\omega_0$, and $\gamma^{-1}$ is the bare exciton lifetime. For more complicated cases, the relation is not necessarily so simple, for there can exist interference effects between different exciton components in normal-mode decay.

If the density of states into which the normal modes decay is not smooth, additional structure reflecting this fact may be observable. This can be the case when an optically accessible exciton band is coupled through phonons to other energy bands not available to direct optical transitions. In this case $\gamma$ will be a function of frequency. Indirect absorption of light by exciton states in a phonon process (photon→optical phonon→exciton +phonon′) is an example of such a process. Here, the absorption is associated with oscillators (optical phonons) of very low energy. There is a sudden change in the lifetime $[\gamma(\omega)]$ of the phonon-photon state as the frequency increases to a value which allows exciton formation, even though the frequency region is far removed from optical phonon frequencies, and the exciton band is not directly accessible to optical transitions.

## VI. SUMMARY AND APPLICATIONS TO EXPERIMENTAL WORK

The qualitative difference between the absorption of light by exciton states in the theory developed here and the usual point of view must be strongly emphasized. In the usual view, light propagating through the crystal directly creates excitons, and the energy flux of the incident beam is reduced by the amount of energy given up in creating excitons. The incorrectness of this point of view was discussed in Sec. II. In the point of view developed here, light inside a crystal mixes strongly with excitons in the crystal, producing a propagating mode of mixed exciton and photon. True absorption takes place when other crystal states are excited by the exciton part of this propagating mode. The energy absorbed by a crystal does not lie in the exciton modes to which the light was directly coupled. Instead, it

---

[22] Fano, reference 3, Appendix A.

lies in the crystal energy modes to which the excitons coupled to the light can make transitions. This qualitative difference, in conjunction with the fact that excitons do not undergo pure radiative decay, can produce large changes in the interpretation of optical phenomena in crystals.[23]

A qualitative distinction between two different types of absorption can be made in order to understand more clearly the absorption process. The kind of absorption usually considered might be called "true absorption." In true absorption, the intensity of a light wave propagating through a crystal is diminished because of the absorption of energy from the light wave by the crystal. The measure of true absorption is classically the spatial rate of attenuation of the Poynting vector. A second kind of absorption might be termed "penetration absorption." A classical dielectric with no damping exhibits total external reflection in a semi-infinite geometry. This total reflection occurs in a frequency region just above the resonant frequency of the dielectric. The dielectric constant is negative in this frequency region. An electromagnetic field exists inside the dielectric even in this total-reflecting frequency region. The wave vector (for normal incidence) is purely imaginary inside the dielectric. If the transmission of a plane parallel sheet of such a dielectric is measured as a function of sheet thickness, the imaginary part of the wave vector can be measured in spite of the fact that there is no absorption of energy by the dielectric.

The problem of interpretation of experimental results is a completely classical one, but one which should be closely examined before applying this theory to experimental results. A differentiation between the two kinds of absorption is not normally made in cases of strong optical absorption, where both types are usually present. The theory developed here relates the imaginary part of the dielectric constant to parameters characteristic of the crystal. It is important for applications of the theory to analyze and interpret experiments in such a way that the optical constants ($n_r$ and $n_i$, $\epsilon_r$ and $\epsilon_i$, or suitable combinations) are obtained. This is especially true in making reflection corrections to transmission experiments for obtaining $n_i$. A trivial and extreme example is the measurement of $n_i$ in the case of pure penetration absorption. If an ordinary reflection correction is made, it will be found that all the energy not reflected from the crystal is transmitted through the crystal. To interpret this fact as a lack of energy absorption by the crystal is completely correct. To interpret this fact as proof that the imaginary part of the index of refraction is zero is definitely incorrect.

A useful approximate expression can be found from the more general Eq. (31) for $\beta$ in terms of the observed absorption coefficient if $\gamma/\omega_0 \ll 1$ and an absorption single line is sufficiently isolated that the following two conditions are met:

1. The contribution of all other bands to the real part of the dielectric constant is positive and essentially constant over the region of study.
2. The contribution of all other bands to the imaginary part of the dielectric constant is zero.

The approximate formula, exact only for $\gamma = 0$, is

$$\int_{\text{absorption line}} n_i(\omega)d\omega = \omega_0 \frac{4\pi\beta}{n} \int_0^1 \frac{(1-y^2)^{\frac{1}{2}}}{[1+(4\pi\beta/n^2)y^2]^{\frac{1}{2}}} dy, \quad (32)$$

where $n^2$ is the dielectric constant due to all other lines, evaluated in the region of absorption of the line under study, and $\omega_0$ is the frequency of the absorption line. (The integral can be expressed in terms of elliptic functions if desired.) The large contribution to the integral occurs when $y$ is near zero. In many physical cases, $4\pi\beta$ is small enough that $4\pi\beta/n^2$ can be neglected in the denominator. For these cases,

$$f_{\text{absorption line}} = \frac{n}{\pi^2} \frac{m}{e^2} \omega_0 V_{\text{cell}} \int_{\text{absorption line}} n_i(\omega)d\omega. \quad (33)$$

This equation resembles closely the Smakula equation[24] for absorption by impurities in a crystal, except that a factor $[3/(n^2+2)]^2$ which occurs in the Smakula expression is missing here. The physical reason for the absence of this term is that, for the perfect crystal, all "local field" effects are taken into account in a correct computation of the crystal wave functions (see Sec. IV). The derivation of (33) does not rest on the assumption $n_i \ll 1$. However, the extension of (33) to the case of two adjacent lines in the form

$$f_1 + f_2 = \text{constant} \times \int_{\text{both lines}} n_i(\omega)d\omega$$

is not correct unless the condition $n_i \ll 1$ is met.

One important result of (33) concerns the estimation of relative oscillator strengths from observed absorption data (i.e., from $n_i$). When two absorption lines lie close together, the lower-energy line is suppressed and the higher-energy line is enhanced in the area under the $n_i(\omega)$ curve. This effect arises because the contribution by the higher-energy line to $n^2$ in (33) for the lower line is large and positive, whereas the contribution

---

[23] In some cases, the applicability of the theory is limited to low temperatures. In order for the theory to be valid, it is necessary that the rate of exchange of energy between the exciton and photon in a mixed eigenstate be fast compared to the transition probability for exciton-phonon scattering. The rate of energy exchange is approximately $\omega_0(\pi\beta)^{\frac{1}{2}}$, as can be seen from (12). For oscillator strengths of $10^{-3}$ or smaller and temperatures high enough that the free-carrier scattering lifetime is around $10^{-14}$ sec, the rate of energy is no longer fast compared to the rate of exciton scattering.

[24] See the "generalized Smakula equation" of D. L. Dexter (reference 19).

by the lower-energy line to $n^2$ in (33) for the higher energy line is large and negative.

The assumptions which have been made to obtain the theory of the dielectric constant were discussed as they were made. The least satisfying of these is probably the assumption that the general theory is valid for actual crystals which do not fit either extreme exciton model. The theory as constructed in Secs. III through V is a more precise theory than the usual one outlined in Sec. II. The division of the crystal into sub-blocks, the use of semiclassical radiation theory, the assumption that $\epsilon-1$ is a small quantity, and an appeal to a group velocity were all avoided.

The formulation given of the complex dielectric constant problem makes it possible, in principle, to compute the complex dielectric constant from first principles. Although it is impossible to make really satisfying calculations on the basis of this theory without much more knowledge of exciton wave functions and the exciton-lattice interaction than is available at present, nevertheless the theory can be of use in providing a framework in which to interpret the optical absorption associated with exciton states.

## VII. ACKNOWLEDGMENTS

The author wishes to thank Professor A. W. Overhauser for suggesting the problem and for many hours of helpful discussion. He also wishes to thank Dr. C. Herring for his criticisms of the manuscript, and Mr. P. A. Carruthers for translating a Russian paper. He wishes to acknowledge the support of a National Science Foundation Predoctoral Fellowship during part of the work.

---

PHYSICAL REVIEW VOLUME 112, NUMBER 5 DECEMBER 1, 1958

# Lorentzian Gas and Hot Electrons

I. Adawi
*RCA Laboratories, Princeton, New Jersey*

(Received April 24, 1958; revised manuscript received August 14, 1958)

The problem of hot electrons in a nonpolar crystal is reconsidered using the Lorentzian gas model more accurately. Scattering by acoustical phonons alone is considered first. The new results are (1) an asymptotic formula for the moments of the velocity distribution which permits calculation of the deviation from the square root law at high fields, and (2) a recursion system allowing the calculation of any velocity polynomial in terms of the average energy, random velocity, and mobility of the electrons. Scattering by ionized impurities in addition to acoustical phonons is considered next and the distribution function is derived. The proportionality constant relating the change in the low-field mobility to $E^2$ is shown to be highly sensitive to ionized impurity scattering. Thus, appreciable changes from its value for pure lattice scattering occur for $\mu_0/\mu_I$ as low as $10^{-3}$. ($E$ is the field strength and $\mu_0$ and $\mu_I$ are the low-field lattice and impurity mobilities, respectively.) It is pointed out that substantial deviations from results obtained using a Maxwellian distribution do occur.

## 1. INTRODUCTION

THIS paper concerns the motion of electrons (or holes) in nonpolar semiconductors or insulators in strong electrostatic fields. We consider a crystal with spherical energy bands and at a high enough temperature so that the equipartition law is valid for the acoustical lattice oscillators with which an electron interacts. With these two assumptions, Shockley[1] shows that the scattering cross section[2] and the average energy losses for an electron interacting with acoustical phonons, remain, to a good approximation, the same if we replace the phonon field by a classical gas of hard spheres of mass[3] $KT/c^2$ (where $c$ is the longitudinal speed of sound and $KT$ is the thermal energy) and of such a density as to make the mean free path (mfp) the same in both cases. This is the Lorentzian[4,5] gas model or the gaseous discharge analogy. Indeed, the velocity distribution function is the same in both cases. (See Sec. 2.)

In Sec. 2 we shall give accurate calculations for the physical properties of hot electrons in Shockley's model. In particular, we wish to emphasize deviations from the square root law in the current voltage characteristics at intemediate fields.

In Sec. 3 we shall consider scatterings by ionized impurities, in addition to acoustical phonons, derive the proper distribution function and obtain deviations from Ohm's law at low fields. The results will be compared to those obtained using a Maxwellian distri-

---

[1] W. Shockley, Bell System Tech. J. **30**, 990 (1951).

[2] See also F. Seitz, Phys. Rev. **73**, 549 (1948); A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, 1953), second edition, Chap. 9.

[3] The validity of equipartition implies that $KT/c^2$ is much greater than the electron effective mass.

[4] H. A. Lorentz, *Theory of Electrons* (Stechert and Company, New York, 1923), p. 267.

[5] S. Chapman and T. G. Cowling, *The Mathematical Theory of Nonuniform Gases* (Cambridge University Press, Cambridge, 1953), second edition, p. 187.