A QUANTUM-MECHANICAL THEORY OF THE CONTRIBUTION OF EXCITONS TO THE COMPLEX DIELECTRIC CONSTANT OF CRYSTALS

A Thesis

Presented to the Faculty of the Graduate School

of Cornell University for the Degree of

Doctor of Philosophy

by

John Joseph Hopfield

June, 1958

Biographical Sketch

John Joseph Hopfield was born July 15, 1933, in Chicago, Illinois. He was educated in public schools in Toledo, Ohio, and Bethesda, Maryland. He received the degree of Bachelor of Arts with Highest Honors from Swarthmore College in June, 1954. He enrolled as a graduate student at Cornell University in September, 1954, where he held a General Electric Fellowship for one year and National Science Foundation Predoctoral Fellowships for two years. During the fall semester of 1957, he was a Teaching Assistant in the department of Physics. He worked for four summers in the Radiation Physics Laboratory of the National Bureau of Standards and one summer at the Johns Hopkins Applied Physics Laboratory.

Acknowledgments

The author wishes to thank Professor A. W. Overhauser for suggesting the thesis problem and for many hours of helpful discussion. He also wishes to thank Mr. J. R. Nelson for making available his computations on sodium chloride and Mr. P. A. Carruthers for translating a Russian paper.

TABLE OF CONTENTS

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 non-conducting excited states has been tentatively verified in both extremes of exciton models, the Frenkel (tight-binding) model and the Wannier (weak-binding) 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 semi-classical 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 peculiar to sets of energy states for which there is but one crystal state having a given wave-number $\underline{k}$ in a finite energy interval. The problem of the description of the fundamental absorption process is the subject of Chapter II. This problem was the motivation for the investigation of the exciton-photon system.

---

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

[2] For a brief review of optical absorption measurements and references to the original experimental and theoretical work, see C. Kittel, Introduction to Solid State Physics (John Wiley & Sons, Inc., New York, 1956), pp. 504-12.

The purpose of the present work is to formulate the problem of the optical properties of excitons in a more rigorous manner than the semi-classical theory through the use of quantum-electrodynamical formalism and to present a new 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.

In Chapter 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. Chapter 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 Chapter III.

In Chapter V the interactions which cause true absorption in crystals are introduced. These interactions result in finite lifetimes for the mixed eigenstates constructed in Chapter IV. The finite lifetimes are interpreted as complex energies. The relation between real wave-vectors and complex

energies is inverted to find a relation between complex wave-numbers and real frequencies. In this way, the complex dielectric constant can be computed. The final chapter 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.[1] 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 non-overlapping identical atoms.[2] For simplicity, the atoms are assumed to have S-type ground states ψ_0 and one (three-fold degenerate) P-type excited state ψ_{P_i} . The atomic positions are denoted by L_m . The zero-order ground state of the crystal is a state with every atom in its ground state (i.e., $\Psi_0 = \prod_m \psi_{0,L_m}$). The elementary excitations of this crystal are states in which one atom at L_m is excited and all other atoms are in their

---

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

[2] 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) .

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

$$\Psi_{k,P_i} = \frac{1}{\sqrt{N}} \sum_{L_m} e^{i k \cdot L_m} \Psi_{P_i, L_m} \prod_{L_n \neq L_m} \Psi_{o, L_n} , \tag{2.1}$$

where N is the total number of atoms in the crystal, and 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. For the usual "golden rule" transition probability[3] the only quantities which need to be calculated are the matrix elements of the perturbation and the density of final states coupled to the initial state. For one-quantum decay to the ground state of the crystal (the crystal analogue to simple optical decay of an excited atom), the matrix element for the transition to the crystal ground

---

[3] See any standard book on quantum mechanics, e.g., L. I. Schiff, Quantum Mechanics (McGraw Hill Book Company, Inc., New York, 1955), pp. 246 ff.

state with emission of a photon of wave-vector $\underline{k}'$ is given by the atomic matrix element for this process times the factor[4]

$$\frac{1}{\sqrt{N}} \sum_{L_m} e^{i(\underline{k}-\underline{k}')\cdot \underline{L}_m} \qquad (2.2)$$

If the box in which the radiation field is given periodic boundary conditions is the same size as the crystal, then the factor (2.2) is zero unless $\underline{k} - \underline{k}' = 2\pi \underline{G}$ where $\underline{G}$ 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 $|\underline{k}|$ 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 ($\underline{G} \neq 0$) couple excitons having optical region wave-vectors with photons of X-ray energy and can be neglected in transition calculations.[5] For optical cases, the wave-number conservation rule is $\underline{k} = \underline{k}'$. This rule states that each exciton $\underline{k}$ is coupled to only one radiation mode for radiative single-photon

---

[4] Seitz, op. cit., p. 647.

[5] 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.

emission. Since transitions, in the framework of the "golden rule," 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.[6] 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 Chapter 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

---

[6] 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 wave-length, 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.

be used to compute the decay behavior,[7] but a calculation based on general damping theory[8] 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 process

---

[7] Ordinary time-dependent perturbation theory transition probability calculations are valid for times defined by $t_2 << t << t_1$. t_1 is defined by the reciprocal of the transition probability as computed from the theory, and is proportional to the square of the matrix element for the transition which conserves energy. For the simple case in which $\underline{k} = \underline{k}'$ conserves energy, $t_1 \propto \frac{1}{N}$ (as can easily be shown from (2.2)). t_2 is defined by the reciprocal of the frequency region over which the matrix elements of H can be considered constant. The energy width of the sharp peak of (2.2) is proportional to $N^{-\frac{1}{3}}$, so t_2 is proportional to $N^{\frac{1}{3}}$. Thus for large crystal (large N) ordinary time-dependent transition theory is not valid.

[8] For the method of performing such a calculation, see W. Heitler, The Quantum Theory of Radiation (Oxford University Press, London, 1954), p. 163 ff.

is a two-step process:

photon $\underline{k}$ + atom in ground state → atom in excited state + no photon → photon $\underline{k}'$ + atom in ground state.

The photon $\underline{k}'$ can be emitted in virtually any direction, and so this process represents the scattering of a photon out of the initial state. The calculated scattering cross section is the same for this process as would be calculated by 1) assigning to the atom a distribution of energy levels which matches the distribution of photon energies emitted from the excited atom in ordinary optical decay, and 2) using the density of states thus calculated for a time-dependent perturbation theory calculation of the absorption cross section.

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 transitions. Energy is again shared between the exciton state and the photon just as it was in the calculation of exciton radiative decay.

Because of the wave-number conservation rule, an arbitrary spreading out of the energy of the exciton state in order to obtain a density of final states for the absorption process is

not a really satisfactory solution to the problem. The fact that re-emitted radiation is indistinguishable from the initial photon makes it essential to consider the removal of energy from the exciton-photon system as an integral part of the absorption process. The fundamental absorption process should not be considered as a photon → exciton process, but rather as a photon → exciton (intermediate state) → 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-energy sink coupling rather than the exciton-photon coupling which causes true optical absorption. Chapters 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.

In order to discuss the semi-classical theory of radiation in a sensible way in a region of exciton absorption, it must be assumed for the analysis to follow that the exciton energy is spread out over a finite frequency interval. If this assumption is made, the current density and polarization density can be computed from first-order time-dependent perturbation theory, with the additional assumption that the results of this calculation for small times will be valid for all time.

The semi-classical theory of the optical properties determines the constitutive relations between $\underline{P}$ and $\underline{E}$ and between $\underline{J}$ and $\underline{E}$ 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 a 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. (If this method is taken seriously, the exciton states have radiative widths which depend on the dimensions of the sub-blocks. This dependence leads to a dependence of the computed optical constants on the size of the sub-blocks used.)

A more satisfactory method of treatment is to use Fourier analysis. The whole crystal may be treated as a unit. A plane

electromagnetic wave of wave-vector $\underline{k}$ and frequency ω is used as a perturbation in the ordinary semi-classical manner. The Fourier transform of the polarization $\underline{P}_{\underline{k}'}$ is computed for this perturbation. Only the component of the polarization field $\underline{k}' = \underline{k}$ is important. The relation between $\underline{P}_{\underline{k}}$ and the perturbing electromagnetic wave are substituted into Maxwell's equations to determine the relation between $\underline{k}$ and ω. Pekar[9] has recently used this method to treat the dielectric tensors of insulators when no absorption is present, including the effects which arise due to the finite effective masses of excitons. This method should be readily extensible to include the case of absorption by computing in addition the relation between $\underline{J}_{\underline{k}}$ 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 $\underline{J}_{\underline{k}}$ cannot be computed.

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 $\underline{k}$. These N

---

[9] C. I. Pekar, J. Exptl. Theoret. Phys. U.S.S.R. 33, 1022 (1957).

states form an energy continuum (in the limit of large), 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 $\underline{k}$ to a particular electron-hole pair state of total wave-number $\underline{k}$ is the order of the atomic matrix element for this transition. Thus, whereas the interaction matrix element is proportional to $\frac{1}{\sqrt{V}}$ for interband transitions, and N electron-hole pairs interact with each photon, the interaction matrix element is proportional to $\sqrt{\frac{N}{V}}$ 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 semi-classical 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 semi-classical theory, the tacit assumption must be made that the electrons and holes created in an absorption process are scattered by the lattice and lose phase memory. 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 semi-classical 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 semi-classical theory. The gross features of the absorption are independent of the collision dephasing mechanism which makes absorption an irreversible process. 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 semi-classical method. The collision dephasing mechanism which makes absorption an irreversible process is completely responsible for the shape of the absorption line.

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 properties is not a really satisfactory procedure. There are technical difficulties[10] involved in the shape-function approach. More important, the

---

[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 actually 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.

semi-classical 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 semi-classical method produces an entirely misleading interpretation of the absorption process.

In the following chapters, a field-theoretic (rather than a semi-classical) 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. THE QUANTUM THEORY OF A CLASSICAL DIELECTRIC

The classical theory of a simple isotropic dielectric with dispersion can be characterized completely by the dependence on frequency of the dielectric constant $\varepsilon(\omega)$. The derivation of $\varepsilon(\omega)$ from first principles for optically isotropic crystals is the problem of this thesis. Since the exciton contribution to the complex dielectric constant can be most easily obtained by use of second quantization, it is useful to begin by developing the quantized form of a classical dielectric. The role of boundary conditions for a semi-infinite medium and possible deviations from simple classical behavior are briefly discussed.

A. The Quantization of an Infinite Classical Dielectric Medium

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

$$\mathcal{L} = \frac{1}{8\pi}\left(\frac{1}{c}\frac{\partial \underline{A}}{\partial t} + \nabla\varphi\right)^2 - \frac{1}{8\pi}\left(\nabla \times \underline{A}\right)^2 + \frac{1}{2\omega_0^2\beta}\left(\frac{\partial \underline{Q}}{\partial t}\right)^2$$

$$-\frac{1}{2\beta}(\underline{Q})^2 + \varphi\left(\nabla\cdot\underline{Q}\right) + \frac{1}{c}\,\underline{A}\cdot\frac{\partial \underline{Q}}{\partial t}. \qquad (3.1)$$

This is the Lagrangian density for an oscillating polarization density $\underline{Q}$ with a restoring force, as can be seen by comparing

(3.1) with the Lagrangian for a moving charged particle. The equations of motion for the field variables of (3.1) are

$$\frac{1}{4\pi c}\frac{\partial}{\partial t}\left(\frac{1}{c}\frac{\partial \underline{A}}{\partial t} + \underline{\nabla}\varphi\right) + \frac{1}{4\pi}\left(\underline{\nabla}\times\underline{\nabla}\times\underline{A}\right) - \frac{1}{c}\frac{\partial \underline{Q}}{\partial t} = 0,$$

$$\frac{1}{4\pi}\underline{\nabla}\cdot\left(\frac{1}{c}\frac{\partial \underline{A}}{\partial t} + \underline{\nabla}\varphi\right) - \underline{\nabla}\cdot\underline{Q} = 0,$$

$$\frac{1}{\omega_0^2\beta}\frac{\partial^2 \underline{Q}}{\partial t^2} + \frac{1}{\beta}\underline{Q} + \frac{1}{c}\frac{\partial \underline{A}}{\partial t} + \underline{\nabla}\varphi = 0. \qquad (3.2)$$

In conjunction with the definitions

$$\underline{B} = \underline{\nabla}\times\underline{A}$$

$$\underline{E} = -\frac{1}{c}\frac{\partial \underline{A}}{\partial t} - \underline{\nabla}\varphi$$

$$\underline{D} = \underline{E} + 4\pi\underline{Q} \qquad (3.3)$$

Equations (3.2) can be written as

$$\frac{1}{c}\frac{\partial \underline{D}}{\partial t} = \underline{\nabla}\times\underline{B} \qquad (a)$$

$$\underline{\nabla}\cdot\underline{D} = 0 \qquad (b)$$

$$\underline{\nabla}\cdot\underline{B} = 0 \qquad (c)$$

$$\frac{1}{c}\frac{\partial \underline{B}}{\partial t} = -\underline{\nabla}\times\underline{E} \qquad (d)$$

$$\frac{1}{\omega_0^2}\frac{\partial^2 \underline{Q}}{\partial t^2} + \underline{Q} = \beta\underline{E}. \qquad (e)$$

(3.4)

The set of Equations (3.4a,b,c,d) are the usual Maxwell equations for a dielectric medium, while Equation (3.4e) gives

the constitutive relation between $\underline{Q}$ and $\underline{E}$. If Equations (3.4) are solved for solutions periodic in time, with angular frequency ω, the dielectric dispersion law determined by (3.4e) is simply

$$\varepsilon = 1 + \frac{4\pi\beta}{1 - \frac{\omega^2}{\omega_0^2}} \tag{3.5}$$

Equation (3.1) is thus a suitable Lagrangian density for a classical dielectric.

In order to quantize the fields, the Coulomb gauge ($\underline{\nabla}\cdot\underline{A} = 0$) and Born-von Kármán periodic boundary conditions in a rectangular parallelopiped box of volume V are used to expand $\underline{A}$, $\underline{Q}$ and φ in plane waves.

$$\underline{A} = \sqrt{\frac{8\pi c^2}{V}} \sum_{\underline{k},\lambda_1}{}' {}^{2} \underline{\varepsilon}_{\underline{k}\lambda} \left(f_{\underline{k}\lambda} \sin \underline{k}\cdot\underline{r} + g_{\underline{k}\lambda} \cos \underline{k}\cdot\underline{r} \right)$$

$$\underline{Q} = \sqrt{\frac{2\beta}{V}} \sum_{\underline{k},\lambda}{}' {}^{3} \underline{\varepsilon}_{\underline{k}\lambda} \left(h_{\underline{k}\lambda} \sin \underline{k}\cdot\underline{r} + j_{\underline{k}\lambda} \cos \underline{k}\cdot\underline{r} \right)$$

$$\varphi = \sqrt{\frac{8\pi}{V}} \sum_{\underline{k}}{}' \left(l_{\underline{k}} \sin \underline{k}\cdot\underline{r} + m_{\underline{k}} \cos \underline{k}\cdot\underline{r} \right) \tag{3.6}$$

$\underline{\varepsilon}_{\underline{k}\lambda_1}$, $\underline{\varepsilon}_{\underline{k}\lambda_2}$, and $\underline{\varepsilon}_{\underline{k}\lambda_3}$ are three orthogonal unit vectors, one of which is parallel to $\underline{k}$. In the Coulomb gauge, $\underline{\nabla}\cdot\underline{A} = 0$, so in the first sum the only plane waves which enter are the two transverse modes. In the second sum, all three polarization

modes must enter the sum. The primes on the summations indicate that they are to be carried out over half of k-space, for definiteness chosen as $k_x > 0$.

Substitution of (3.6) into (3.1) and integration over the volume V yields the Lagrangian (3.7)

$$L = \sum_{k,\lambda_\perp}{}' \Big\{ \tfrac{1}{2}\left(\dot{f}^2_{k\lambda} + \dot{g}^2_{k\lambda}\right) - \tfrac{1}{2} c^2 k^2 \left(f^2_{k\lambda} + g^2_{k\lambda}\right) + \tfrac{1}{2}\,\tfrac{1}{\omega_0^2}\left(\dot{h}^2_{k\lambda} + \dot{j}^2_{k\lambda}\right) - \tfrac{1}{2}\left(h^2_{k\lambda} + j^2_{k\lambda}\right) + \sqrt{4\pi\beta}\left(f_{k\lambda}\dot{h}_{k\lambda} + g_{k\lambda}\dot{j}_{k\lambda}\right)\Big\} + \sum_{\lambda \parallel k}{}' \Big\{ \tfrac{1}{2}\left(\dot{l}^2_k + \dot{m}^2_k\right) + \tfrac{1}{2\omega_0^2}\left(\dot{h}^2_{k\lambda} + \dot{j}^2_{k\lambda}\right) - \tfrac{1}{2}\left(h^2_{k\lambda} + j^2_{k\lambda}\right) + \sqrt{4\pi\beta}\, k \left(l_k j_{k\lambda} - m_k h_{k\lambda}\right)\Big\} \tag{3.7}$$

in terms of the new variables f, g, h, j, l, and m. The transverse modes (first sum) and longitudinal modes (second sum) are separated in the Lagrangian, and may thus be treated separately. For consideration of the optical properties, the transverse modes are the only ones of interest. The longitudinal modes represent an electrostatic potential and a set of longitudinal oscillator modes which do not interact with radiation.

The Hamiltonian derivable from the first half of Equation (3.7) is

$$H_{k\lambda} = \left[\frac{1}{2}(P_f^2 + P_g^2) + \frac{1}{2}c^2k^2(f^2+g^2)\right] + \left[\frac{\omega_0^2}{2}(P_h^2 + P_j^2)\right.$$

$$\left. + \frac{1}{2}(h^2+j^2)\right] + \sqrt{4\pi\beta}\,\omega_0^2\left[-P_h f - P_j g\right] + \frac{1}{2}4\pi\beta\omega_0^2\left[f^2+g^2\right]. \tag{3.8}$$

where P_f, P_g, P_h, P_j are the momenta canonically conjugate to f, g, h, and j respectively. Only one k and one λ need be treated at a time, since modes of different k or λ are independent. Thus the subscripts k, λ may be dropped on f, P_f, etc. P_f, P_g, P_h, P_j may be obtained from the Lagrangian by the usual method, and are related to the coordinates and velocities by

$$P_f = \dot{f}$$

$$P_g = \dot{g}$$

$$P_h = \frac{1}{\omega_0^2}\dot{h} + \sqrt{4\pi\beta}\,f$$

$$P_j = \frac{1}{\omega_0^2}\dot{j} + \sqrt{4\pi\beta}\,g.$$

By means of a series of canonical transformations given in Appendix A (of the type used to produce quantization in running wave modes for the ordinary Maxwell equations) applied to the f_g and h_j systems, this Hamiltonian may be

rewritten as

$$H = \sum_{k,\lambda_1} \Big\{ \hbar c|k| \left(a^*_{k\lambda} a_{k\lambda} + \tfrac{1}{2} \right) + \hbar \omega_o \left(b^*_{k\lambda} b_{k\lambda} + \tfrac{1}{2} \right)$$

$$+ \frac{i\hbar\omega_o^2 \sqrt{4\pi\beta}}{2\sqrt{ck\omega_o}} \left[(a^*_{k\lambda} b_{k\lambda} - a_{k\lambda} b^*_{k\lambda}) + (a_{-k\lambda} b_{k\lambda} - a^*_{-k\lambda} b^*_{k\lambda}) \right]$$

$$+ \frac{\pi\beta\omega_o^2\hbar}{ck} \left[a_{k\lambda} a^*_{k\lambda} + a^*_{k\lambda} a_{k\lambda} + a^*_{k\lambda} a^*_{-k\lambda} + a_{-k\lambda} a_{k\lambda} \right] \Big\} \tag{3.9}$$

where the a's and b's are those combinations of p's and q's which, when quantum-mechanical commutation rules[1] are applied, are boson creation and destruction operators. $a^*_{k\lambda}$ is the Hermitian conjugate operator to $a_{k\lambda}$, etc.

$$\left[a_{k\lambda}, a_{k'\lambda'} \right] = \left[a_{k\lambda}, b_{k'\lambda'} \right] = \left[a_{k\lambda}, b^*_{k'\lambda'} \right] = \left[b_{k\lambda}, b_{k'\lambda'} \right] = 0$$

$$\left[a_{k\lambda}, a^*_{k'\lambda'} \right] = \left[b_{k\lambda}, b^*_{k'\lambda'} \right] = \delta_{kk'} \delta_{\lambda\lambda'} \tag{3.10}$$

The operators $a^*_{k\lambda}$ are exactly the photon creation operators of the usual Maxwell field while the $b^*_{k\lambda}$ 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 Chapter IV. Optical phonons are another example of polaritons.) The sum is now taken over all k-space. The field operators are given in terms

---

[1] Schiff, op. cit., p. 352, or Heitler, op. cit., p. 57. The definitions of creation and annihilation operators used here differ slightly from those of Schiff and of Heitler.

of a's and b's by

$$\underline{A} = \sqrt{\frac{2\pi c\hbar}{V k}} \sum_{k,\lambda_\perp} \underline{\varepsilon}_{k\lambda} \left(a_{k\lambda} e^{i\underline{k}\cdot\underline{r}} + a^*_{k\lambda} e^{-i\underline{k}\cdot\underline{r}} \right)$$

$$\underline{Q} = \sqrt{\frac{\hbar\omega_0\beta}{2V}} \sum_{k,\lambda_\perp} \underline{\varepsilon}_{k\lambda} \left(b_{k\lambda} e^{i\underline{k}\cdot\underline{r}} + b^*_{k\lambda} e^{-i\underline{k}\cdot\underline{r}} \right). \tag{3.11}$$

The Hamiltonian (3.9) represents a system of linearly coupled harmonic oscillators. It has harmonic oscillator normal modes, as does the classical system it represents. These normal modes will be expressed in terms of a new set of creation and annihilation operators. It is sufficient to work with a single wave-number $\underline{k}$ and polarization λ, since H is invariant under translation and different polarizations are not coupled. Define

$$\alpha_k = w a_k + x b_k + y a^*_{-k} + z b^*_{-k}. \tag{3.12}$$

If α_k is to be a normal-mode annihilation operator,[2] then

$$\left[a_k, H \right] = E_k \alpha_k \tag{3.13}$$

for, in terms of normal mode operators,

$$H = \sum_{k,\lambda,n} E_{k\lambda n} \alpha^*_{k\lambda n} \alpha_{k\lambda n} \tag{3.14}$$

where n is an index referring to the different normal modes of a given wave-vector and polarization. Using definition (3.12)

---

[2] α_k is a linear combination of operators which belong to the same representation k of the translation group; thus α_k belongs to this representation also.

and Equations (3.9) and (3.10), the eigenvalue problem (3.13) may be written in matrix form,

$$\begin{pmatrix} \hbar c|k| + 2D & -iC & -2D & -iC \\ +iC & \hbar\omega_0 & -iC & 0 \\ +2D & -iC & -\hbar c|k| - 2D & iC \\ -iC & 0 & +iC & -\hbar\omega_0 \end{pmatrix} \begin{pmatrix} w \\ x \\ y \\ z \end{pmatrix} = E \begin{pmatrix} w \\ x \\ y \\ z \end{pmatrix} \tag{3.15}$$

where

$$C = \frac{\hbar\omega_0^2\sqrt{\pi\beta}}{\sqrt{c|k|\omega_0}}, \qquad D = \frac{\pi\beta\omega_0^2\hbar}{c|k|}.$$

In units of $\hbar = c = 1$, the eigenvalues of (3.15) are determined by the equation

$$E^4 + E^2\left(-k^2 - \omega_0^2 - 4\pi\beta\omega_0^2\right) + k^2\omega_0^2 = 0 \tag{3.16}$$

which may be written in a more familiar form as

$$\varepsilon = \frac{k^2}{\omega^2} = 1 + \frac{4\pi\beta}{1 - \frac{E^2}{\omega_0^2}}. \tag{3.17}$$

(In the present units, $n \equiv$ index of refraction $= \frac{|k|}{E}$, and $\varepsilon = n^2 = \frac{k^2}{E^2}$.) As might be expected, there is the same relation 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

$$\left[\alpha_{k_i}, \alpha_{k'_j}\right] = \left[\alpha^*_{k_i}, \alpha^*_{k'_j}\right] = 0$$

$$\left[\alpha_{k_i}, \alpha^*_{k'_j}\right] = \delta_{kk'}\delta_{ij} \tag{3.18}$$

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.

$$\begin{pmatrix} \alpha_{k_1} \\ \alpha_{k_2} \\ \alpha^*_{-k_1} \\ \alpha^*_{-k_2} \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{13} & c_{14} \\ c_{21} & c_{22} & c_{23} & c_{24} \\ c_{31} & c_{32} & c_{33} & c_{34} \\ c_{41} & c_{42} & c_{43} & c_{44} \end{pmatrix} \begin{pmatrix} a_k \\ b_k \\ a^*_{-k} \\ b^*_{-k} \end{pmatrix} \tag{3.19}$$

The combination of the commutation rules for the α representation and for the ab representation yield the following relations between the c_{ij},

$$\begin{aligned} |c_{11}|^2 + |c_{12}|^2 - |c_{13}|^2 - |c_{14}|^2 &= 1 \\ |c_{21}|^2 + |c_{22}|^2 - |c_{23}|^2 - |c_{24}|^2 &= 1 \\ -|c_{31}|^2 - |c_{32}|^2 + |c_{33}|^2 + |c_{34}|^2 &= 1 \\ -|c_{41}|^2 - |c_{42}|^2 + |c_{43}|^2 + |c_{44}|^2 &= 1 \\ c_{i1}c^*_{j1} + c_{i2}c^*_{j2} - c_{i3}c^*_{j3} - c_{i4}c^*_{j4} &= 0 \quad \text{for } i \neq j \end{aligned} \tag{3.20}$$

It is then easy to show that C^{-1} is given by

$$C^{-1} = \begin{pmatrix} c_{11}^* & c_{21}^* & -c_{31}^* & -c_{41}^* \\ c_{12}^* & c_{22}^* & -c_{32}^* & -c_{42}^* \\ -c_{13}^* & -c_{23}^* & c_{33}^* & c_{43}^* \\ -c_{14}^* & -c_{24}^* & c_{34}^* & c_{44}^* \end{pmatrix} \tag{3.21}$$

A plot of $E(k)$ and some useful combinations of $c_{ij}(k)$ are given in Figures 1 and 2 for the particular case $4\pi\beta = 0.1$. The transformation[3] C is given in detail in (3.22).

$$c_{11} = \frac{\left(1-\frac{E_1}{\omega_0}\right)\left(\frac{|k|}{\omega_0}+\frac{E_1}{\omega_0}\right)\left(1+\frac{E_1}{\omega_0}\right)}{2\left(\frac{|kE_1|}{\omega_0^2}\right)^{\frac{1}{2}}\left[\left(1-\frac{E_1^2}{\omega_0^2}\right)^2+4\pi\beta\right]^{\frac{1}{2}}}$$

$$c_{12} = \frac{-i(\pi\beta)^{\frac{1}{2}}\left(1+\frac{E_1}{\omega_0}\right)}{\left(\frac{|E_1|}{\omega_0}\right)^{\frac{1}{2}}\left[\left(1-\frac{E_1^2}{\omega_0^2}\right)^2+4\pi\beta\right]^{\frac{1}{2}}}$$

---

[3] C is not unitary; the "Hamiltonian" matrix of (3.15) 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 (3.15) 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 $b_k^\dagger b_k$, $d_k^\dagger d_k$, etc. are diagonal to the representation in which the number operators $\alpha_k^\dagger \alpha_k$ are diagonal is a unitary transformation.

$$C_{13} = -\frac{\left(1-\frac{E_1}{\omega_0}\right)\left(\frac{|k|}{\omega_0}-\frac{E_1}{\omega_0}\right)\left(1+\frac{E_1}{\omega_0}\right)}{2\left(\frac{|k E_1|}{\omega_0^2}\right)^{\frac{1}{2}}\left[\left(1-\frac{E_1^2}{\omega_0^2}\right)^2+4\pi\beta\right]^{\frac{1}{2}}}$$

$$C_{14} = -\frac{i(\pi\beta)^{\frac{1}{2}}\left(1-\frac{E_1}{\omega_0}\right)}{\left(\frac{|E_1|}{\omega_0}\right)^{\frac{1}{2}}\left[\left(1-\frac{E_1^2}{\omega_0^2}\right)^2+4\pi\beta\right]^{\frac{1}{2}}} \qquad (3.22)$$

$C_{j1}, C_{j2}, C_{j3}, C_{j4}$ 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 Equation (3.17), 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 $|k| < \omega_0$ and $\beta \to 0$, $a_k = \alpha_{k_1}$, $b_k = \alpha_{k_2}$, $a^*_{-k} = \alpha^*_{-k_1}$, $b^*_{-k} = \alpha^*_{-k_2}$.

The ground state in the α, or uncoupled, system can now be written in terms of the wave functions for the unperturbed system. If attention is focused on the two wave-vectors, $\underline{k}$ and $-\underline{k}$ and one polarization, and the eigenstates of the unperturbed system are denoted by Ψ_{n_1,n_2,n_3,n_4} (the product of four harmonic oscillator functions representing n_1 photons of wave number $\underline{k}$, n_2 polaritons of wave number $\underline{k}$, n_3 photons of wave number $-\underline{k}$, and n_4 polaritons of wave number $-\underline{k}$), then

$$\Psi^{\alpha}_{\text{Ground}} = \sum_{n_1,n_2,n_3,n_4=0}^{\infty} A_{n_1,n_2,n_3,n_4}\, \Psi_{n_1,n_2,n_3,n_4} \qquad (3.23)$$

The conditions $\alpha_{k_1} \Psi^{\alpha}_{\text{Ground}} = \alpha_{k_2} \Psi^{\alpha}_{\text{Ground}} = \alpha_{-k_1} \Psi^{\alpha}_{\text{Ground}} = \alpha_{-k_2} \Psi^{\alpha}_{\text{Ground}} = 0$

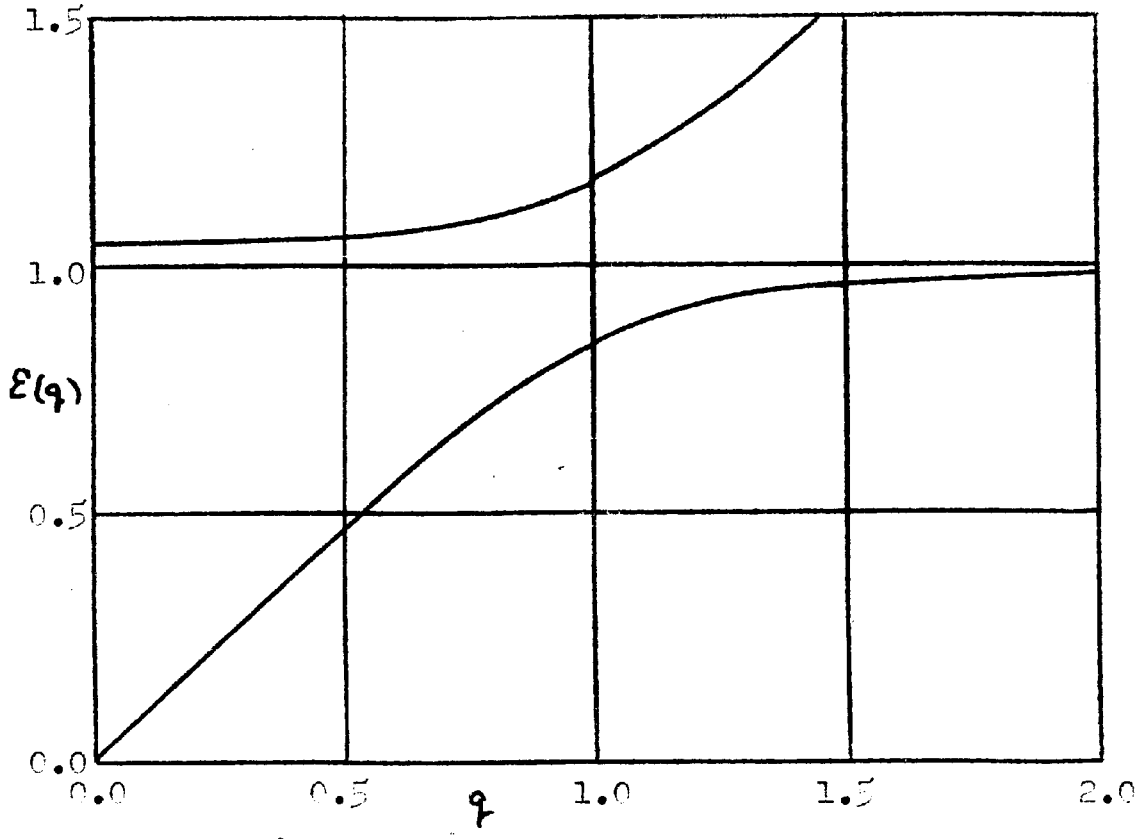

FIGURE 1. $E(k)$ for $4\pi\beta = 0.1$. Units of $\hbar = c = 1$, and $\mathcal{E} = \frac{E}{\omega_0}$, $q = \frac{k}{\omega_0}$

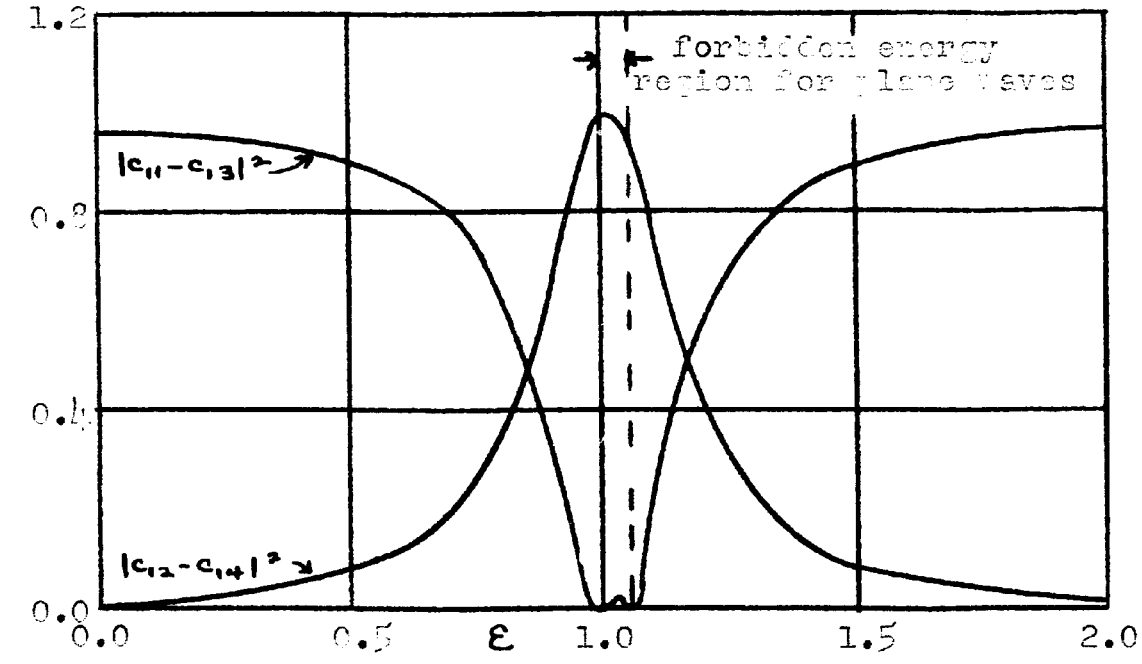

FIGURE 2. $|c_{11} - c_{13}|^2$ and $|c_{12} - c_{14}|^2$ as functions of energy. Units $\hbar = c = 1$. $4\pi\beta = 0.1$ and $\mathcal{E} = \frac{E}{N_0}$

generate four recursion relations between the coefficients A_{n_1,n_2,n_3,n_4} (with the convention $A_{n_1,n_2,n_3,n_4}=0$ if any $n<0$).

$$\begin{aligned}
&\sqrt{n_1+1}\, c_{11} A_{n_1+1,n_2,n_3,n_4} + \sqrt{n_2+1}\, c_{12} A_{n_1,n_2+1,n_3,n_4} \\
&+\sqrt{n_3}\, c_{13} A_{n_1,n_2,n_3-1,n_4} + \sqrt{n_4}\, c_{14} A_{n_1,n_2,n_3,n_4-1} = 0 \\
&\sqrt{n_1+1}\, c_{21} A_{n_1+1,n_2,n_3,n_4} + \sqrt{n_2+1}\, c_{22} A_{n_1,n_2+1,n_3,n_4} \\
&+\sqrt{n_3}\, c_{23} A_{n_1,n_2,n_3-1,n_4} + \sqrt{n_4}\, c_{24} A_{n_1,n_2,n_3,n_4-1} = 0 \\
&\sqrt{n_1}\, c^*_{31} A_{n_1-1,n_2,n_3,n_4} + \sqrt{n_2}\, c^*_{32} A_{n_1,n_2-1,n_3,n_4} \\
&+\sqrt{n_3+1}\, c^*_{33} A_{n_1,n_2,n_3+1,n_4} + \sqrt{n_4+1}\, c^*_{34} A_{n_1,n_2,n_3,n_4+1} = 0 \\
&\sqrt{n_1}\, c^*_{41} A_{n_1-1,n_2,n_3,n_4} + \sqrt{n_2}\, c^*_{42} A_{n_1,n_2-1,n_3,n_4} \\
&+\sqrt{n_3+1}\, c^*_{43} A_{n_1,n_2,n_3+1,n_4} + \sqrt{n_4+1}\, c^*_{44} A_{n_1,n_2,n_3,n_4+1} = 0
\end{aligned} \tag{3.24}$$

Only the states for which $n_1+n_2+n_3+n_4$ is even will occur in the ground-state wave function, as can be seen from the recursion relations or alternatively from the fact that H (Equation (3.9)) couples pairs of polaritons and photons. There will be no admixture of states belonging to a total wave-number not equal to zero, so $n_1+n_2-n_3-n_4 \neq 0 \Rightarrow A_{n_1,n_2,n_3,n_4} = 0$. For normalization of $A_{0000} = 1$, the first few expansion coefficients are

$$A_{0000} = 1$$

$$A_{1000} = A_{0100} = A_{0010} = A_{0001} = A_{1100} = A_{0011} = 0$$

$$A_{1001} = A_{0110} = \frac{4i(\pi\beta)^{\frac{1}{2}}\left(\frac{E_2-E_1}{\omega_0}\right)\left(\frac{|k|}{\omega_0}\right)^{\frac{1}{2}}}{\left(1+\frac{E_1}{\omega_0}\right)\left(1+\frac{E_2}{\omega_0}\right)\left[\left(1-\frac{E_1}{\omega_0}\right)\left(\frac{|k|}{\omega_0}+\frac{E_1}{\omega_0}\right)-\left(1-\frac{E_2}{\omega_0}\right)\left(\frac{|k|}{\omega_0}+\frac{E_2}{\omega_0}\right)\right.}$$

$$A_{0101} = \frac{\left(1-\frac{E_1}{\omega_0}\right)\left(1-\frac{E_2}{\omega_0}\right)\left[\frac{|k|}{\omega_0}+\frac{E_2}{\omega_0}\right)\left(1+\frac{E_2}{\omega_0}\right)-\left(\frac{|k|}{\omega_0}+\frac{E_1}{\omega_0}\right)\left(1+\frac{E_1}{\omega_0}\right)\right]}{\left(1+\frac{E_1}{\omega_0}\right)\left(1+\frac{E_2}{\omega_0}\right)\left[\left(1-\frac{E_1}{\omega_0}\right)\left(\frac{|k|}{\omega_0}+\frac{E_1}{\omega_0}\right)-\left(1-\frac{E_2}{\omega_0}\right)\left(\frac{|k|}{\omega_0}+\frac{E_2}{\omega_0}\right)\right]}$$

$$A_{1010} = \frac{i\left(1-\frac{E_1}{\omega_0}\right)\left(1-\frac{E_2}{\omega_0}\right)\left(\frac{|k|}{\omega_0}\right)^{\frac{1}{2}}\left(\frac{E_1-E_2}{\omega_0}\right)}{(\pi\beta)^{\frac{1}{2}}\left[\left(1-\frac{E_1}{\omega_0}\right)\left(\frac{|k|}{\omega_0}+\frac{E_1}{\omega_0}\right)-\left(1-\frac{E_2}{\omega_0}\right)\left(\frac{|k|}{\omega_0}+\frac{E_2}{\omega_0}\right)\right]}$$

For $E_1 = k$, $E_2 = \omega_0$ these reduce to the first-order perturbation expressions in powers of $\beta^{\frac{1}{2}}$. For example, by making these substitutions into A_{1001}, (A_{1001}) perturbation $= \frac{i\sqrt{\pi\beta\omega_0}}{(1+k/\omega_0)}$.[4]

Although it will prove advantageous to work in the α system with "clothed" photons and polaritons, nevertheless for the problems to be worked out it will never be necessary

---

[4] It should be noted in passing as an example of an exact treatment of a quantum-electrodynamical problem in such a way as to avoid the infra-red divergence, that the perturbation result tends to infinity as $(k/\omega_0)^{-\frac{1}{2}}$ if k approaches zero, whereas the exact expression tends to zero as $(k/\omega_0)^{\frac{1}{2}}$ if k approaches zero.

to calculate the "clothed" wave functions. 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. An oscillator immersed in the dielectric is an example of such a system. An oscillator, rather than an atom, is picked as the test system in order that the modification of the subsystem Hamiltonian due to the altered Coulomb interaction represented by the scalar terms of the Lagrangian (3.7) may reasonably be omitted. The matrix elements for coupling of the first excited state (denoted by a subscript 1) to the ground state (denoted by a subscript 0) of the oscillator by means of radiative interaction will be computed.

For a charged oscillator, one term of the perturbation in the Hamiltonian of the oscillator due to the radiation field may be written[5]

$$H' = \frac{e}{mc} \underline{A} \cdot \underline{p} \tag{3.25}$$

where $\underline{A}$ is the vector potential operator and $\underline{p}$ is the oscillator momentum operator. $\underline{A}$ is given in operator form by Equation (3.11).

---

[5] Heitler, op. cit., p. 190.

The matrix elements of the oscillator which enter H' involving photons of wave number $\underline{k}$ and $-\underline{k}$ and polarization $\underline{\varepsilon}$ are

$$\frac{e}{m}\sqrt{\frac{2\pi\hbar c}{V k}}\left\{\langle 1|\,\underline{p}\cdot\underline{\varepsilon}\,e^{i\underline{k}\cdot\underline{r}}\,|0\rangle\, a_{\underline{k},\varepsilon} + \langle 1|\,\underline{p}\cdot\underline{\varepsilon}\,e^{-i\underline{k}\cdot\underline{r}}\,|0\rangle\, a^{*}_{\underline{k},\varepsilon}\right.$$

$$\left. + \langle 1|\,\underline{p}\cdot\underline{\varepsilon}\,e^{-i\underline{k}\cdot\underline{r}}\,|0\rangle\, a_{-\underline{k},\varepsilon} + \langle 1|\,\underline{p}\cdot\underline{\varepsilon}\,e^{i\underline{k}\cdot\underline{r}}\,|0\rangle\, a^{*}_{-\underline{k},\varepsilon}\right\} \tag{3.26}$$

In the usual dipole approximation, valid when the linear dimensions of the oscillator are small compared to the wavelength of the emitted radiation, the exponentials may be omitted.

In treating radiative problems in a non-dispersive dielectric, one may simply start from the Lagrangian (3.1) with $\mathcal{G}=0$ and multiply the first term by ε, the dielectric constant. For this system,

$$\mathcal{L} = \frac{\varepsilon}{8\pi}\left(\frac{1}{c}\frac{\partial \underline{A}}{\partial t} + \underline{\nabla}\varphi\right)^2 - \frac{1}{8\pi}\left(\underline{\nabla}\times\underline{A}\right)^2 \tag{3.27}$$

The equations of motion of the field variables are

$$\frac{1}{4\pi}\frac{\varepsilon}{c}\frac{\partial}{\partial t}\left(\frac{1}{c}\frac{\partial \underline{A}}{\partial t} + \underline{\nabla}\varphi\right) + \frac{1}{4\pi}\left(\underline{\nabla}\times\underline{\nabla}\times\underline{A}\right) = 0$$

$$\frac{1}{4\pi}\underline{\nabla}\cdot\left(\frac{1}{c}\frac{\partial \underline{A}}{\partial t} + \underline{\nabla}\varphi\right) = 0 \tag{3.28}$$

With the definitions

$$\underline{B} = \underline{\nabla}\times\underline{A} \qquad \underline{E} = -\frac{1}{c}\frac{\partial \underline{A}}{\partial t} - \underline{\nabla}\varphi \qquad \underline{D} = \epsilon\,\underline{E}$$

(3.28) reduce to Maxwell's equations as desired. In the Coulomb gauge, it is easy to see what the quantized vector potential operator is, for it is sufficient to compare Lagrangian (3.1) and (3.27), and note that as far as $\underline{A}$ is concerned, (3.27) may be obtained by replacing c in (3.1) by $\frac{c}{n}$ $(n^2=\varepsilon)$. By making such a change in (3.11), it is found, in units of $\hbar=c=1$, that in the presence of a dielectric, the operator $\underline{A}$ becomes

$$\underline{A} = \sqrt{\frac{2\pi}{nVk}} \sum_{k,\lambda} \underline{\varepsilon}_{k\lambda} \left(a_{k\lambda} e^{i\underline{k}\cdot\underline{r}} + a^{*}_{k\lambda} e^{-i\underline{k}\cdot\underline{r}} \right) \tag{3.29}$$

If, therefore, the matrix elements for radiative interaction with an electric dipole oscillator are computed, for this system of index of refraction n, they will be exactly those of Equation (3.25) or (3.26) multiplied by a factor $\frac{1}{\sqrt{n}}$.

In the formalism developed here for the quantum-mechanical dielectric with dispersion, in order to compute the matrix elements of H' the field operators must first be transformed to the α or "clothed" system. By using the transformation (3.21) the matrix elements corresponding to (3.25) may be written[6] (in units of $\hbar=c=1$) as

---

[6] Use can be made of the fact that since the Lagrangian was isotropic, the matrix elements of C^{-1} for $\underline{k}$ and $-\underline{k}$ are related.

$$\sqrt{\frac{2\pi}{Vk}}\,\frac{e}{m}\left\{\langle 1|\,\underline{p}\cdot\underline{\varepsilon}\,e^{i\underline{k}\cdot\underline{r}}\,|0\rangle\left[(c^*_{11}-c^*_{13})\alpha_{k_1}+(c^*_{21}-c^*_{23})\alpha_{k_2}\right.\right.$$

$$\left.+(-c^*_{31}+c^*_{33})\alpha^*_{-k_1}+(-c^*_{41}+c^*_{43})\alpha^*_{-k_2}\right]+\langle 1|\,\underline{p}\cdot\underline{\varepsilon}\,e^{-i\underline{k}\cdot\underline{r}}\,|0\rangle$$

$$\left.\left[(c^*_{11}-c^*_{13})\alpha^*_{k_1}+(c^*_{21}-c^*_{23})\alpha^*_{k_2}+(-c^*_{31}+c^*_{33})\alpha_{-k_1}+(-c^*_{41}+c^*_{43})\alpha_{-k_2}\right]\right\}$$

(3.30)

Well below the dispersion region ($k \ll \omega_0$), the coefficients c_{ij} reduce to a simple form.

$$c_{11}=\frac{n+1}{2n^{3/2}} \qquad c_{13}=-\frac{(n-1)}{2n^{3/2}}$$

$$c_{21}=\frac{i\left(1-\frac{E_2}{\omega_0}\right)}{2\left(\frac{|k|}{\omega_0}\right)^{\frac{1}{2}}\left[\left(1-\frac{E_2^2}{\omega_0^2}\right)^2+4\pi\beta\right]^{\frac{1}{2}}} \qquad c_{23}=\frac{i\left(1-\frac{E_2}{\omega_0}\right)}{2\left(\frac{|k|}{\omega_0}\right)^{\frac{1}{2}}\left[\left(1-\frac{E_2^2}{\omega_0^2}\right)^2+4\pi\beta\right]^{\frac{1}{2}}}$$

$$c_{31}=-\frac{(n-1)}{2n^{3/2}} \qquad c_{33}=\frac{n+1}{2n^{3/2}}$$

$$c_{41}=\frac{i\left(1-\frac{E_2}{\omega_0}\right)}{2\left(\frac{|k|}{\omega_0}\right)^{\frac{1}{2}}\left[\left(1-\frac{E_2^2}{\omega_0^2}\right)^2+4\pi\beta\right]^{\frac{1}{2}}} \qquad c_{43}=\frac{i\left(1-\frac{E_2}{\omega_0}\right)}{2\left(\frac{|k|}{\omega_0}\right)^{\frac{1}{2}}\left[\left(1-\frac{E_2^2}{\omega_0^2}\right)^2+4\pi\beta\right]^{\frac{1}{2}}}$$

$$n=\left[1+4\pi\beta\right]^{\frac{1}{2}}$$

(3.31)

Therefore, when $k \ll \omega_0$, (3.30) reduces to a very simple form,

$$\sqrt{\frac{2\pi}{Vk}}\,\frac{e}{m}\left\{\langle 1|\underline{p}\cdot\underline{\varepsilon}\,e^{i\underline{k}\cdot\underline{r}}|0\rangle\left[\frac{1}{n^{\frac{1}{2}}}\alpha_{k_1}+\frac{1}{n^{\frac{1}{2}}}\alpha^{*}_{-k_1}\right]\right.$$
$$\left.+\langle 1|\underline{p}\cdot\underline{\varepsilon}\,e^{-i\underline{k}\cdot\underline{r}}|0\rangle\left[\frac{1}{n^{\frac{1}{2}}}\alpha^{*}_{k_1}+\frac{1}{n^{\frac{1}{2}}}\alpha_{-k_1}\right]\right\}. \tag{3.32}$$

Equation (3.32) is identical with (3.26) multiplied by $\frac{1}{\sqrt{n}}$. Far above the region of dispersion, the polarization oscillators will drop out completely, and ordinary quantum electrodynamics with $n=1$ will hold. Thus as long as the behavior of the dielectric in only a non-dispersive region is of importance, it is sufficient to replace the velocity of light c by $\frac{c}{n}$ in ordinary quantum electrodynamics. This will not be true in a dispersive region.

The proof has in no way depended upon the properties of the oscillator or the oscillator states chosen. Thus it will be true for any subsystem coupled only to the radiation field inserted in the quantum-mechanical dielectric. A similar proof will hold for the A^2 perturbation of the Hamiltonian.

B. Boundary Conditions and the Quantization of a Semi-Infinite Dielectric Medium

The equations of motion of the classical electromagnetic field variables for a semi-infinite medium with a plane boundary

may be written in terms of Lagrangian densities for the two regions of space under consideration. If semi-infinite space $x \geqq 0$ contains the dielectric discussed in Section A, and the region $x < 0$ is free space, the Lagrangian density may be taken to be

$$\mathcal{L}(x,y,z) = \frac{1}{8\pi}\left(\frac{1}{c}\frac{\partial \underline{A}}{\partial t} + \underline{\nabla}\varphi\right)^2 - \frac{1}{8\pi}\left(\underline{\nabla}\times\underline{A}\right)^2$$

$$+ S(x)\left[\frac{1}{2\omega_0^2\beta}\left(\frac{\partial \underline{Q}}{\partial t}\right)^2 - \frac{1}{2\beta}\left(\underline{Q}\right)^2 + \frac{1}{c}\underline{A}\cdot\frac{\partial \underline{Q}}{\partial t} + \varphi\,\underline{\nabla}\cdot\underline{Q}\right].$$

$$S(x) = 0, \quad x < 0 \qquad\qquad S(x) = 1, \quad x \geqq 0 \tag{3.33}$$

For $x<0$, (3.33) is the Lagrangian density of the electromagnetic field in empty space; for $x>0$, (3.33) is the Lagrangian density of Equation (3.1). Therefore, the equations of motion in these two regions of space will be those associated with those two regions; i.e., the Maxwell equations in free space and the Maxwell equations plus a constitutive equation in the dielectric medium.

Equation (3.33) contains implicitly the boundary conditions which must hold on the surface $x=0$. The field equations obtainable from (3.33) are

$$\frac{1}{4\pi c}\frac{\partial}{\partial t}\left(\frac{1}{c}\frac{\partial \underline{A}}{\partial t} + \underline{\nabla}\varphi\right) + \frac{1}{4\pi}\left(\underline{\nabla}\times\underline{\nabla}\times\underline{A}\right) - \frac{1}{c}S(x)\frac{\partial \underline{Q}}{\partial t} = 0$$

$$\frac{1}{4\pi}\underline{\nabla}\cdot\left(\frac{1}{c}\frac{\partial \underline{A}}{\partial t} + \underline{\nabla}\varphi\right) + S(x)\,\underline{\nabla}\cdot\underline{Q} = 0$$

$$S(x)\left[\frac{1}{\omega_0^2\beta}\frac{\partial^2 \underline{Q}}{\partial t^2} + \frac{1}{\beta}\underline{Q} + \frac{1}{c}\frac{\partial \underline{A}}{\partial t} + \underline{\nabla}\varphi\right] = 0 \tag{3.34}$$

If $\underline{D}$ is defined by $\underline{D} = \underline{E} + 4\pi \underline{Q}$, and the ambiguity which arises from the fact that the equations of motion of $\underline{Q}$ are not defined for $x<0$ is removed by specifying the solution $\underline{Q}=0$ for $x<0$, then (3.34) reduce to Maxwell's equations at every point in space, including the boundary.

The quantization of such a semi-infinite system is slightly more difficult than the quantization of the infinite system of Section A. In general, a set of field equations can be quantized by expanding the field in terms of a complete countable set of functions. In order to obtain a mathematically tractable quantum-mechanical form of the field, it is customary to use the classical normal modes of the field as the expansion functions. For a classical Hermitian Hamiltonian and suitable boundary conditions, these normal modes will be orthogonal, and the expansion coefficients will be independent variables.

The classical normal modes of the coupled radiation and dielectric were not used as expansion functions in Section A. When the normal modes of the pure radiation field and pure polarization field were used as expansion functions, the coupling between them in the quantum-mechanical equations was tractable. Unfortunately the use of this procedure for a semi-infinite medium is difficult. If an expansion of the fields is made as in Section A, the Lagrangian will couple many different modes

of both fields. This coupling arises because

$$\int_0^\infty e^{ikx}\,dx = \pi\delta(k) + i\frac{P}{k}$$

where $\frac{P}{k}$ is defined in integrated form[7] by

$$\int_a^b f(k)\frac{P}{k}\,dk = \lim_{\varepsilon\to 0}\left[\int_a^{-\varepsilon}\frac{f(k)\,dk}{k} + \int_\varepsilon^b \frac{f(k)\,dk}{k}\right].$$

If the range of integration extended from $-\infty$ to ∞, the $\frac{P}{k}$ term does not occur. The $\delta(k)$ term by itself yields a tractable coupling in the quantum-mechanical equations; the $\frac{P}{k}$ term produces an unwieldy amount of coupling between different modes.

To treat more easily the case of the semi-infinite dielectric, an expansion in the normal modes of the coupled system must be made. For any given set of boundary conditions at infinity there will exist for the Lagrangian density (3.33) a set of solutions (normal modes) which are independent in the sense that the Lagrangian may be expressed in terms of the expansion coefficients with no cross terms. To find this set for particular boundary conditions at infinity is difficult, but in principle possible.

This procedure will not be carried out, for the fact that it can be done actually implies that it would yield no new

---

[7] See, for example, Heitler, op. cit., p. 69.

information about the dielectric. The boundary conditions at $x=0$ that have been built into the Lagrangian density and which will be obeyed by the normal modes are the classical boundary conditions. Further, to each classical normal mode will correspond a frequency ω and two wave numbers k and k', one in the dielectric medium and one en vacuo. The normal mode quantization will be the quantization of harmonic oscillators, so the quantum-mechanical oscillator frequency will be the same as the classical normal mode frequency. Thus the quantum-mechanical relation between ω and k or ω and k' will be the same as the classical relation. (This was, of course, found to be the case for an infinite medium.)

Therefore, if an infinite quantum-mechanical dielectric medium is treated and the relation between frequency and wave-number determined, it is not necessary to perform the correct quantum-mechanical treatment of semi-infinite or other geometry to predict experimental results. It is sufficient merely to find the Lagrangian of the classical dielectric which corresponds to the infinite quantum-mechanical dielectric. The equations of motion and boundary conditions derived from the Lagrangian contain correctly all[8] the classical properties of the dielectric. This result can be more concisely stated in

---

[8] To treat problems involving the interaction of a foreign subsystem with the dielectric, it is necessary to use some quantized form of the dielectric or at least a semi-classical radiation theoretic dielectric.

terms of the dielectric constant. If the dielectric constant is a function only of the frequency, the propagation of light from free space into the dielectric is determined by the dispersion relation $\varepsilon(\omega) = \frac{c^2 k^2}{\omega^2}$. This dispersion relation can be derived for an infinite medium. Assuming the dispersion relation is an analytic function, $\varepsilon(\omega)$ can be extended to all frequencies for use with non-infinite geometries.

C. More Complex Dielectrics

Sections A and B dealt with 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.[9] In the classical model the polarization $\underline{\mathcal{Q}}(\underline{r})$ depends only on the electric field $\underline{E}$ at the point $\underline{r}$. A generalization of this dependence would allow $Q(\underline{r},t)$ to depend on $\mathcal{T}\underline{E}(\underline{r}',t')$, where $\mathcal{T}$ is a linear operator.[10] Another generalization which might be made would be to replace the classical restoring force proportional to $\underline{Q}$ in the equation of motion of $\underline{Q}$ by a more general linear restoring force. Both of these modifications will be present to some extent in a real physical dielectric.[11]

---

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

[10] There are restrictions on the form of $\mathcal{T}$ if there is to exist a causal relation between $\underline{E}$ and $\underline{Q}$.

[11] Pekar (op. cit.) has derived these effects from the semi-classical 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.

This section treats the simplest case of the second general modification mentioned above, a case which is known to arise in the theory of the contribution to the dielectric constant of excitons. A discussion of the second case and the physical instances in which it arises is deferred to Chapter IV.

A phenomenological modification of the dielectric which includes the fact that excitons have finite effective masses may be arrived at by inspecting the equation of motion of the polarization if the electric field is zero.

$$\frac{\partial^2 \underline{Q}}{\partial t^2} + \omega_0^2 \underline{Q} = 0 \tag{3.35}$$

The plane wave solutions to (3.35) are

$$\underline{Q} = \underline{Q}_0 e^{i\underline{k}\cdot\underline{r}} e^{i\omega t} \quad ; \quad \omega^2 = \omega_0^2 \tag{3.36}$$

An effective mass would introduce a dependence of ω on $|\underline{k}|$. The simplest differential equation which has approximately an effective mass dependence of ω on $|\underline{k}|$ is

$$\frac{\partial^2 \underline{Q}}{\partial t^2} + \omega_0^2 \underline{Q} - \gamma \nabla^2 \underline{Q} = 0. \tag{3.37}$$

The plane wave solutions of (3.37) have ω given by $\omega = \sqrt{\omega_0^2 + \gamma k^2}$ which, for small k, may be approximated by $\omega = \omega_0 + \frac{\gamma k^2}{2\omega_0}$. The "effective mass" of this relation is given by its k^2 dependence: $\frac{\hbar^2 k^2}{2m^*} = \frac{\hbar \gamma k^2}{2\omega_0}$, or $m^* = \frac{\omega_0 \hbar}{\gamma}$.

The Lagrangian density (3.33) may be modified to include such an effect in the transverse modes by adding to it a term $S(x)\frac{\gamma}{2\beta\omega_0^2}(\nabla\times\underline{Q})^2$. The equations of motion of the electromagnetic field remain the same as those derived from (3.33). The constitutive equation is changed to

$$S(x)\left[\frac{1}{\omega_0^2}\frac{\partial^2\underline{Q}}{\partial t^2}+\underline{Q}\right]+S(x)\frac{\gamma}{\omega_0^2}\nabla\times\nabla\times\underline{Q}+\frac{\gamma}{\omega_0^2}\left[(\nabla S(x)\times\nabla\times\underline{Q}\right]=\beta\,\underline{E} \tag{3.38}$$

The plane wave solutions to these equations of motion for $x>0$ are more complex than those of a simple classical dielectric. There are now <u>two</u> plane wave propagation modes for any given direction and frequency. The plane wave solutions are

$$\underline{E}=\underline{E}_0 e^{i\underline{k}\cdot\underline{r}}e^{i\omega t} \quad (a) \qquad \frac{k^2c^2}{\omega^2}=1+\frac{4\pi\beta}{1-\frac{\omega^2}{\omega_0^2}-\frac{k^2\gamma}{\omega_0^2}} \quad (d)$$

$$\underline{B}=\underline{B}_0 e^{i\underline{k}\cdot\underline{r}}e^{i\omega t} \quad (b) \qquad |\underline{B}_0|=|\underline{E}_0|\left|\frac{\omega}{kc}\right| \quad (e)$$

$$\underline{Q}=\underline{Q}_0 e^{i\underline{k}\cdot\underline{r}}e^{i\omega t} \quad (c) \qquad |\underline{Q}_0|=|\underline{E}_0|\frac{\beta}{1-\frac{\omega^2}{\omega_0^2}-\frac{k^2\gamma}{\omega_0^2}} \quad (f)$$

(3.39)

where $\underline{E}$ and $\underline{Q}$ are parallel, and $\underline{k}$, $\underline{E}$, and $\underline{B}$ are mutually perpendicular as in ordinary plane electromagnetic waves. (3.39d) is a quadratic equation in k^2, with two roots of k^2 for any given frequency ω .

In addition to introducing a second normal mode for every frequency, the additional term $S(x)\frac{\gamma}{2\beta\omega_0^2}(\nabla\times\underline{Q})^2$ produces another boundary condition to be met on the surface of the

dielectric. The last term on the left hand side of (3.38) may be written $\frac{\gamma}{\omega_0^2}\delta(x)\hat{i}\times\nabla\times\underline{Q}$. If $\underline{Q}$ and $\underline{E}$ are everywhere finite, this implies that $\hat{i}\times\nabla\times\underline{Q}=0$ for $x=0$, or thus that the tangential component of $\nabla\times\underline{Q}$ vanishes at the boundary (cf. the tangential component of $\underline{B}=\nabla\times\underline{A}$ is continuous anywhere where $\underline{j}=0$; the spatial derivatives of $\underline{A}$ and $\underline{Q}$ enter the Lagrangian density in the same form). This additional boundary condition is sufficient to determine unique solutions to boundary problems such as the reflection of electromagnetic waves from the dielectric surface. For instance, the amplitude reflection coefficient at normal incidence may be shown to be

$$R = \frac{n_2(n_2^2-1) - n_1(n_1^2-1) - n_1 n_2(n_2^2-n_1^2)}{n_1(n_1^2-1) - n_2(n_2^2-1) - n_1 n_2(n_2^2-n_1^2)} \qquad (3.40)$$

where $n_1=\frac{k_1 c}{\omega}$, $n_2=\frac{k_2 c}{\omega}$, and k_1 and k_2 are the wave vectors for the two modes of frequency ω in the dielectric.

For a realistic physical case, either $n_1 >> n_2$ or $n_2 >> n_1$ in the region which corresponds to optical frequencies except near what was previously ($\gamma = 0$) the total reflection region. In a real material, there will be damping and absorption present in this region, which may be accounted for in classical dielectric theory by introducing a phenomenological damping constant into the equations of motion. If the damping constant is

chosen so as to give an absorption width comparable to that observed in the exciton absorption spectra of the alkali halides, then R is well approximated by $\frac{n_1-1}{n_1+1}$ where n_1 is the smaller of the two complex indices of refraction. Further, n_1 will be approximately that which would be computed for $\gamma = 0$ (infinite effective mass). The physical reason for this result is that energy is transferred most efficiently to the mode of propagation which has a phase velocity near the velocity of light. The second, or "exciton propagation" mode always has a phase velocity much smaller than the velocity of light in the spectral region of interest, which results in the dominance of the usual propagation mode.

Since the physical reason for the failure of the finite effective mass to alter appreciably the reflection coefficient is common to all problems of wave propagation in dielectrics, it is to be expected that the finite effective mass effects will not produce appreciable modifications of any observable electromagnetic quantity. 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. THE INTERACTION OF PHOTONS WITH EXCITONS

An exciton band in an insulating or semiconducting crystal is thought of as a band of non-conducting 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 will 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 either model. Terms which can cause absorption will be dropped from the approximate Hamiltonian until Chapter 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 (3.9) of Chapter III-A.

A. The Extreme Tight-binding Model

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 always be neglected. From a purely theoretical point of view this implies an infinite lattice constant, but from the point of view of a model the lattice constant may be given any value whatsoever and overlaps simply ignored. If the lattice sites of the atoms are $\underline{L}_m$ and the atomic number of the atoms is Z, then the Hamiltonian for the electrons in the absence of radiation is

$$H = \sum_i \frac{p_i^2}{2m} - \frac{1}{2}\sum_{i\neq j}\frac{e^2}{r_{ij}} + \sum_{i,m}\frac{Ze^2}{|\underline{r}_i - \underline{L}_m|} - \frac{1}{2}\sum_{m\neq n}\frac{Z^2e^2}{|\underline{L}_m - \underline{L}_n|}. \tag{4.1}$$

The fourth term of the Hamiltonian represents the Coulomb interaction of the nuclei, which has been written in the electronic Hamiltonian to provide a convenient zero for the potential energy of the electronic system.

If the atomic wave functions never overlap, it is possible to associate a set of Z electrons with each atom, for exchange effects will not occur between non-overlapping wave functions. For an electron j on the m-th atom and an electron i on the n-th atom, $1/r_{ij}$ can be expanded as

$$\frac{1}{r_{ij}} \approx \frac{1}{|\underline{L}_m - \underline{L}_n|} + \frac{(\underline{x}_{jm} - \underline{x}_{in})\cdot(\underline{L}_m - \underline{L}_n)}{|\underline{L}_m - \underline{L}_n|^3} + \frac{\underline{x}_{in}\cdot\underline{x}_{jm}}{|\underline{L}_m - \underline{L}_n|^3} - \frac{3[\underline{x}_{in}\cdot(\underline{L}_m - \underline{L}_n)][\underline{x}_{jm}\cdot(\underline{L}_m - \underline{L}_n)]}{|\underline{L}_m - \underline{L}_n|^5} \tag{4.2}$$

where $\underline{x}_{in} = \underline{L}_n - \underline{r}_i$: $\underline{x}_{jm} = \underline{L}_m - \underline{r}_j$. Only terms through the dipole-dipole terms have been included in the multipole expansion. With this approximation and a similar expansion for

$\frac{1}{|r_i - L_m|}$, the Hamiltonian (4.1) can be written as

$$H = \sum_{n=1}^{N}\left[\sum_{i=1}^{Z}\left(\frac{p_{in}^2}{2m} - \frac{Ze^2}{|x_{in}|}\right) + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|x_{in}-x_{jn}|}\right] + \sum_{n\neq m=1}^{N}\frac{\underline{X}_n\cdot\underline{X}_m}{|L_m - L_n|^3} - 3\frac{[\underline{X}_n\cdot(L_m-L_n)][\underline{X}_m\cdot(L_m-L_n)]}{|L_m-L_n|^5} \qquad (4.3)$$

where $\underline{X}_n = \sum_{i=1}^{Z} x_{in}$, and N is the number of atoms in the crystal. The first term in (4.3) is the sum of N isolated atom Hamiltonians; the second term represents the dipole-dipole interaction between different atoms.

A suitable set of $(-1)^{th}$ order wave functions for describing the electronic state of the crystal is $\Psi = \prod_m \psi_{tm}$, where ψ_{tm} is the wave function of atomic state t on atom m, having atomic energy eigenvalue E_t . The ground state wave function is $\Psi_o = \prod_m \psi_{om}$, and its expectation value of H is $\langle \Psi_o | H | \Psi_o \rangle = NE_o$. It is convenient to redefine the zero of energy by subtracting NE_o from all energies, and all energies from here on will be considered to be measured from NE_o.

The zero-order lowest energy excited states of the crystal should not be taken as $\Psi_t = \psi_{tn}\prod_{m\neq n}\psi_{om}$, 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 $\Psi_{tk} = \frac{1}{\sqrt{N}}\sum_n \psi_{tn} e^{i\underline{k}\cdot L_n}\prod_{m\neq n}\psi_{om}$ are used, when $\underline{k}$ 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 Ψ_{tk} are orthonormal wave functions for which matrix elements of H between states tk and tk' vanish. For these states, $\langle H \rangle$ can be shown[1] to have the form given by (4.4) for $kV^{\frac{1}{3}} >> 1$.

$$\langle H \rangle_{tk} = E_t + \frac{N}{V} \frac{8\pi}{3} |X_{ot}|^2 P_2(\cos\theta)\left[j_0(kr) + j_2(kr)\right]. \tag{4.4}$$

θ is the angle between $\underline{k}$ and $\langle \psi_o | \underline{X} | \psi_t \rangle$, and

$$|X_{ot}|^2 \equiv \langle \psi_o | \underline{X} | \psi_t \rangle \langle \psi_t | \underline{X} | \psi_o \rangle. \tag{4.5}$$

It is convenient to define a set of operators d_{tm} and d^*_{tm} (for $t \neq o$) which operate on the wave function and obey the following rules[2]

$$\begin{aligned} d_{tm}\psi_{t'm'} &= \psi_{om}\delta_{mm'}\delta_{tt'} \\ d^*_{tm}\psi_{t'm'} &= \psi_{tm}\delta_{mm'}\delta_{t'o} \\ d_{tm}d_{t'm'} - d_{tm}d_{t'm'} &= 0 \quad \text{for } m \neq m' \end{aligned} \tag{4.6}$$

d^*_{tm} operates only on the wave function of atom m, raising the atom to state t if the atom was previously in state ψ_o ,

---

[1] Heller and Marcus, op. cit.

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

and giving a zero result otherwise. d_{tm} acts only on the wave function of atom m and yields zero unless the atom m was in state t, in which case d_{tm} produces the ground state function. The products of these raising and lowering operators are given by (4.7) as can be proved from the definitions.

$$d_{tm}d_{t'm} = d^*_{tm}d^*_{t'm} = d_{t'm}d^*_{tm} = 0 \quad \text{for } t \neq t' \tag{4.7}$$

The state Ψ_{tk} can be expressed in terms of these operators and the ground-state wave function by

$$\Psi_{tk} = \left[\frac{1}{\sqrt{N}}\sum_m e^{i\underline{k}\cdot\underline{L}_m} d^*_{tm}\right]\Psi_o \quad ; \quad \Psi_o = \left[\frac{1}{\sqrt{N}}\sum_m e^{-i\underline{k}\cdot\underline{L}_m} d_{tm}\right]\Psi_{tk}. \tag{4.8}$$

Particularly useful linear combinations of the raising and lowering operators are

$$b^*_{tk} = \frac{1}{\sqrt{N}}\sum_m e^{i\underline{k}\cdot\underline{L}_m} d^*_{tm} \quad ; \quad b_{tk} = \frac{1}{\sqrt{N}}\sum_m e^{-i\underline{k}\cdot\underline{L}_m} d_{tk}. \tag{4.9}$$

In terms of these operators, $\Psi_{tk} = b^*_{tk}\Psi_o \quad ; \Psi_o = b_{tk}\Psi_{tk}$. The inverse transformation between the operators b and d is

$$d^*_{tm} = \frac{1}{\sqrt{N}}\sum_k b^*_{tk} e^{-i\underline{k}\cdot\underline{L}_m} \quad ; \quad d_{tm} = \frac{1}{\sqrt{N}}\sum_k b_{tk} e^{i\underline{k}\cdot\underline{L}_m} \tag{4.10}$$

The Hamiltonian (4.3) can be exactly expressed in terms of

the operators d_{tm}. The operator $\underline{X}_m$ can be written as

$$\underline{X}_{m\,\text{operator}} = \sum_t \langle 0|\underline{x}_m|t\rangle d_{tm} + \sum_t \langle t|\underline{x}_m|0\rangle d^*_{tm} + \sum_{t\neq t'} \langle t|\underline{x}_m|t'\rangle d^*_{tm} d_{t'm}. \tag{4.11}$$

The atomic Hamiltonian of atom m can be written

$$H_m = \sum_t E_t\, d^*_{tm} d_{tm}. \tag{4.12}$$

Substitution of (4.10) into (4.12) yields

$$\sum_m H_m = \frac{1}{N} \sum_{t,m,k,k'} E_t\, e^{i(\underline{k}-\underline{k}')\cdot \underline{L}_m}\, b^*_{tk'} b_{tk} = \sum_{k,t} E_t\, b^*_{tk} b_{tk}.$$

The complete Hamiltonian will not be written out, but instead only the terms of $X_m X_n$ 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 by justified will be more readily apparent. The approximate Hamiltonian is

$$H=\sum_{k,t} E_t b^*_{tk} b_{tk} + \frac{1}{N}\sum_{k,k',t,t',m\neq m'}\left\{\left[\langle 0|\underline{x}_m|t\rangle b^*_{tk} e^{i\underline{k}\cdot\underline{L}_m} + \langle t|\underline{x}_m|0\rangle b_{tk} e^{-i\underline{k}\cdot\underline{L}_m}\right]\cdot\right.$$

$$\frac{\left[\langle 0|\underline{x}_{m'}|t'\rangle b^*_{t'k'} e^{i\underline{k}'\cdot\underline{L}_{m'}} + \langle t'|\underline{x}_{m'}|0\rangle b_{t'k'} e^{-i\underline{k}'\cdot\underline{L}_{m'}}\right]}{|\underline{L}_m-\underline{L}_{m'}|^3}$$

$$+\left[\left(\langle 0|\underline{x}_m|t\rangle b^*_{tk} e^{i\underline{k}\cdot\underline{L}_m} + \langle t|\underline{x}_m|0\rangle b_{tk} e^{-i\underline{k}\cdot\underline{L}_m}\right)\cdot\left(\underline{L}_m-\underline{L}_{m'}\right)\right]\times$$

$$\left.\frac{\left[\left(\langle 0|\underline{x}_{m'}|t'\rangle b^*_{t'k'} e^{i\underline{k}'\cdot\underline{L}_{m'}} + \langle t'|\underline{x}_{m'}|0\rangle b_{t'k'} e^{-i\underline{k}'\cdot\underline{L}_{m'}}\right)\cdot\left(\underline{L}_m-\underline{L}_{m'}\right)\right]}{|\underline{L}_m-\underline{L}_{m'}|^5}\right\}$$

(4.13)

The sum can be carried out in the continuum approximation.[3] For small ($kr<<1$) but non-zero k, the Hamiltonian is

$$H = \sum_{k,t} E_t b^*_{tk} b_{tk} + \frac{4\pi}{3}\frac{Ne^2}{V}\sum_{k,t,t'}\left\{P_2(\cos\theta)\left[\underline{X}_t\cdot\underline{X}_{t'} b^*_{tk} b^*_{t',-k}\right.\right.$$

$$\left.\left.+\underline{X}^*_t\cdot\underline{X}^*_{t'} b_{tk} b_{t',-k} + \underline{X}^*_t\cdot\underline{X}_{t'} b_{tk} b^*_{t'k} + \underline{X}_t\cdot\underline{X}^*_{t'} b^*_{tk} b_{t'k}\right]\right\}$$

(4.14)

---

[3] Heller and Marcus, op. cit.

The commutator $[b_{tk}, b^*_{t'k'}]$ of b_{tk} and $b^*_{t'k'}$ is given by

$$b_{tk}b^*_{t'k'} - b^*_{t'k'}b_{tk} = \frac{1}{N}\sum_{m,m'} e^{i\underline{k}\cdot\underline{L}_m - \underline{k}'\cdot\underline{L}_{m'}} d_{tm}d^*_{t'm'} - e^{i\underline{k}\cdot\underline{L}_m - \underline{k}'\cdot\underline{L}_{m'}} d^*_{t'm'}d_{tm}$$

which reduces by use of (4.6) to

$$\left[b_{tk}, b^*_{t'k'}\right] = \frac{1}{N}\sum_m e^{i(\underline{k}-\underline{k}')\cdot\underline{L}_m}\left[d_{tm}d^*_{t'm} - d^*_{t'm}d_{tm}\right]$$

$$\left[b^*_{t'k'}, b^*_{tk}\right] = 0 \qquad (4.15)$$

$d^*_{tm}d_{tm}$ is the number operator for the state tm; $d_{tm}d^*_{tm}$ is a number operator for the ground state om (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 non-zero matrix elements of $d^*_{tm}d_{tm}$ 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 $t=t'$, $[b_{tk}, b^*_{t'k'}] = \delta_{kk'}$ to order $\frac{M}{N}$, where N is the total number of atoms in the crystal. Similarly for $t\neq t'$, $d^*_{tm}d_{t'm}$ has a non-zero value for the order of M atoms, zero for the rest, while $d_{tm}d^*_{t'm}$ is zero for $t\neq t'$. To order $\frac{M}{N}$,

$$\left[b_{tk}, b^*_{t'k'}\right] = \delta_{kk'}\delta_{tt'}. \qquad (4.16)$$

In the approximation (4.16), the Hamiltonian (4.15) represents a set of coupled harmonic oscillators. The coupling is quadratic, involving only pairs of operators. The Hamiltonian (4.15) can in principle be diagonalized by a unitary transformation of the type used in Chapter III and can be expressed in terms of a new set of uncoupled harmonic oscillators as

$$H = \sum_{k,s} E_s \, g^*_{ks} \, g_{ks} . \tag{4.17}$$

The g_{ks} will be a linear combination of the old operators of the form $g_{ks} = \sum_t \alpha_{ts} b_{tk} + \beta_{ts} b^*_{t,-k}$.

It is now possible to give a physical interpretation of the operators b_{tk} and b^*_{tk}. b^*_{tk} is so constructed that acting on the ground state it produces an exciton of wavenumber k and atomic state t. The operator $b^*_{t'k'}$ applied to the exciton state k,t produces a crystalline state in which <u>two</u> atoms are excited. (This may be verified by direct recourse to the definitions of $b^*_{t'k'}$ and b^*_{tk}.) Such double-excitations are correctly generated by the b^+_{tk} 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 $\frac{1}{N}$. The zero-order wave functions for multiple-excitations can then be represented by boson operators in a

manner analogous to spin-waves in a lattice,[4] with the same restriction to states with numbers of excited atoms much less than N.

The terms which were omitted from the model Hamiltonian (4.14) have two physical interpretations. Firstly, the b^*_{tk} 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 $\frac{M}{N}$. 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 from the model.

---

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

The perturbation Hamiltonian for the interaction of atom m with the radiation field in the Coulomb gauge is

$$H' = \sum_{k,\lambda} \sum_{\substack{\text{electrons } i \\ \text{of atom}}} \frac{e}{m} \sqrt{\frac{2\pi\hbar c}{Vk}}\, \underline{p}_i \cdot \left[e^{-i\underline{k}\cdot\underline{x}_i}\, \underline{\varepsilon}_\lambda a^*_{k\lambda} + e^{+i\underline{k}\cdot\underline{x}_i}\, \underline{\varepsilon}_\lambda a_{k\lambda} \right]$$

$$+ \sum_i \frac{e^2}{2m} \left[\sum_{k,\lambda} \left(e^{-i\underline{k}\cdot\underline{x}_i}\, \underline{\varepsilon}_\lambda a^*_{k\lambda} + e^{+i\underline{k}\cdot\underline{x}_i}\, \underline{\varepsilon}_\lambda a_{k\lambda} \right) \sqrt{\frac{2\pi\hbar c}{Vk}} \right]^2 \qquad (4.18)$$

where V is the volume of the box of quantization, $\underline{\varepsilon}_{k\lambda}$ is the polarization vector of a photon of wave number $\underline{k}$ (note $\underline{\varepsilon}_{k\lambda} \cdot \underline{k} = 0$), and $\underline{p}_i$ and $\underline{x}_i$ are respectively the momentum and position operators for the i^{th} electron. In the dipole approximation,[5] (valid if the atomic radius $<< \frac{1}{k}$, which is always the optical case of interest unless dipole transitions are forbidden)

$$H' = \frac{e}{m} \sum_{k,\lambda} \sqrt{\frac{2\pi\hbar c}{Vk}}\, \underline{P} \cdot \left[e^{-i\underline{k}\cdot\underline{L}_m}\, \underline{\varepsilon}_\lambda a^*_{k\lambda} + e^{i\underline{k}\cdot\underline{L}_m}\, \underline{\varepsilon}_\lambda a_{k\lambda} \right]$$

$$+ \frac{e^2}{2m} \sum_{k,\lambda} \frac{2\pi\hbar c}{Vk} \left[a^*_{k\lambda} a^*_{-k\lambda} + a_{k\lambda} a_{-k\lambda} + a^*_{k\lambda} a_{k\lambda} + a_{k\lambda} a^*_{k\lambda} \right]$$

where $\underline{P}$ is the momentum operator for all the electrons of the atom. In the atomic wave function representation, the matrix elements of $\underline{P}$ can be written $\underline{P}_{st} = \frac{i}{\hbar} (E_s - E_t)\, \underline{X}_{st}$. With the notation $\omega_{st} = \frac{E_s - E_t}{\hbar}$, the atomic matrix elements of the

---

[5] Schiff, op. cit., p. 252.

perturbation may be written

$$\langle s|H'|t\rangle = \frac{e}{m}\sum_{k,\lambda}\sqrt{\frac{2\pi\hbar c}{Vk}}\,\frac{i\langle s|\underline{x}|t\rangle}{\omega_{st}}\cdot\underline{\varepsilon}_{k\lambda}\left[a^{*}_{k\lambda}e^{-i\underline{k}\cdot\underline{r}_m}+a_{k\lambda}e^{i\underline{k}\cdot\underline{r}_m}\right]$$

$$+\frac{e^2}{2m}Z\delta_{st}\sum_{k,\lambda}\frac{2\pi\hbar c}{Vk}\left[a^{*}_{k\lambda}a^{*}_{-k\lambda}+a_{k\lambda}a_{-k\lambda}+a^{*}_{k\lambda}a_{k\lambda}+a_{k\lambda}a^{*}_{k\lambda}\right]. \tag{4.19}$$

These matrix elements may be converted into a perturbation Hamiltonian operator by use of the operators d_{tm} and d^{*}_{tm}.

$$H'_{atom}=\frac{ie}{m}\sum_{\substack{s\neq 0,\,t\neq 0\\ s\neq t\\ k,\lambda}}\sqrt{\frac{2\pi\hbar c}{Vk}}\,\omega_{st}d^{*}_{sm}d_{tm}\langle s|\underline{x}|t\rangle\cdot\underline{\varepsilon}_{k\lambda}\left[a^{*}_{k\lambda}e^{-i\underline{k}\cdot\underline{r}_m}+a_{k\lambda}e^{i\underline{k}\cdot\underline{r}_m}\right]$$

$$+\frac{ie}{m}\sum_{s,k,\lambda}\sqrt{\frac{2\pi\hbar c}{Vk}}\,\omega_{os}\left[\langle 0|\underline{x}|s\rangle d_{sm}-\langle s|\underline{x}|0\rangle d^{*}_{sm}\right]\cdot\underline{\varepsilon}_{k\lambda}\left[a^{*}_{k\lambda}e^{-i\underline{k}\cdot\underline{r}_m}+a_{k\lambda}e^{i\underline{k}\cdot\underline{r}_m}\right]$$

$$+\frac{e^2}{2m}\sum_{k,\lambda}\frac{2\pi\hbar c}{Vk}Z\left[a^{*}_{k\lambda}a^{*}_{-k\lambda}+a_{k\lambda}a_{-k\lambda}+a^{*}_{k\lambda}a_{k\lambda}+a_{k\lambda}a^{*}_{k\lambda}\right] \tag{4.20}$$

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 can be expressed

in terms of the exciton creation and annihilation operators as

$$H' = ie\sqrt{N} \sum_{\substack{s,\lambda,\underline{G} \\ \underline{k} \text{ in } 1^{st} \text{ Brillouin zone}}} \sqrt{\frac{2\pi\hbar c}{V|\underline{k}+2\pi\underline{G}|}}\, \omega_{os} \langle 0|\underline{X}|s\rangle \Big[\underline{\varepsilon}_{k\lambda} \left(b_{sk}\, a^{*}_{\underline{k}+2\pi\underline{G},\lambda} - b^{*}_{sk}\, a_{\underline{k}+2\pi\underline{G},\lambda} \right) + \underline{\varepsilon}_{-k,\lambda} \left(b_{sk}\, a_{-\underline{k}+2\pi\underline{G},\lambda} - b^{*}_{sk}\, a^{*}_{-\underline{k}+2\pi\underline{G},\lambda} \right) \Big]$$

$$+ \frac{e^2}{2m} \sum_{\text{all } k,\lambda} \frac{2\pi\hbar c}{Vk} \Big[a^{*}_{k\lambda} a^{*}_{-k\lambda} + a_{k\lambda} a_{-k\lambda} + a^{*}_{k\lambda} a_{k\lambda} + a_{k\lambda} a^{*}_{k\lambda} \Big] . \tag{4.21}$$

$\underline{G}$ is any vector of the reciprocal lattice. $\underline{X}$ is assumed to have only real matrix elements for convenience (the atomic wave functions may be chosen to be real). The terms in H' for $\underline{G} \neq 0$ will be omitted. The matrix elements for $\underline{G} \neq 0$ are small compared to the matrix elements for $\underline{G} = 0$ in the optical range in the ratio of $\sqrt{\frac{1}{\lambda G}}_{\text{optical}} \approx \frac{1}{50}$. It will also be energetically unfavorable to mix in appreciable amounts of photon states for $G \neq 0$ because the photon energies for $\underline{G} \neq 0$ are of the order of two thousand times the exciton or optical photon energies. 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 $\underline{X}$ from the ground-state only to P-states. The three degenerate P-states may be always so arranged that the state created by b^{*}_{sk} has matrix elements of $\underline{X}$ for a single atom only in directions perpendicular or parallel to $\underline{X}$. Such an arrangement divides the excitons

into two categories: transverse excitons with $\langle 0|\underline{X}|S\rangle$ perpendicular to $\underline{k}$ and longitudinal excitons with $\langle 0|\underline{X}|S\rangle$ parallel to $\underline{k}$. There is no interaction between the longitudinal excitons and photons since $\underline{e}_{k\lambda}\cdot\langle 0|\underline{X}|S\rangle=0$ for longitudinal excitons of wave-number $\underline{k}$. Similarly there is no interaction between any of the three exciton modes in the Hamiltonian (4.14). For consideration of optical interactions, the longitudinal excitons can be omitted. In (4.14) and (4.21) only P-states have interactions with each other, 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 λ. By utilizing the atomic f-sum rule,[6]

$$\sum_S \frac{2m}{3\hbar}\omega_{S0}|\langle 0|\underline{X}|S\rangle|^2=Z, \text{ or } \sum_S \frac{2m}{\hbar}\omega_{S0}|\langle 0|i X_i|S\rangle|^2=Z \tag{4.22}$$

($\underline{X}=iX_1+jX_2+\underline{k}X_3$) and the interaction Hamiltonian, (4.21) can be rewritten as

$$H'=\sum_n\left\{\sum_{k,\lambda}\left[i\sqrt{\frac{2\pi\hbar c}{Vk}}\,\frac{e\omega_{on}}{c}\langle 0|X_i|n\rangle\left(b_{n\lambda k}a^*_{k\lambda}-b^*_{n\lambda k}a_{k\lambda}\right.\right.\right.$$
$$\left.+b_{n\lambda k}a_{-k\lambda}-b^*_{n\lambda k}a^*_{-k\lambda}\right)+\frac{2\pi e^2cN}{c^2kV}\,\omega_{os}|\langle 0|X_i|n\rangle|^2$$
$$\left.\left.\left(a^*_{k\lambda}a_{k\lambda}+a_{k\lambda}a^*_{k\lambda}+a^*_{k\lambda}a^*_{-k\lambda}+a_{k\lambda}a_{-k\lambda}\right)\right]\right\}. \tag{4.23}$$

---

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

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 $H_{\text{photon}} = \sum_{k,\lambda} \hbar c k \left(a^*_{k\lambda} a_{k\lambda}\right)$

$$H_{\text{exciton}} = \sum_{k,n,\lambda} E_n \left(b^*_{n\lambda k} b_{n\lambda k}\right)$$

$$H_{\text{exciton-exciton}} = -\frac{2\pi}{3} \frac{Ne^2}{V} \sum_{n,n',k,\lambda} \left(X_n X_{n'} b^*_{n\lambda k} b^*_{n'\lambda,-k} + X^*_n X^*_{n'} b_{n\lambda k} b_{n'\lambda,-k} + X^*_n X_{n'} b_{n\lambda k} b^*_{n'\lambda k} + X_n X^*_{n'} b^*_{n\lambda k} b_{n\lambda k}\right)$$

and $H_{\text{exciton-photon}}$ is given by (4.23). (4.24)

A comparison of (4.23) with (3.9) shows that each exciton type n 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 Chapter 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 Chapter III. Direct application of the diagonalization procedure yields the secular equation

$$\begin{vmatrix} \hbar ck + \frac{4\pi e^2 N|x|^2}{\hbar ckV} - \omega & i\sqrt{\frac{2\pi\hbar cN}{kV}}\frac{eE|x|}{\hbar c} & \frac{4\pi e^2 N|x|^2}{\hbar ckV} & -i\sqrt{\frac{2\pi\hbar cN}{kV}}\frac{eE|x|}{\hbar c} \\ -i\sqrt{\frac{2\pi\hbar cN}{kV}}\frac{eE|x|}{\hbar c} & E - \frac{4\pi}{3}\frac{Ne^2|x|}{V} - \omega & -i\sqrt{\frac{2\pi\hbar cN}{kV}}\frac{eE|x|}{\hbar c} & -\frac{4\pi}{3}\frac{Ne^2|x|^2}{V} \\ -\frac{4\pi e^2 N|x|^2}{\hbar ckV} & -i\sqrt{\frac{2\pi\hbar cN}{kV}}\frac{eE|x|}{\hbar c} & -\hbar ck - \frac{4\pi e^2 N|x|^2}{\hbar ckV} - \omega & i\sqrt{\frac{2\pi\hbar cN}{Vk}}\frac{eE|x|}{\hbar c} \\ -i\sqrt{\frac{2\pi\hbar cN}{kV}}\frac{eE|x|}{\hbar c} & \frac{4\pi}{3}\frac{Ne^2|x|}{V} & -i\sqrt{\frac{2\pi\hbar cN}{kV}}\frac{eE|x|}{\hbar c} & -E + \frac{4\pi Ne^2|x|^2}{3V} - \omega \end{vmatrix} = 0$$

(4.25)

The most convenient form of the solution is (in units of $\hbar = c = 1$)

$$\frac{k^2}{\omega^2} = 1 + \frac{8\pi\frac{N}{V}e^2|x|^2 E}{\left(E - \frac{8\pi}{3}\frac{N}{V}e^2|x|^2\right)E - \omega^2}$$

(4.26)

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 $\frac{2e^2|x|^2 E}{E^2-\omega^2}$ is the polarizability of a free atom, (4.25) can be rewritten in the more familiar Lorenz-Lorentz form

$$\varepsilon = \frac{k^2}{\omega^2} = 1 + \frac{4\pi \frac{N}{V}\alpha}{1-\frac{4\pi}{3}\frac{N}{V}\alpha} \quad \text{or} \quad \frac{\varepsilon-1}{\varepsilon+2} = \frac{4\pi}{3}\alpha\frac{N}{V} \tag{4.27}$$

The energy of the coupled excitons is $E_{coupled} = E\sqrt{1-\frac{8\pi}{3}\frac{N}{V}\frac{e^2|x|^2}{E}}$ The expansion of the square root to first order yields $E-\frac{4\pi}{3}\frac{Ne^2}{V}|x|^2$, which agrees with the expression obtained by Dexter[7] or Equation (4.4), both from perturbation theory. The use of a boson formalism makes it possible to iterate selected terms of ordinary perturbation theory to obtain higher-order corrections due to multiple excitations. (The energy shift obtained here agrees with the shift directly derivable from $H_{exciton} + H_{exciton\text{-}exciton}$.)

There are two points of view which can be adopted for treating the "local field" effects in the extreme tight-binding model. The semi-classical 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

---

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

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 non-interacting 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 electro-dynamics 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 $\frac{4\pi}{3}$ catastrophe of the semi-classical theory at a finite frequency ω 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.[8] 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 semi-classical 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 tight-binding model Hamiltonian will be taken to be $H_{exciton} + H_{photon} + H_{exciton\text{-}photon}$ 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.

---

[8] 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 polarizability of the atom is given by $\underline{P} = \alpha \underline{E} + \gamma \underline{E} E^2$ (there will be no E^2 term for spherically symmetric atoms), then the time averaged polarization $\bar{P}$ in the presence of an applied field $\underline{E}_a$ (small) and a large fluctuating field $E_0(t)$ will be approximately $\bar{P} = [\alpha + \frac{5}{3}\gamma \overline{(E_0(t))^2}]\, \underline{E}_a$. The observed polarization is proportional to $\underline{E}_a$, but the observed polarizability is not α. This effect is not included in classical local field formulae.

B. The Extreme Weak-binding Model

In the idealized weak-binding exciton model to be treated here, the electronic structure of the solid is characterized by two energy bands: the valence band and the conduction band, denoted here by subscripts v and c respectively. Both bands are assumed to be S-bands. The valence band is assumed to have one relative maximum located at $k=0$, and the conduction band is assumed to have one relative minimum located at $k=0$. There is an energy gap at $k=0$. In the ground state of the crystal the valence band is filled and the conduction band is empty.

The electronic wave function of the crystal can be specified in terms of the occupation number of the electronic states; i.e., a designation of which electronic states are to enter the Slater determinant of one-particle wave functions can be made. A wave function can be written in terms of the ground-state wave function and creation and annihilation operators for particles in the valence and conduction band. c^*_{vq}, $[c^*_{cq}]$ is defined to be the creation operator for an electron of wave-number q in the valence [conduction] band, and c_{vq}, $[c_{cq}]$ is the corresponding annihilation operator. These operators obey the usual anti-commutation rules for fermion creation and annihilation operators.

$$c_{vq}\, c^{*}_{vq'} + c^{*}_{vq'}\, c_{vq} = \delta_{qq'} \qquad c_{vq} c^{*}_{cq'} + c^{*}_{cq'} c_{vq} = 0$$

$$c_{cq}\, c^{*}_{cq'} + c^{*}_{cq'}\, c_{cq} = \delta_{qq'} \qquad c_{vq} c_{cq'} + c_{cq'} c_{vq} = 0$$

(4.28)

In the independent electron approximation the Hamiltonian for this electronic system can be written

$$H_o = \sum_q E_{cq}\, c^{*}_{cq}\, c_{cq} + \sum_q E_{vq}\, c_{vq}\, c^{*}_{vq} \tag{4.29}$$

where E_{cq} is the energy eigenvalue of the state q in the conduction band and E_{vq} is the energy of state q in the valence band. The zero of energy has been taken as the ground-state energy. The occupied states of the conduction band will be referred to in the usual way as electron states, and the unoccupied states in the valence band as hole states.

By including the interactions of electrons in a more exact manner than in the Hartree-Fock scheme, the energy levels and eigenstates of the crystal will be slightly modified from those of Equation (4.29). There will, in general, exist exciton states lower in energy than the lowest energy electron-hole pair of (4.29). These bound states of electrons and holes will be shown to have the same approximate boson character as the tight-binding excitons of Section A.

The real Hamiltonian of the crystal will contain the Coulomb interaction between all pairs of electrons. It is commonly assumed that an approximate first-order Hamiltonian can be written in which there is a simple Coulomb interaction between electrons and holes. The effect of all the electrons in lower energy states and the modification of the $N-1$ one-electron states when one state in the Slater determinant is changed is assumed to be represented by an effective dielectric constant.[9] The first order Hamiltonian H_1, in operator notation, has the form

$$H_1 = H_0 + \frac{1}{2}\sum_{k,k',K} B_K \left[c^*_{v,k'-K}\, c_{vk'}\, c^*_{c,k+K}\, c_{ck} + c^*_{c,k'-K}\, c_{ck'}\, c^*_{c,k+K}\, c_{c,k} + c^*_{v,k'-K}\, c_{vk'}\, c^*_{v,k+K}\, c_{vk} \right]. \tag{4.30}$$

B_K is the Fourier transform of the Coulomb potential.

$$B_K = \frac{4\pi e^2}{\varepsilon (2\pi)^{3/2}} \frac{1}{V} \frac{1}{K^2} \tag{4.31}$$

ε is the effective dielectric constant and V is the volume of the crystal. The form implies that the electron and hole can be exactly localized. It is impossible to define a position operator for a hole or a position operator for an electron

---

[9] For a treatment of excitons in this approximation and further references to the literature, see G. Dresselhaus, J. Phys. Chem. Solids 1, 4 (1956).

without a complete set of functions. The interaction written here assumes that the electrons and holes are always far enough apart that localization within a unit cell is sufficient to define position. Even with this proviso, (4.30) is still not exactly correct. Terms referring to "vacuum polarization" have been omitted and there should be present terms such as $c_{vk} c^*_{ck}$ which modify the vacuum state. It is usually supposed that the effects of such terms can be absorbed either in ε or in the effective masses of the bands.

Let ψ_{mq} be a one-exciton (i.e., one electron coupled to one hole) eigenstate of (4.30) of energy E_{mq};

$$\psi_{mq} = \left[\sum_k A_{mk,k+q} \, c_{vk} \, c^*_{c,k+q} \right] \psi_0 . \tag{4.32}$$

If this state represents a bound state of electron and hole, then the sum over k extends over many k vectors. By the general uncertainty result obtainable from the Fourier transform, if the "radius" of the bound electron-hole pair is r_0, the spread of k around q is approximately $\frac{1}{r_0}$.

Define b^*_{mq} as the bracket in (4.32), i.e., $\psi_{mq} = b^*_{mq} \psi_0$, and let b_{mq} be the Hermitian conjugate to the operator b^*_{mq}. The general properties of b_{mq} and b^*_{mq} will be investigated, for these are the operators which will appear in the dielectric

theory. It will be shown that for matrix elements between exciton states,

$$b_{m'q'}\, b^{*}_{mq} - b^{*}_{mq}\, b_{m'q'} = \delta_{mm'}\,\delta_{qq'} \qquad (a)$$

$$b_{mq}\, b_{m'q'} - b_{m'q'}\, b_{mq} = 0 \qquad (b)$$

$$b_{mq}\, H - H\, b_{mq} = E_{mq}\, b_{mq} \qquad (c) \qquad (4.33)$$

within order $M\frac{r_o^3}{V}$, where V is the volume of the crystal and M is the number of excitons in the crystal. Equations (4.33a,b, and c) together are equivalent to the statement that excitons are bosons, and have a dispersion relation given by E_{mq}.

The proof of (4.33a) is straightforward. If the eigenfunctions ψ_{mq} are normalized, then from the general orthogonality relations between eigenfunctions of different energies or belonging to different representations of the translation group, $\langle \psi_{mq} | \psi_{m'q'} \rangle = \delta_{mm'}\,\delta_{qq'}$. This expression can be evaluated in terms of the $A_{mk,k+q}$ by using (4.32) and the definitions of c_{vk} and c_{ck}, and yields

$$\delta_{mm'}\,\delta_{qq'} = \delta_{qq'} \sum_{k} A^{*}_{mk,k+q}\, A_{m'k,k+q}\,. \qquad (4.34)$$

The commutator (4.33a) can be evaluated directly from the

definitions of the b_{mq} and is

$$b_{m'q'} b^*_{mq} - b^*_{mq} b_{m'q'} = \sum_{k,k'} A_{mk,k+q} A^*_{m'k',k'+q'}$$

$$\left[c_{c,k'+q'} c^*_{vk'} c_{vk} c^*_{c,k+q} - c_{vk} c^*_{c,k+q} c_{c,k'+q'} c^*_{vk'} \right]. \quad (4.35)$$

An application of the commutation rules (4.28) shows that the bracket of (4.35) is zero if both $k' \neq k$ and $k'+q' \neq k+q$. The other terms of the sum will be divided into two parts. Part I contains the terms $k=k'$ and part II contains all other terms.

$$I = \sum_k A_{mk,k+q} A^*_{m'k,k+q'} \left[c_{c,k+q'} c^*_{vk} c_{vk} c^*_{c,k+q} - c_{vk} c^*_{c,k+q} c_{c,k+q'} c^*_{vk} \right]$$

which reduces to

$$I = \sum_k A_{mk,k+q} A^*_{m'k,k+q} \left[\delta_{qq'} - \delta_{qq'} c_{vk} c^*_{vk} - c^*_{c,k+q} c_{c,k+q'} \right]. \quad (4.36)$$

The only terms which enter II are those for which $k+q = k'+q'$, (but $q \neq q'$).

$$II = \sum_k A_{mk,k+q} A^*_{m',k+q-q',k+q} \left[c_{c,k+q} c^*_{v,k+q-q'} c_{vk} c^*_{c,k+q} \right.$$

$$\left. - c_{vk} c^*_{c,k+q} c_{c,k+q} c^*_{v,k+q-q'} \right]$$

$$= \sum_k A_{mk,k+q} A^*_{m',k+q-q',k+q} c^*_{v,k+q-q'} c_{vk} \quad (4.37)$$

For $q=q'$, II gives no contribution to the commutator, while I reduces to

$$\left[b_{m'q'}, b^*_{mq} \right] = \sum_k A_{mk,k+q} A^*_{m'k,k+q} \left[1 - c_{vk} c^*_{vk} - c^*_{c,k+q} c_{c,k+q} \right]. \quad (4.38)$$

For exciton states the occupation number of any electron state is of order $M\frac{r_o^3}{V}$, where M is the total number of electron-hole pairs (excitons) in the crystal. The last two terms in (4.38) can be neglected in comparison to 1 to order $M\frac{r_o^3}{V}$, and (4.38) then reduces to (4.33a) by use of (4.34) for $q=q'$. For $q\neq q'$, the last term in I and the sum II occur. Matrix elements between exciton states of $c^*_{c,k+q}\,c_{c,k+q}$ are of order $M\frac{r_o^3}{V}$. Each of the terms $A_{mk,k+q}\,A_{m'k,k+q'}$ is of order $\frac{r_o^3}{V}$, and there are approximately $\frac{V}{r_o^3}$ such terms. Therefore for $q\neq q'$, the commutator is of order $M\frac{r_o^3}{V}$. (4.33a) has thus been verified for exciton states. (4.33b) can be proved in the same manner so its proof will not be given here.

Although a direct proof of (4.33c) is possible, it is more convincing to show the validity of (4.33c) by arguments based on physical grounds. The approximations will be more obvious and the generality more clear in the semi-quantitative treatment to follow than in a more mathematical proof where the same approximations must be made.[10]

---

[10] The basic reason that a direct proof is difficult is that the Hamiltonian cannot be expressed directly in terms of the operators b_{mq}, although the commutators of b_{mq} and H can be expressed in terms of b_{mq}. In order to do even this properly it is necessary to express $c_{vk}\,c_{c,k+q}$ in terms of the b^*_{mq}. This transformation must exist, for the set $\{b^*_{mq}\}$ all m,q and the set $\{c_{vk}, c^*_{c,k+q}\}$ for all k and q both generate (acting on ψ_o) the space of all one-electron plus one-hole excitations. Unfortunately this transformation is not known in general, so it is very difficult to discuss the approximations which must be made to arrive at (4.33c) in a more than semi-quantitative way.

$b^*_{mq}\Psi_o$ is an eigenfunction of H with eigenvalue E_{mq}. The set $\{b^*_{mq}\psi_o\}$ for all m and q describes the wave functions of all exciton states of one electron bound to one hole. There exist eigenfunctions of H which describe states of many holes and many electrons. In the zero-order approximation, the independent electron model, no correlations are allowed between electrons except those produced by anti-symmetrization. In the exciton approximation, states containing correlated pairs of electrons and hole are constructed. Higher excitations involving several correlated electrons and holes can be constructed. Of these higher excitations only those in which one electron is coupled to one hole will be treated here. (There will be other correlation effects produced by antisymmetrization.)

The state $b^*_{mq}\psi_o$ is a linear combination of approximately $\frac{V}{r_o^3}$ Slater determinants, each determinant differing by one hole-electron pair from the ground-state Slater determinant. The wave function produced by $b^*_{m'q'}$ operating on one of these determinants resembles closely the wave function produced by $b^*_{m'q'}$ acting on ψ_o. All of the pair creation operators of $b^*_{m'q'}$ will "act" on the chosen Slater determinant as usual except the one pair-creation operator which has already been used to produce this new Slater determinant from the ground-state wave function. $b^*_{m'q'}b^*_{mq}\psi_o$ is a state of double excitation with two correlated electron-hole pairs, each pair not correlated with

the other pair except insofar as the exclusion principle causes such correlations. There will exist a slight error in normalization of the double excitation wave functions due to the $\frac{V}{r_o^3}$ terms of $b^*_{m'q'} b^*_{mq}$ which act on the same electron or hole wave functions, out of a total of $\left(\frac{V}{r_o^3}\right)^2$ terms in the product.

For the case $m,q = m',q'$ there is an additional error of normalization which is a consequence of the description of the excited states in terms of boson operators. By direct computation using boson commutation rules, it can be shown that

$$\langle b^*_{mq} b^*_{mq} \Psi_o | b^*_{mq} b^*_{mq} \Psi_o \rangle = 2 \langle b^*_{mq} \Psi_o | b^*_{mq} \Psi_o \rangle = 2$$

In general, if Ψ_o is the normalized ground state, $\frac{(b^*_{mq})^n \Psi_o}{\sqrt{n!}}$ is the normalized excited state with n excitations of type mq. This is the usual result for harmonic oscillator operators.

The expectation value of the Hamiltonian will contain three types of terms. One of these terms will be the energy of one exciton mq with a slight error due to the "overlap" which produced the normalization error. A second will be the energy of an exciton $m'q'$ with a similar error. The third type of terms will contain the effects of the interaction between the two excitons. In the case of the independent electron model, the effects of electronic interactions are assumed to be taken into account by the band structure, whereas it will be assumed that the mean exciton-exciton interaction is an adequate expression of the exciton interactions and can be included in the

exciton energies and effective masses. These arguments lead to an approximate Hamiltonian for excitons of the form

$$H = \sum_{m,q} E_{mq}\, b^*_{mq}\, b_{mq} \tag{4.39}$$

valid when the number of excitons in the crystal is small compared to $\frac{V}{r_o^3}$.

A specific calculation of the expectation value of the Hamiltonian for the simple case of double excitations can be carried out fairly easily in the Wannier representation if some of the effects of exchange are neglected.[11] This calculation will show in detail the nature of the terms which have been neglected in the argument for the validity of (4.33c). In an effective mass approximation the Hamiltonian for a single exciton[12] is

$$H = -\frac{\hbar^2}{2m_e}\nabla^2_{r_e} - \frac{\hbar^2}{2m_h}\nabla^2_{r_h} - \frac{e^2}{\varepsilon|r_e - r_h|}. \tag{4.40}$$

An eigenfunction $\varphi_{nk}(r_e, r_h)$ of (4.40) with energy E_{nk} is to be interpreted in real space as the function

---

[11] It is customary to neglect exchange in working with Wannier excitons. If the analogy between Wannier excitons and positronium is good, the exchange effects in excitons, as in positronium, are small and produce only fine structure.

[12] See Dresselhaus, op. cit.

$$\Psi(\text{"}r_e\text{"},\text{"}r_h\text{"}) = \sum_{L_i L_j} \varphi_{nk}(L_i, L_j)\, \psi_{v,L_i}(r_h)\, \psi_{c,L_j}(r_e) \tag{4.41}$$

where L_i are the lattice sites, $\psi_{cL_j}(r_e)$ is the Wannier function for an electron in the conduction band at L_j, and $\psi_{vL_i}(r_h)$ is a Wannier function of $N-1$ electrons in the valence band corresponding to a hole at L_i. This function will be an eigenfunction (within the assumptions necessary to derive (4.40)) of the crystal Hamiltonian. The exclusion principle has been properly taken into account, but exchange effects have been neglected in the theory. The eigenfunctions $\varphi_{nk}(r_e, r_h)$ have the form

$$\varphi_{nk}(r_e, r_h) = e^{\frac{1}{2} i \underline{k}\cdot(\underline{r}_e + \underline{r}_h)}\, u_n(|\underline{r}_e - \underline{r}_h|).$$

The generalization of (4.40) to double excitations is

$$H = -\frac{\hbar^2}{2m_e}\left(\nabla_{r_{e_1}}^2 + \nabla_{r_{e_2}}^2\right) - \frac{\hbar^2}{2m_h}\left(\nabla_{r_{h_1}}^2 + \nabla_{r_{h_2}}^2\right)$$

$$-\frac{e^2}{\varepsilon}\left[\frac{1}{|\underline{r}_{e_1} - \underline{r}_{h_1}|} + \frac{1}{|\underline{r}_{e_2} - \underline{r}_{h_2}|} + \frac{1}{|\underline{r}_{e_1} - \underline{r}_{h_2}|} + \frac{1}{|\underline{r}_{e_2} - \underline{r}_{h_1}|} - \frac{1}{|\underline{r}_{e_1} - \underline{r}_{e_2}|} - \frac{1}{|\underline{r}_{h_1} - \underline{r}_{h_2}|}\right]. \tag{4.42}$$

A wave function $\Phi = \psi_{nk}(r_{e_1}, r_{h_1})\, \psi_{nk}(r_{e_2}, r_{h_2})$ has an expectation value of the energy

$$\langle \Psi | H | \Psi \rangle = 2E_{nk} - \frac{e^2}{\varepsilon} \Big\langle e^{\frac{i}{2}\underline{k}\cdot(\underline{r}_{e_1}+\underline{r}_{h_1}+\underline{r}_{e_2}+\underline{r}_{h_2})} u_n(|\underline{r}_{e_1}-\underline{r}_{h_1}|)\, u_n(|\underline{r}_{e_2}-\underline{r}_{h_2}|)$$

$$\left| \frac{1}{|\underline{r}_{e_1}-\underline{r}_{h_2}|} + \frac{1}{|\underline{r}_{e_2}-\underline{r}_{h_1}|} - \frac{1}{|\underline{r}_{e_2}-\underline{r}_{e_1}|} - \frac{1}{|\underline{r}_{h_2}-\underline{r}_{h_1}|} \right| e^{\frac{i}{2}\underline{k}\cdot(\underline{r}_{e_1}+\underline{r}_{h_1}+\underline{r}_{e_2}+\underline{r}_{h_2})} u_n(|\underline{r}_{e_1}-\underline{r}_{h_1}|) u_n(|\underline{r}_{e_2}-\underline{r}_{h_2}|) \Big\rangle$$

(4.43)

Since $u_n(|\underline{r}_e-\underline{r}_h|)$ generally will fall to zero exponentially for $|\underline{r}_e-\underline{r}_h| > r_0$, where r_0 is the exciton "radius," the only contributions occur when $|\underline{r}_{e_1}-\underline{r}_{h_1}|$ and $|\underline{r}_{e_2}-\underline{r}_{h_2}|$ are $\lesssim r_0$. In most of the region of integration, $|\underline{r}_{e_1}-\underline{r}_{e_2}| >> r_0$, and the denominators of the potential can be expanded in a multipole expansion. The charge distribution $|u_n(|\underline{r}_{e_1}-\underline{r}_{h_1}|)|^2$ has as its first non-vanishing moment the quadrupole moment. If new integration variables $\frac{\underline{r}_{e_1}+\underline{r}_{h_1}}{2}$, $\frac{\underline{r}_{e_2}+\underline{r}_{h_2}}{2}$, $\underline{r}_{e_1}-\underline{r}_{h_1}$, $\underline{r}_{e_2}-\underline{r}_{h_2}$ are taken and Ψ is normalized to 1 in the volume of the crystal, the second term of $\langle \Psi | H | \Psi \rangle$ consists of two parts, a near-zone interaction and a quadrupole-quadrupole interaction of quadrupoles spread uniformly through the volume of the box. Both near-zone and quadrupole interaction integrals will converge independent of the volume of the box, and since the normalization constant is $\frac{1}{\sqrt{V}}$,

$$\langle \Psi | H | \Psi \rangle = 2E_{nk} + O\left(\frac{1}{V}\right). \tag{4.44}$$

The wave function (4.43) cannot be interpreted without modification in real space. The real space wave function is

$$\psi(r_{e_1}, r_{e_2}, r_{h_1}, r_{h_2}) = \sum_{L_i, L_j, L_m, L_n} \Psi(L_i, L_j, L_m, L_n)$$

$$\psi_{cL_i}(r_{e_1})\, \psi_{cL_j}(r_{e_2})\, \psi_{vL_m}(r_{h_1})\, \psi_{vL_n}(r_{h_2}) \qquad (4.45)$$

This wave function contains terms with two electrons in the same Wannier conduction state ψ_{cL_i} and terms with two holes in the same Wannier hole state ψ_{vL_m}. The exclusion principle for the Wannier states can be properly taken into account by using a wave function Ψ' which can be constructed from Ψ by antisymmetrizing with respect to the two holes and antisymmetrizing with respect to electrons. This wave function is produced by the operator $b^*_{n\uparrow} b^*_{n\downarrow}$ acting on the ground state. The expectation value of the near-zone interaction will be somewhat modified by this antisymmetrization. If the effects of antisymmetrization are neglected, but the exclusion principle taken into account,

$$\psi(r_{e_1}, r_{e_2}, r_{h_1}, r_{h_2}) = \sum_{L_i \neq L_j} \sum_{L_m \neq L_n} \Psi(L_i, L_j, L_m, L_n) \cdot$$

$$\psi_{cL_i}(r_{e_1})\, \psi_{cL_j}(r_{e_2})\, \psi_{vL_m}(r_{h_1})\, \psi_{vL_n}(r_{h_2}) \qquad (4.46)$$

For an exciton "radius" of n lattice constants, there are approximately $(n^3 N)^2$ terms in the sum (4.45) and only $(n^3(N-1))^2$ terms in the sum (4.46). This is the

cause of the normalization error in the multiple exciton functions generated by products of b^*_{nk}.

All the qualitative features of the arguments leading to an approximate exciton Hamiltonian (4.39) have been born out in detail for the specific case of double excitations, neglecting exchange. The physical situation can be well described in terms of the behavior of He^4. At low densities (gaseous state), helium atoms (bound units of an even number of fermions) can be treated as bosons. At high densities (nuclear matter) an alpha particle can no longer be correctly treated as a boson. Until the mean separation of the alpha particles becomes of the order of the range of nuclear forces between them, the boson approach is adequate.

The exciton-photon interaction Hamiltonian will next be derived. The actual interaction Hamiltonian is Equation (4.18), which will be revised into a more useful form. The approximate interaction Hamiltonian will be shown to have a form identical with that of the tight-binding model. The interaction Hamiltonian will be constructed by first computing the lowest state interaction in the crystal-equivalent to the dipole approximation, then by generalizing to all crystal states by use of the exciton field operators.

The term of (4.18) linear in the photon field operators, H_1', will be treated first. The matrix element of this first

term between the state $b^*_{mq}\psi_o$ and ψ_o is (leaving the photon term in operator form)

$$\langle \psi_o | H_1' | b^*_{mq} \psi_o \rangle =$$

$$\left\langle \psi_o \left| \sum_{k,\lambda} \sum_{\text{electrons } i} \sqrt{\frac{2\pi\hbar c}{Vk}}\, \underline{\varepsilon}_{k\lambda} \cdot \underline{p}_i \left[a^*_{k\lambda} e^{-i\underline{k}\cdot\underline{r}_i} + a_{k\lambda} e^{i\underline{k}\cdot\underline{r}_i} \right] \right| b^*_{mq} \psi_o \right\rangle . \tag{4.47}$$

Each term in the sum over k' is exactly the matrix element of the perturbation Hamiltonian between the ground state and a state of free electron $k'+q$ and free hole k'. A general wave-number conservation rule (within $2\pi\underline{G}$) for such matrix elements eliminates most of the terms in the sum over $\underline{k}$ in (4.47), leaving

$$\langle \psi_o | H_1' | b^*_{mq} \psi_o \rangle = \sqrt{\frac{2\pi\hbar c}{q}} \sum_{k'} A_{mk';k'+q} M_{\lambda k'} \left[a^*_{-q\lambda} + a_{q\lambda} \right] \tag{4.48}$$

where $M_{\lambda k'}$ is defined by

$$M_{\lambda k'} = \left\langle \psi_o \left| \sum_{\text{electrons } i} \underline{\varepsilon}_{q\lambda} \cdot \underline{p}_i\, e^{-i\underline{q}\cdot\underline{x}_i} \right| c_{ck'} c_{c,k'+q} \psi_o \right\rangle . \tag{4.49}$$

(4.49) can be written in terms of one-electron Bloch functions as

$$M_{\lambda k'} = \int_{\text{entire crystal}} u^*_{vk'} e^{-i\underline{k}'\cdot\underline{x}} \left(\underline{\varepsilon}_{q\lambda} \cdot \underline{p} \right) e^{-i\underline{q}\cdot\underline{x}} u_{c,k'+q} e^{i(\underline{k}'+\underline{q})\cdot\underline{x}} \, d^3x \tag{4.50}$$

This matrix element is, of course, a function of q. The usual procedure will be followed here of expanding the matrix element

around $q=0$ and keeping the first non-vanishing term. The constant term of this expansion is given by (4.51) for Bloch functions normalized in a unit cell.

$$M_{\lambda k'} = \int_{\text{unit cell}} u^*_{vk'} (\underline{\varepsilon}_{q\lambda} \cdot \underline{P}) u_{ck'} \, d^3x \tag{4.51}$$

At the beginning of this section it was specified that both the valence and conduction bands were S-bands. The matrix elements (4.51) vanish between S-bands at $k'=0$, but for general k' they are non-zero. (4.48) has the dependence $\sqrt{\frac{1}{q}}$ on q and is zero or non-zero depending upon the coefficients $A_{mk',k'+q}$. For S-bands, (4.48) is non-zero only if the exciton is formed in a P-state. If P-bands[13] had been considered, it would have proved possible to create excitons in S-states. In the simplest cases, $B_{mq} = \sum_{k'} A_{mk',k'+q} M_{\lambda k'}$ will be independent of q. This will be the case as long as the exciton wave function is not appreciably distorted by the exciton motion and an isotropic effective mass approximation is valid. In any event, for small q,

$$\langle \psi_0 | H' | b^*_{mq} \psi_0 \rangle \approx \sqrt{\frac{2\pi\hbar c}{q}} \, B_m \left[a^*_{-q\lambda} + a_{q\lambda} \right] \tag{4.52}$$

where $B_m = B_{mq}$ evaluated at $q=0$.

---

[13] Dresselhaus, op. cit.

There are no matrix elements of H_1' between the ground state and states of more than one exciton. Each term of H_1' involves only one electron. If initial and final states differ in two electron states, the orthogonality of the single particle wave functions makes $\langle \Psi_0 \mid H_1' \mid$ state of more than one exciton $\rangle = 0$.

As in Section A, only the exciton states for which there exist non-zero matrix elements of H_1' from the ground state will be considered. The argument of the previous paragraph shows that matrix elements of H_1' exist only between exciton states differing by but one exciton. Therefore H_1' as an operator can be written as a linear combination of pair operators and photon operators, conserving wave-number.

$$H_1' = \sum_{k,q,\lambda} \Big[\alpha_{qk\lambda}\, c^*_{c,k+q}\, c_{vk}\, (a_{q\lambda} + a^*_{-q\lambda}) + \alpha^*_{qk\lambda}\, c^*_{vk}\, c_{c,k+q}\, (a^*_{q\lambda} + a_{-q\lambda}) \Big] \tag{4.53}$$

As long as the scattering of light by excitons without the formation of new excitons is unimportant, it is sufficient to treat only electron-hole pairs as has been done in (4.53) (i.e., electron-electron pairs can be omitted in H_1'). There exists a linear transformation between the pair operators in (4.53) and the exciton operators b_{mq}, so H_1' operator can be expressed as

$$H_1' = \sum_{m,q,\lambda} \beta_{mq\lambda}\, b^*_{mq} \left[a_{q\lambda} + a^*_{-q\lambda} \right] + \beta^*_{mq\lambda}\, b_{mq} \left[a^*_{q\lambda} + a_{-q\lambda} \right]. \tag{4.54}$$

The conservation of wave-number has been utilized in deriving (4.54) from (4.53) and the unknown linear transformation. The coefficients of (4.54) are evaluated by requiring the matrix element (4.52) to be a special case of (4.54). From this criterion,

$$\beta^{*}_{mq\lambda} = \sqrt{\frac{2\pi\hbar c}{q}}\ B_m \tag{4.55}$$

B_m will be taken to be a pure imaginary number. If this is not now the case, a transformation $b_{mq} \rightarrow e^{i\theta} b_{mq}$ can be made such that B_m is a pure imaginary number without altering the commutation rules of the b_{mq} operators.

The second term of the perturbation Hamiltonian (4.18) is easily evaluated. An expansion is again made about $q=0$ and only the lowest-order term kept. In this approximation the matrix elements of H_1' are matrix elements of $\underline{P}$ between Bloch states of the same wave-number belonging to different bands. In the same approximation, matrix elements of the number N occur between Bloch states of different bands for H_2'. No part of the operator of H_2' refers to the excitons in this approximation. The result is

$$H_2' = \frac{e^2}{2m}\ \frac{2\pi\hbar c}{Vk}\ N \sum_{k,\lambda} \left(a_{k\lambda}\, a_{-k\lambda} + a^{*}_{k\lambda}\, a^{*}_{-k\lambda} + a^{*}_{k\lambda}\, a_{k\lambda} + a_{k\lambda}\, a^{*}_{k\lambda} \right). \tag{4.56}$$

The H_2' calculated here represents the contribution of all energy bands of the crystal to H_2'. In order to make the exciton-photon Hamiltonian look like the exciton-photon Hamiltonian of Section A, part of H_2' is split off to be combined with H_1', and the rest of H_2' is attributed to the other excited states of the crystal. Each exciton will then have the interaction with the photons of the form given by (4.23).

A brief summary of the derived results is given here for review and future reference. An approximate Hamiltonian H and the interaction of excitons in an optically isotropic crystal with photons were derived for both models of exciton states. In this Hamiltonian the excitons are bosons and are represented in second-quantized form by boson operators. "Local field" effects are taken into account in assuming that the exciton states which enter (4.57) are eigenfunctions of the crystal Hamiltonian (i.e., exciton-exciton interactions are not present in (4.57)). If the order of interaction is defined by the sum of number of "particles" (excitons or photons) involved in both "initial" and "final" states, the Hamiltonian can be qualitatively described as containing only two-body interactions (which conserve wave-number). Higher order couplings exist, of course, and will be discussed in the next chapter on the complex dielectric constant. The

approximate Hamiltonian is

$$H = \sum_{k,\lambda} \Big\{ \hbar c|k|\, a^*_{k\lambda} a_{k\lambda} + \sum_{\substack{\text{exciton}\\ \text{modes } j}} \hbar\omega_j\, b^*_{j\lambda k}\, b_{j\lambda k}$$

$$+ \sum_j \Big[i\hbar\omega_j^2 \sqrt{\frac{\pi\beta_j}{c|k|\omega_j}} \left(a^*_{k\lambda} b_{j\lambda k} - a_{k\lambda} b^*_{j\lambda k} + a_{k\lambda} b_{j\lambda,-k} - a^*_{k\lambda} b^*_{j\lambda,-k} \right)$$

$$+ \pi\beta_j \omega_j^2 \frac{\hbar}{c|k|} \left(a^*_{k\lambda} a_{k\lambda} + a_{k\lambda} a^*_{k\lambda} + a^*_{k\lambda} a^*_{-k\lambda} + a_{k\lambda}\, a_{-k\lambda} \right) \Big] \Big\}. \tag{4.57}$$

The coupling parameters β_j can be written in terms of wave function matrix elements for either model of exciton.

V. THE COMPLEX DIELECTRIC CONSTANT

In this chapter use is made of the correspondence between the quantum theory of a classical dielectric and the exciton-photon interaction Hamiltonian to define an exciton contribution to the dielectric constant for the simple approximate Hamiltonian of Chapter IV. An extension to include absorption and complex dielectric constants will then be made by use of assumptions about the classical form of the dielectric constant due to excitons.

An infinite classical dielectric having one dispersion frequency ω_0 was quantized in Chapter III. It was shown that if the classical dielectric constant as a function of frequency ω was given by

$$\varepsilon = 1 + \frac{4\pi\beta}{1 - \frac{\omega^2}{\omega_0^2}} \tag{5.1}$$

then there are two independent modes of boson propagation in the dielectric. In general, both modes were mixtures of the original polarization waves and electromagnetic waves, although in limiting cases the modes become "pure electro-magnetic wave" and "pure polarization wave." The two independent propagation modes were shown to have the dispersion relation (5.1) if ε is defined as $\frac{c^2k^2}{\omega^2}$. In Appendix B this proof is extended to include an arbitrary number of polarization fields if each polarization field is coupled only to the electromagnetic field.

For real wave-vectors and real energies, the quantum-mechanical definition of the dielectric constant will be taken to be the dispersion relation expressing the dependence of $\frac{c^2k^2}{\omega^2}$ on ω for all mixed polarization and transverse electromagnetic field propagation modes.

As an aid to extending the definition of the dielectric constant to include absorption, several assumptions will be made concerning the form of the classical dielectric constant which represents the quantum-mechanical properties of the crystal system. In terms of the relation between $\underline{D}$ and $\underline{E}$ these assumptions are:

1. There is a linear point relation between $\underline{D}$ and $\underline{E}$.

2. If the electric field at $\underline{r}$ is given by $\underline{E}_0 \sin \omega t$, then $\underline{D}$ at $\underline{r}$ is given by $\underline{D} = \varepsilon(\omega)\underline{E}_0 \sin[\omega t + \eta(\omega)]$, which will be expressed in terms of a complex dielectric constant as $\underline{D} = \varepsilon(\omega)\underline{E}_0 e^{i\omega t}$. $\varepsilon(\omega)$ in this notation can be complex. (If this complex notation is to represent a real relation between $\underline{D}$ and $\underline{E}$, then $\varepsilon(\omega) = \varepsilon^*(-\omega)$.) $\varepsilon(\omega)$ is an analytic function of the complex variable ω . For $\omega \to \infty$, $\varepsilon(\omega) \to 1$.

3. $\varepsilon(\omega)$ is uniquely defined for real ω .

It is not to be expected that these relations will hold exactly for the dielectric constant of a solid. Indeed, it was pointed out in Chapter III-C and in Chapter IV-B that small deviations

from Assumptions 1 and 3 must actually exist in solids, although the effects are small in and below the region of ultraviolet frequencies. Beyond the ultraviolet spectral region, these effects can and will occur. Since the dielectric constants of insulators fall rapidly to a value very near unity beyond the ultraviolet range, it is expected that these deviations will have a small effect on calculations in the optical and near-ultraviolet spectral regions.

Assumptions 1 and 3 can be regarded as defining the simplifications of the quantum-mechanical model that must be made in order to yield results which bear any resemblance to the dielectric constant of the usual classical model of Chapter III-A. Assumption 2 has no real physical justification. The assumption is valid for the usual classical model of a dielectric and is often used in dispersion theory[1] to obtain relations between the real and imaginary parts of $\varepsilon(\omega)$. It is regrettable that this chapter must be based upon this perhaps insufficiently justified assumption, but it must be admitted that there is an abundance of precedents (at least in Physics) for assuming any function to be analytic.

---

[1] The derivations of the Kramers-Kronig relations are often based on Assumption 2. J. S. Toll, Phys. Rev. 104, 1760 (1956) shows that Assumption 1 combined with the assumption of a causal relation between $\underline{E}$ and $\underline{D}$ is sufficient to prove Assumption 2 for the complex frequency half-plane in which Assumption 2 is needed for the results here. Toll's work is probably the most convincing justification of Assumption 2.

The use of these three assumptions to derive the complex dielectric constant will be illustrated for the simple classical dielectric of Chapter III-A with an added damping term. The quantum-mechanical damping term is represented by coupling the polarization field to an energy sink of harmonic oscillators. Lifetimes for decay of plane-wave eigenstates (mixed polarization and electromagnetic waves) of Chapter III-A are computed in terms of the coupling to the energy sink. These lifetimes are interpreted as complex energies for states of real wave-number. The relation between real wave-numbers and complex frequencies can then be inverted to find the relation between real frequencies and complex wave-numbers. This relation between real frequencies and complex wave-numbers is equivalent to a complex dielectric constant expressed as a function of real frequencies. The classical expression for the complex dielectric constant in the presence of velocity damping is given for comparison.

Adding a term $\frac{\gamma}{\omega_o^2}\dot{\underline{Q}}$ to the equation of motion (3.4e) of a classical polarization field produces a classical dielectric medium with damping. The added term represents a dissipative force. The complex dielectric constant can now be found by solving Equations (3.2) as modified above for solutions in which all variables have the spatial and time dependence

$e^{i\underline{k}\cdot\underline{r}}\, e^{i\omega t}$. The dielectric constant obtained is now

$$\varepsilon = 1 + \frac{4\pi\beta}{1 - \frac{\omega^2 - i\gamma\omega}{\omega_0^2}}. \tag{5.2}$$

The dielectric constant derived satisfies Assumptions 1 through 3. (5.2) was derived with real ω in mind but is valid for <u>all</u> frequencies, both real and complex.

A quantum-mechanical equivalent to a classical damped harmonic oscillator can be taken to be a quantum-mechanical oscillator coupled to a continuum of other harmonic oscillators with velocity coupling, as shown in Appendix C. The quantum-mechanical Hamiltonian for an oscillator with damping constant γ and the classical equations of motion are

$$H = \frac{p_a^2}{2m} + \frac{\kappa}{2} x_a^2 + \int_0^\infty E\left(d_E^* d_E + \tfrac{1}{2}\right)\rho\, dE + \frac{p_a}{m}\left(\frac{\gamma\hbar}{\pi\rho_0}\right)^{\frac{1}{2}} \int_0^\infty \left(d_E + d_E^*\right)\rho\, dE$$

$$m\ddot{x}_a + \gamma \dot{x}_a + \kappa x_a = 0 \tag{5.3}$$

where $\rho = \frac{\rho_0}{E}$ is the number of states per unit energy (ρ_0 is a constant), and d_E^* and d_E are creation and annihilation operators for the absorption harmonic oscillators.

This damping for one oscillator can be extended to treat

the case of a continuum of harmonic oscillators.[2] If this is done, the Hamiltonian (3.9) can be modified to include the absorption oscillators by including the term

$$\sum_{k,\lambda}\int_0^\infty (d^*_{Ek\lambda}\, d_{Ek\lambda}+\tfrac{1}{2})E\rho\, dE + \hbar i\sqrt{\frac{\gamma\omega_0}{2\pi\rho_0}}\int_0^\infty \sum_{k,\lambda}\Big[b^*_{k\lambda}\, d_{Ek\lambda} - b_{k\lambda}\, d^*_{Ek\lambda} + b^*_{k\lambda}\, d^*_{E,-k\lambda} + b_{k\lambda}\, d_{E,-k\lambda}\Big]\rho\, dE. \tag{5.4}$$

The absorption oscillators d which are coupled to Ω at every point in space have been written in plane wave representation.

The coupling (5.4) of the absorption oscillators to the polarization oscillators produces a decay of the normal modes derived in Chapter III. The transition probability per unit time from the radiation-polarization field initially in a state in which there were n bosons in mode α_{k_1} (in the notation of Chapter III) to the state in which $n-1$ bosons are present in mode α_{k_1} will now be computed. In order to compute this transition probability, the perturbation (5.4) must first be

---

[2] There are many properties of a damping force besides the variation of the damping forces with mass and spring constant. For instance, the behavior of an undamped system coupled to the damped oscillator could be investigated to see whether or not this corresponds to the classical result. By investigating this kind of property, it should be possible to find a quantum-mechanical damping model with exact correspondence to the classical damping for the system under consideration.

Because the damping inserted was not specifically designed to have this correspondence, it is not too surprising that the results obtained do not correspond exactly to the classical theory.

expressed in terms of the operators α by means of the transformation (3.19). Since all the absorption oscillators are initially in their ground states (by assumption), only those terms of (5.4) containing creation operators for excitations of the absorption system need be included. Only the terms which will involve α_{k_1} will cause decay. These terms are

$$-i\hbar\sqrt{\frac{\gamma\omega_0}{2\pi\rho_0}}\left[+b_{k\lambda}\,d^*_{Ek\lambda}+b^*_{-k\lambda}\,d^*_{Ek\lambda}\right]. \tag{5.5}$$

By using (3.19), (5.5) can be reduced to

$$i\hbar\sqrt{\frac{\gamma\omega_0}{2\pi\rho_0}}\,d^*_{Ek\lambda}\,\alpha_{k\lambda}\left[+c^*_{12}-c^*_{1+}\right] \tag{5.6}$$

and can be expressed by using (3.22) as

$$\hbar\sqrt{\frac{\gamma\omega_0}{2\pi\rho_0}}\,d^*_{Ek\lambda}\,\alpha_{k\lambda}\left\{\frac{(\pi\beta)^{\frac{1}{2}}\,2\left(\frac{E_1}{\omega_0}\right)^{\frac{1}{2}}}{\left[\left(1-\left(\frac{E_1}{\omega_0}\right)^2\right)^2+4\pi\beta\right]^{\frac{1}{2}}}\right\}. \tag{5.7}$$

Since $\langle n|\alpha_{k_1}|n-1\rangle=\sqrt{n}$, the transition probability (in units of $\hbar=c=1$) is

$$P=\frac{n\gamma\,4\pi\beta}{\left(1-\left(\frac{E_1}{\omega_0}\right)^2\right)^2+4\pi\beta} \tag{5.8}$$

and the mean rate of energy loss $\overline{\frac{dE}{dt}}$ of this mode is

$$\overline{\frac{dE}{dt}} = \frac{E\gamma 4\pi\beta}{\left[1-\left(\frac{E_1}{\omega_0}\right)^2\right]^2 + 4\pi\beta} \qquad (5.9)$$

where $E = nE_1$, as in Appendix C.

Use will now be made of Assumptions 1, 2 and 3 to express the classical form of the dielectric constant. The classical dielectric constant is normally expressed as a function of real frequency and gives the relationship between a complex wave-number and a real frequency. If the dielectric constant is analytic, it is also possible to express the dielectric constant in terms of the relation between <u>real</u> wave-numbers and <u>complex</u> frequencies. The imaginary part of the frequency gives the rate of decay in time of the amplitude of a plane spacial wave. The correspondence between the classical dielectric for plane spatial waves and the quantum-mechanical dielectric is, for a given wave-number k, (units $\hbar = c = 1$),

$$(E)_{\text{quantum-mechanical}} \rightarrow (\text{real part of } \omega)_{\text{classical}}$$

$$\left(\tfrac{1}{2}\frac{P}{n}\right)_{\text{quantum-mechanical}} \rightarrow -(\text{imaginary part of } \omega)_{\text{classical}}$$

The factor of $\frac{1}{2}$ in the second correspondence relation is due to the difference between amplitude decay and energy decay. The energy is proportional to the square of the amplitude (in

complex notation, proportional to AA^*), so decays twice as fast as the amplitude.

To obtain the usual classical form of the dielectric constant it is necessary to solve the quantum-mechanical dispersion relations

$$\frac{k^2}{\omega_1^2} = 1 + \frac{4\pi\beta}{1-\frac{\omega_1^2}{\omega_0^2}} \quad ; \quad \omega_2 = \frac{-\frac{1}{2}\gamma\, 4\pi\beta}{\left[1-\left(\frac{\omega_1}{\omega_0}\right)^2\right]^2 + 4\pi\beta} \tag{5.10}$$

for $\omega_c = \omega_1 + i\omega_2$, and find the expression for $\frac{k^2}{\omega_c^2}$ for real ω_c (k will then be complex). The first relation of (5.10) defines the real part of the frequency of a plane wave normal mode in terms of its wave-vector. The second equation defines the imaginary part of the frequency of a normal mode in terms of its wave-vector through the dependence of ω_1 on k. The algebra about to be done is equivalent to solving (5.10) for $\omega_c = \omega_1 + i\omega_2$ in terms of k for real wave-vectors. This equation is then analytically inverted to express k in terms of ω_c. k^2/ω_c^2 is then expressed in terms of ω_c. For real values of ω_c, this final expression is the complex dielectric constant as a function of real frequency.

ω_1 can be written in terms of ω_c as the solution of the quintic equation

$$(\omega_1 - \omega_c)\left(\left[1-\frac{\omega_1^2}{\omega_0^2}\right]^2 + 4\pi\beta\right) - 2\pi i\gamma\beta = 0. \tag{5.11}$$

Four of the roots of this equation correspond to the solutions of

$$\left[1-\left(\frac{\omega_1}{\omega_0}\right)^2\right]^2+4\pi\beta=0 \tag{5.12}$$

for the case $\gamma \to 0$. These roots are not physically meaningful and will produce results which violate Assumption 3. The root of (5.11) which does not violate Assumption 3 is the root corresponding to $\omega_1=\omega_c$ when $\gamma \to 0$. This root may be found by perturbation methods in an expansion in powers of $\frac{\gamma}{\omega_1}$. The first-order root is

$$\omega_1=\omega_c-\frac{2\pi i\gamma\beta}{\left[1-\left(\frac{\omega_c}{\omega_0}\right)^2\right]^2+4\pi\beta} \tag{5.13}$$

By substituting (5.13) into (5.10a) the complex dielectric constant can now be found. Since $\omega_2 \to$ constant for $\omega_1 \to 0$, the perturbation solution to (5.13) is not valid for ω_r near zero and will be valid only for $\left|\frac{\gamma}{\omega_c}\right| >> 1$. The simplest case from a mathematical point of view is the case $\left|\frac{\gamma}{\omega_1}\right| << 1$, $4\pi\beta >> \left|\frac{\gamma}{\omega_1}\right|$. The first of these two inequalities is easily understood as a limitation to weak damping.[3] The second inequality can be interpreted in terms of the energy shift

---

[3] The condition $\omega_1 >> \gamma$ for states of real wave-vector does <u>not</u> imply $k_r >> k_i$ for real energies. Indeed, for $\gamma=0$, there are frequency regions in which $k_r=0$, $k_i \neq 0$.

which must occur due to coupling to the damping oscillators. $4\pi\beta\omega_1$ is a measure of the shift of energy of the eigenstates from the energy levels of the uncoupled photon-polariton system. γ is a measure of the energy shift due to the damping oscillators. The condition $4\pi\beta\omega_1 >> \gamma$ requires that the energy shift due to the dielectric coupling of photons and polaritons be large compared to the energy shifts due to the damping oscillators. If this is not the case, then the real part of the energy is not accurately given by (5.10). Other terms which would occur in (5.14) are neglected because of the $4\pi\beta >> \frac{\gamma}{\omega_1}$ criterion. They are small in the region of interest (the absorption region), and are believed to arise here from the neglect of the energy shift. In the frequency region of physical interest $\omega_c \simeq \omega_0$, $\omega_1 \simeq \omega_c - \frac{\gamma}{2}i$, and

$$\varepsilon = \frac{k^2}{\omega_c^2} \simeq 1 + \frac{4\pi\beta}{1 - \frac{(\omega_c - \frac{\gamma}{2}i)^2}{\omega_0^2}} \qquad (5.14)$$

Except for an energy shift of order $\left(\frac{\gamma}{\omega_0}\right)^2$, this result is in exact agreement with the classical result, Equation (5.2). Since the energy shift is of order $\left(\frac{\gamma}{\omega_0}\right)^2$, since the quantum-mechanical energy shift due to the absorption oscillators was ignored, and since (5.11) was solved only to first order in $\frac{\gamma}{\omega_0}$, the shift should probably be ignored in (5.14).

The method of solving the quantum-mechanical problem cannot be extended directly to the low frequency region, for the

transition probability becomes large compared to the frequency of oscillation. Since the semi-classical method of treating a dielectric medium gives unambiguous answers in frequency regions far removed from the dielectric resonant frequency ω_o, no attempt will be made to derive a quantum-electrodynamical result in the low frequency region.

The contribution of excitons to the complex dielectric constant will now be computed. This problem is attacked in the same way as the damping problem just solved. In this physical case, the role of the energy sink is played by crystal states to which the excitons can decay, and to which the excitons are coupled in several-body processes. The model Hamiltonian of Equation (4.57), in conjunction with the extension in Appendix B of the classical results for a single dispersion oscillator, yields a dielectric constant

$$\varepsilon = \frac{c^2 k^2}{\omega^2} = 1 + 4\pi \sum_i \frac{\beta_i}{1 - \left(\frac{\omega}{\omega_i}\right)^2} \tag{5.15}$$

where ω_i is the frequency of the uncoupled exciton modes, and β_i is the parameter defined in Chapter III and can be written in terms of appropriate matrix elements for either exciton model. The oscillator strength[4] f_{io} (between the ground

---

[4]. In the notation of Seitz, op. cit., p. 644, these f_{io} are "f-factors" or "line strengths."

state and exciton i) is defined to be

$$f_{i0} = \frac{m}{e^2} \frac{\beta_i}{(N/V)} \omega_i^2 . \tag{5.16}$$

$\frac{N}{V}$ is the number of atoms per unit volume in the crystal. The definition (5.16) is equivalent to the usual definition of oscillator strengths in terms of matrix elements of the operator X for free atoms, as can be immediately verified by inserting the definition of β_i for tight-binding excitons into (5.16) and neglecting "local field" effects.

If it is assumed that for any given frequency only one exciton mode will be responsible for absorption, it is possible to separate out that one mode and treat it separately. In Chapter III-A the method of separation was derived. It was shown that for ω not too near the dispersion frequency ω_i , the quantum electrodynamics of a dielectric could be properly represented by replacing c in the vector potential (either classical or quantum-mechanical) by $\frac{c}{n}$, where n is the index of refraction due to that one oscillator in the frequency region under study.

In the Hamiltonian (4.57) the coupling term linear in the photon field operator has a coefficient proportional to $\sqrt{\frac{f_i}{c}}$, and the coupling term quadratic in the photon field operator has a coefficient proportional to $\frac{f_i}{c}$. The vector

potential itself is proportional to the photon field operators times $\sqrt{c}$. To express (5.15) for all oscillators but the one j which is to be eliminated, it is necessary to do more than simply substitute $\frac{c}{n_j}$ for c in Equation (5.15). In order to make a substitution of $\frac{c}{n}$ for c , it is necessary to take into account the fact that the dependence of the Hamiltonian on c is <u>not</u> the same dependence of the vector potential operator on c . Since $\sqrt{\frac{f_i}{c}} = \sqrt{c}\,\sqrt{\frac{f_i}{c^2}}$, (5.15) can be expressed in terms of one less oscillator by replacing c by $\frac{c}{n_j}$, <u>and</u> replacing f_i for each of the other oscillators by f_i/n_j^2 . Thus

$$\left(\frac{c}{n_j}\right)^2 \frac{k^2}{\omega^2} = 1 + \frac{e^2}{\hbar}\frac{N}{V}\frac{1}{n_j^2}\sum_{i\neq j}\frac{8\pi|x_i|^2\omega_i}{\omega_i^2-\omega^2}$$

or

$$\varepsilon = \frac{k^2c^2}{\omega^2} = n_j^2 + \frac{e^2}{\hbar}\frac{N}{V}\sum_{i\neq j}\frac{8\pi|x_i|^2\omega_i}{\omega_i^2-\omega^2}. \qquad (5.17)$$

In the non-dispersive region (or anywhere else)

$$n_j^2 = 1 + \frac{e^2}{\hbar}\frac{N}{V}\frac{8\pi|x_j|^2\omega_j}{\omega_j^2-\omega^2} \qquad (5.18)$$

so (5.17) reduces to the usual expression (5.15).

This procedure can be extended to eliminate all oscillators but one oscillator i , by replacing c by $c' = \frac{c}{n}$ in (4.57), and omitting all oscillators in (4.57) but the oscillator i .

Oscillator i is given a new oscillator strength $f_i' = \frac{f_i}{n^2}$. n is the index of refraction due to all other dispersion oscillators in the frequency region under study.

An estimate of the range of validity of this approximate isolation of one dispersion oscillator in an actual physical case can be made by a brief study of Figure 2, Chapter III. The case plotted ($4\pi\beta = 0.1$) represents an oscillator strength of about 0.2 for values of ω_i and $\frac{N}{V}$ appropriate for the exciton lines of NaCl. The deviations of $|c_{11} - c_{13}|^2$ and $|c_{12} - c_{14}|^2$ from their asymptotic values as a function of energy are the quantities which measure the validity of the elimination of an oscillator in the method described. In Figure 2 the range of ϵ where separation is <u>not</u> valid is roughly $0.6 < \epsilon < 1.3$. The width of this region is proportional to the oscillator strength of the oscillator to be eliminated. Fortunately this restricted range of validity can often be extended by an argument presented later in this chapter.

It will be assumed for the present treatment that all the exciton lines lie far enough apart that this separation is valid. The complications which arise when this assumption is not valid and the appropriate method of treatment will be discussed at the end of this chapter. The exciton-photon Hamiltonian (4.57) now reduces to Equation (3.9) with the substitution of c' for c, and β' for β.

Absorption, from the point of view of the present paper, is due to terms which have been left out of the Hamiltonian (4.57). In Chapter 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):

$$\begin{aligned}
&\text{exciton} \longleftrightarrow \text{exciton}' + \text{photon} && \text{(a)}\\
&\text{exciton} \longleftrightarrow 2 \text{ photons} && \text{(b)}\\
&\text{exciton} \longleftrightarrow \text{exciton}' + \text{phonon} && \text{(c)}\\
&\text{exciton} \longleftrightarrow 2 \text{ phonons} && \text{(d)}\\
&\text{exciton} \longleftrightarrow \text{phonon} + \text{photon} && \text{(e)}
\end{aligned} \qquad (5.19)$$

and their variations.[5] 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 sizable 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 quantitative 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.

---

[5] 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 Chapter III is also applicable) can decay into exciton states. This gives rise to so-called indirect absorption processes.

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 $\underline{k}$ into modes of wave-vector not equal to $\underline{k}$. 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 of (5.19) 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.

The transition probability per unit time of the clothed excitons can be computed as was done for the simple damping

case earlier in the chapter by using the transformation to clothed excitons as given in (3.22). Let the states to which an unclothed exciton of wave-vector $\underline{k}$ is coupled in three-body processes be represented by $\Psi_{n E \underline{k}}$ and have energies E, n being an additional parameter which describes all energy degeneracies of these states. The matrix element connecting unclothed exciton state $\underline{k}$ and $\Psi_{n E \underline{k}}$ will be denoted by $H_{\underline{k} n E}$. For a crystal with optical symmetry, $H_{\underline{k} n E}$ is independent of the direction of $\underline{k}$ for wave-vectors in the optical region. Near the resonant frequency, only c_{12} is important, since c_{14} is zero at $E = \omega_0$ and the other two coefficients c_{11} and c_{13} refer to photon operators. The same method that was used to obtain (5.14) from (5.10) will now yield

$$\varepsilon \simeq n^2 + \frac{4\pi\beta}{1 - \left(\frac{\omega - \frac{\sigma}{2} i}{\omega_0}\right)^2} \tag{5.20}$$

where n is the index of refraction due to all the other crystal states. In the present case, γ is defined by

$$\gamma = \frac{2\pi}{\hbar} \left| H_{\underline{k} n E} \right|^2 \rho_f (E = \hbar\omega). \tag{5.21}$$

Additional approximations must be made in order to derive (5.20). It must be assumed that for small $\underline{k}$ (the optical region) $H_{\underline{k} n E}$ is independent of $\underline{k}$. The further assumption

is made that $|\gamma(\omega_1) - \gamma(\omega_2)| << \gamma(\omega_1)$. All other assumptions are the same as those leading up to (5.14). ρ_f is the density of final states $\psi_{\underline{k},n\underline{E}}$ of an energy corresponding to the clothed exciton.

All these assumptions are unnecessary assumptions in the sense that if $\gamma(\omega)$ is a known function and the energy shifts due to the damping are also known, the inversion of (5.10) is a well defined mathematical problem. Because $\gamma(\omega)$ is not a known function, the additional assumptions are made in order to obtain an approximate result for physical applications.

It is not necessary in a real physical case that $\gamma(\omega)$ be a slowly varying function. It is easy to construct very reasonable exciton band schemes like the one in Figure 3 for which the density of final states for band-to-band exciton transitions with phonon emission varies extremely rapidly. The exciton band (1) is the band coupled directly to the photon field. Band 2 is coupled through the phonon field to band 1.

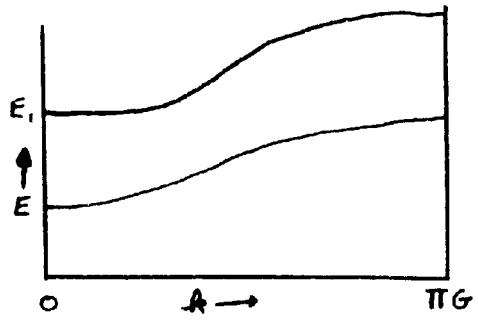

FIGURE 3

For energies slightly below E_1, $\gamma(\omega)$ will be large, but will fall off rapidly with increasing energy.

Although (5.20) has a form much like the classical damped oscillator complex dielectric constant, nevertheless the dependence of γ on ω can produce marked deviation of the line shape from the classical Lorentzian form. Some of the minor structure and "edges" observed in the absorption spectra of solids in the ultraviolet region are probably due to this dependence of γ on ω. (The same qualitative effect would be obtained if the problem is looked at from the point of view of second-order perturbation theory.) From the point of view developed here, the fundamental reason for transparency of ionic crystals in the visible region is the fact that $\rho_j(\hbar\omega)=0$ for three-body processes, four-body processes, and on up to about ten-body processes (multiple-phonon emission). Where $\rho_f \neq 0$ the matrix elements for ten-phonon emission are negligibly small. On the other hand, it is the dependence of ω_1 on k (in the notation used earlier in this chapter) which is chiefly responsible for the shape of the absorption line near the region of maximum absorption.

It is tempting to extend the general complex dielectric constant for all energy levels to[6]

$$\varepsilon = 1 + 4\pi \sum_j \frac{\beta_j}{1 - \frac{\omega^2 - i\omega\gamma_j}{\omega_j^2}} \qquad (5.22)$$

where γ_j depends weakly on ω. This is not always justifiable unless the lines are sufficiently far apart. In the absence of absorption, it happens that the exact dielectric constant is correctly given by the separation method, as can be seen from Equations (5.17) and (5.18) even if the criterion for its application is not met. (This kind of exact result of an inexact calculation occurs in other places for a harmonic oscillator, e.g., in the perturbation calculation of the harmonic oscillator energy levels for a perturbation λx.) In order to treat correctly the case of two or more exciton lines which lie close together, it is necessary to treat both lines together and to obtain through the methods of Chapter III-A the transformation analogous to (3.21). This transformation will involve finding the eigenfunctions of a $2+2\ell$ matrix, where ℓ is the number of excitons which lie close together. The decay of the clothed excitons can then be computed if the coupling which produces decay is known and a complex index of refraction computed by use of Assumptions 1 through 3.

---

[6] Because the contribution to the complex dielectric constant of excitons has the same form as the contribution of interband transitions, this equation is valid for all electronic contribution to the complex dielectric constant if the sum is generalized to include the possibility of a continuous distribution of energy levels. This equivalence can be demonstrated by treating the electron-hole pairs as bosons to which the results of Chapter III are applicable. The boson approximation seems poor but it is equivalent to the application of semi-classical radiation theory. (Semi-classical radiation theory for an atom of two states is in most applications equivalent to replacing the atom by a harmonic oscillator.)

The reason for the failure of (5.22) to be universally valid lies in the form of the decay of the clothed excitons formed from nearby exciton bands. If two or more unclothed excitons have a decay mode to the same final state, then the clothed exciton decay is complicated by the phase relations between the different bare exciton components. This can be qualitatively expressed in the language of second-order perturbation theory. Suppose transitions can be made from an initial state i to a particular range of final states f by way of two different intermediate states, 1 and 2. The expression for the total transition probability is not the sum of the transition probabilities for transitions via each of the intermediate states. The phase relations between the compound matrix elements $H_{i\to 1\to f}$ and $H_{i\to 2\to f}$ are very important. The net transition probability for the transition $i\to f$ is proportional to $|H_{i\to 1\to f} + H_{i\to 2\to f}|^2$.

If cooperative bare-exciton decay effects are not present,[7] and argument can be made for the validity of (5.22) without having to perform any further quantum-mechanical transformations. In this case the finite lifetime of each bare exciton can be regarded as due to coupling to its own set of absorption oscillators. The result (5.22) is well known for classical

---

[7] If the dominant exciton scattering process is intra-band scattering, cooperative decay effects will not be present.

damped oscillators with δ_j constant, and can be extended to include a frequency-dependent damping force. The almost one to one correspondence between the classical and quantum-mechanical solutions to problems involving coupled harmonic oscillators strongly suggests that since (5.22) holds for the classical system, it holds for the quantum-mechanical system also. An electrical analogue to a quantum-mechanical case of cooperative damping is a pair of resonant circuits with a common resistive element as in Figure 4.

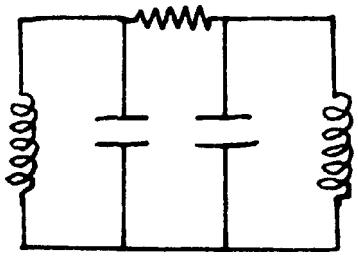

FIGURE 4

Any particular form of exciton-phonon coupling would permit proper computation of the complex dielectric constant due to excitons by the methods developed here. Such a computation should, of course, be extended to include the exciton absorption line shift due to the presence of the absorption causing coupling. The treatment of any particular model is beyond the scope of the present work.

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 Chapter 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 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.

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 , ε_r and ε_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.[1]

The theory of Chapters III through V will be used to estimate the oscillator strength in the fundamental absorption band for NaCl from experimental values of the absorption coefficient obtained by Hartman, Nelson, and Siegfried.[2] It is worthwhile to compute the fundamental band oscillator strength, for the process of making an actual numerical computation provides a convenient framework for a discussion of the application and interpretation of this dielectric theory. The assumption is made that the theory developed for the two exciton models treated could be extended to any model of exciton. The fact that the same exciton-photon Hamiltonian can be derived for

---

[1] In short, "caveat experimentor."

[2] Hartman, Nelson and Siegfried, Phys. Rev. 105, 123 (1957).

the two extreme exciton models of Chapter III suggests strongly that the general results of Chapter V should apply to any exciton model.

The fundamental absorption band of the alkali halides is thought to contain several exciton absorption lines.[3,4] The lack of knowledge of the form of the exciton-phonon coupling which is responsible for finite exciton lifetimes makes it impossible to treat correctly the multiplet structure of the fundamental absorption band. (Indeed, it is impossible to treat correctly any exciton line at all without knowledge of the coupling which is responsible for decay.) To circumvent this difficulty it will be assumed, for lack of any better estimate, that $\gamma(\omega)$ does not depend strongly on ω in the absorption region. With this assumption the equation for the complex dielectric constant in the fundamental absorption region is

$$\varepsilon = n_1^2(\omega) + \sum_{\text{lines } j} \frac{4\pi\beta_j}{1-\left(\frac{\omega^2 - i\gamma\omega}{\omega_j^2}\right)}. \tag{6.1}$$

n_1^2 is not the dielectric constant $\varepsilon(\omega)$, but is the contribution to the high-frequency dielectric constant of all

---

[3] For experimental observations of the structure, see Hartman, Nelson, and Siegfried, op. cit. or Figure 5 which is based on computations from their data.

[4] For a theory of the multiplet structure, see A. W. Overhauser, Phys. Rev. 101, 1702 (1956).

excited electronic states except those in the fundamental absorption band. Therefore $n_1^2(\omega)$ is given by

$$n_1^2(\omega) = 1 + \sum_{\substack{\text{all other} \\ \text{lines } i}} \frac{4\pi\beta_i}{1 - \left(\frac{\omega^2 - i\delta\omega}{\omega_i^2}\right)} \cong \varepsilon_\infty - \sum_{\substack{\text{exciton} \\ \text{lines } j}} 4\pi\beta_j . \tag{6.2}$$

The imaginary part of ε can be approximated in the frequency range when ε_i is large (valid for $\frac{\delta_j}{\omega_j} << 1$) by

$$\varepsilon_i = - \sum_j \frac{2\pi\beta_j \omega_j \left(\frac{\delta_j}{2}\right)}{(\omega_j - \omega)^2 + \left(\frac{\delta_j}{2}\right)^2} . \tag{6.3}$$

The oscillator strengths per primitive cell f_j are related directly to the β_j by

$$f_j = \frac{m}{e^2} \beta_j \omega_j^2 V_{cell} . \tag{6.4}$$

There are two simple computational methods of obtaining β_j if $\varepsilon_i(\omega)$ is known. The first is to try to fit the observed data near the absorption peaks by Equation (6.3). The second method is to compute the area under the absorption curve and to relate it to the sum of the β_j by integrating (6.3). (The integral of (6.3) from $-\infty$ to ∞ is independent of δ.)

Nelson[5] has computed the real and imaginary parts of the index of refraction from reflectivity data on NaCl of Hartman, Nelson and Siegfried[6] by using the Kramers-Kronig relations.

---

[5] J. R. Nelson (private communication).

[6] Hartman, Nelson and Siegfried, op. cit.

The results of his computation for n_r and n_i, and the product $2 n_r n_i = \varepsilon_i$ are plotted in Figure 5. (The plotted n_i and n_r are for cleaved crystals at 6° K.) Numerical integration of the area under the ε_i curve from 7.55 to 8.40 ev. yields a total oscillator strength of 1.2 for the fundamental band. An approximate fit of the two peaks of ε_i to Equation (6.3) yields oscillator strengths of about 0.6 for the line at 7.92 ev. and 0.4 for the line at 8.04 ev. The fit to the experimental curves is not very good due to the tails on $\varepsilon_i(\omega)$ and the bump at 7.75 ev., which are due either to additional absorption lines or to the dependence of γ_i on ω. There is some ambiguity in performing the Kramers-Kronig calculation of n_i and n_r, (the low-energy tail of ε_i is probably not real), so it is not really worthwhile to attach any more significant figures to the oscillator strengths given here, if indeed the Kramers-Kronig calculation is reliable to even one significant figure.[7] There are, unfortunately, no really good calculations of oscillator strengths for NaCl with which to compare these results.

---

[7] The calculation of n_r and n_i from the Kramers-Kronig relations is made difficult by the fact that $n_r(\omega)$ is expressed as an integral of a function of the reflection coefficient over all frequencies. The computed values of n_i and n_r are somewhat sensitive to the assumptions made about the behavior of the reflection coefficient outside the measured spectral region. For further details and references, see F. C. Jahoda, Phys. Rev. 107, 1261 (1957).

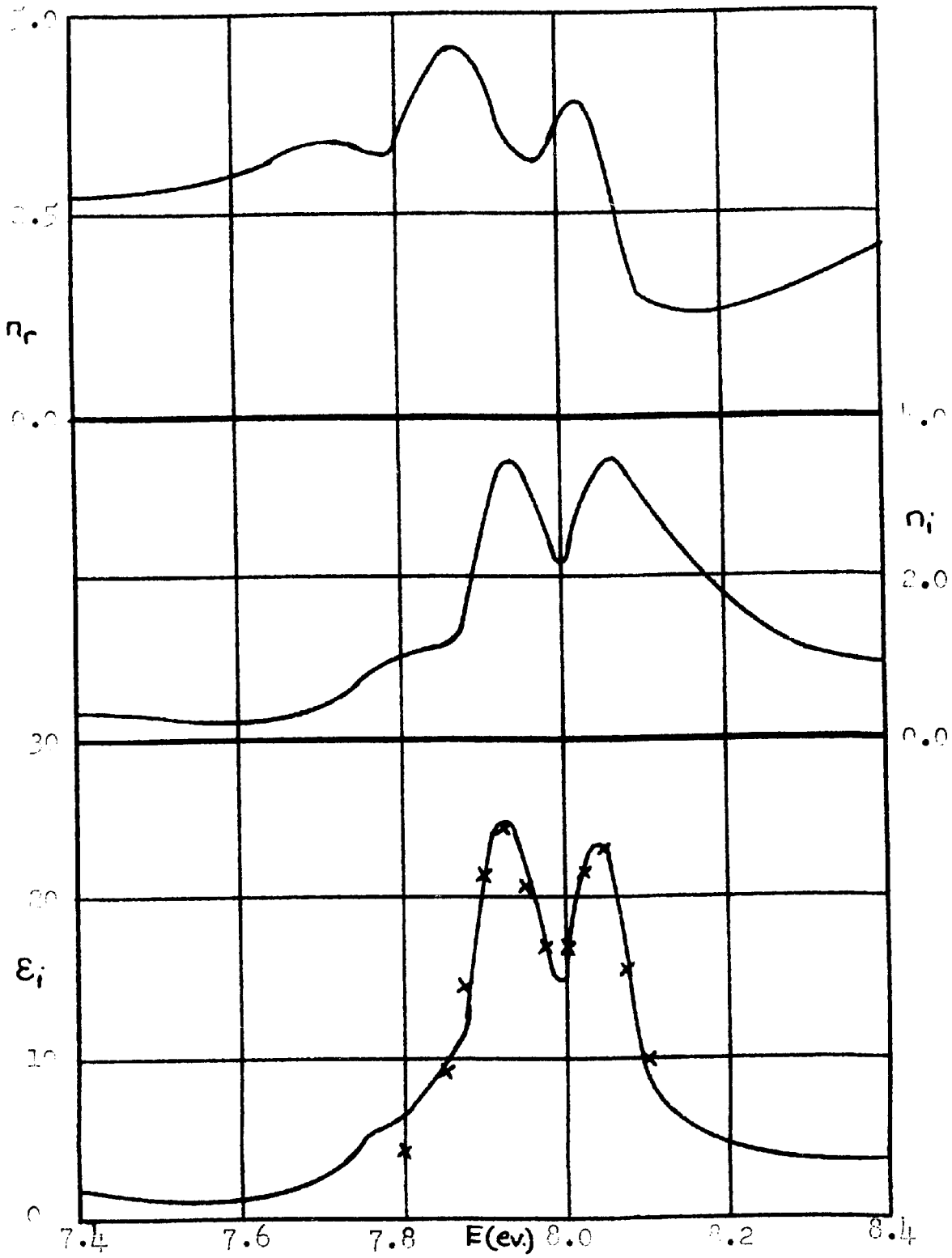

FIGURE 5. n_r, n_i, and ε_i as functions of the energy for NaCl at 6° Kelvin. n_i and n_r were computed by Nelson from the experimental reflectivity data of Hartman, Nelson, and Siegfried. The points × plotted for ε_i are calculated from (1.3) with the oscillator strengths given in the text.

A useful approximate expression can be found for β in terms of the observed absorption coefficient if $\frac{\gamma}{\omega_0} << 1$ 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 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

$$\int_{\text{absorption line}} n_i(\omega)\,d\omega = \omega_0 \frac{4\pi\beta}{n} \int_0^1 \frac{(1-y^2)^{\frac{1}{2}}}{\left(1 + \frac{4\pi\beta}{n^2} y^2\right)^{\frac{1}{2}}}\,dy \tag{6.5}$$

where n^2 is the dielectric constant due to all other lines, evaluated in the region of absorption of the line under study, and ω_0 is the frequency of the absorption line. The large contribution to the integral occurs when y is near zero. In many physical cases, $4\pi\beta$ is small enough that $\frac{4\pi\beta}{n^2}$ can be neglected in the denominator. For these cases,

$$\int_{\text{absorption line}} n_i(\omega)\,d\omega \approx \frac{\pi^2 \omega_0 \beta}{n} \tag{6.6}$$

which can be rewritten as

$$f_{\text{absorption line}} = \frac{n}{\pi^2} \frac{m}{e^2} \omega_0 V_{\text{cell}} \int_{\text{absorption line}} n_i(\omega)\,d\omega. \tag{6.7}$$

This equation resembles closely the Smakula equation[8] for absorption by impurities in a crystal, except that a factor $\left(\frac{3}{n^2+2}\right)^2$ 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 Chapter III-A).

The derivation of (6.6) does not rest on the assumption $n_i \ll 1$. However, the extension of (6.8) 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 conditon $n_i \ll 1$ is met.

Although the separation criteria justifying (6.7) are not met for the two NaCl absorption lines of Figure 5, a qualitative argument can be made from the n_r curve to the effect that the "average" n for Equation (6.7) must be the order of 2. In the theory here, oscillator strengths are twice some observed constant, whereas if the Smakula equation were (inappropriately) applied, the oscillator strengths would be evaluated as $\frac{9 \cdot 2}{(2^2+2)^2} = \frac{1}{2}$ times the same constant.

One important result of this theory concerns the estimation of relative oscillator strengths from observed absorption data (i.e., from n_i). When two absorption lines lie close together

---

[8] cf. the "generalized Smakula equation" of D. L. Dexter, op. cit.

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 of Equation (6.7) for the lower line is large and positive, whereas the contribution by the lower energy line to n^2 of Equation (6.7) for the higher energy line is large and negative. The effect is very marked in Figure 5, where the area under the n_i curve of the second peak is at least half again as large as the area under the first peak, while the oscillator strength of the first line is larger than that of the second line. It should also be noted that the observed absorption maxima are at slightly higher energies than the exciton energies. The effect in NaCl is a shift of about 0.02 ev.

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 are probably the assumption that $\varepsilon(\omega)$ is an analytic function and the assumption that the general theory is valid for actual crystals which do not fit either extreme exciton model. The theory as constructed in Chapters III through V is a more exact theory than the usual one outlined in Chapter II. The division of the crystal into sub-blocks, the use of semi-classical radiation theory, the assumption that $\varepsilon - 1$ 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 there are several general results of the theory which may be useful in the interpretation of experimental results.

1. Substructure can exist in the exciton absorption spectrum due to the dependence of $\gamma(\omega)$ on ω.

2. For exciton wave functions independent of temperature, the integrated absorption coefficient or the integrated imaginary part of the dielectric constant can depend on temperature through the dependence of $\gamma(\omega)$ on phonon population. (There can also be changes in the exciton wave function as a function of temperature due to the exciton-lattice interaction. These would alter the actual oscillator strengths and frequencies of the exciton lines.)

3. Approximate oscillator strengths can be computed by the methods given in this chapter.

The most important result of this theory is an understanding of the fundamental radiative processes involving excitons. Excitons in perfect crystals cannot decay to the crystal ground state with emission of a single quantum radiation; the absorption of light by excitons in solids does not create free excitons by a direct process. Instead, light travels through the

crystal as a mixture of exciton and electromagnetic wave. Energy absorption from this mixed wave is caused by the interaction of the exciton part of this wave with other energy modes of the crystal.

APPENDIX A

The following canonical transformations can be used to derive Equation (3.9) from Equation (3.8). These equations are for one particular polarization λ, and only wave vector k is considered. Starting with the Hamiltonian of Equation (3.8)

$$H = \frac{1}{2}\left(P_f^2 + P_g^2\right) + \frac{1}{2}c^2k^2\left(f^2+g^2\right) + \left[\frac{\omega_o^2}{2}\left(P_h^2+P_j^2\right) + \frac{1}{2}\left(h^2+j^2\right)\right]$$
$$+ \sqrt{4\pi\beta\omega_o^2}\left[-P_h f - P_j g\right] + \frac{1}{2}4\pi\beta\omega_o^2\left[f^2+g^2\right],$$

apply the canonical transformation defined by

$$f = \frac{1}{\sqrt{2}}\left(\alpha + \frac{P_{\beta_+}}{ck}\right) \qquad P_f = \frac{1}{\sqrt{2}}\left(P_\alpha - ck\beta_+\right)$$

$$g = \frac{1}{\sqrt{2}}\left(\beta_+ + \frac{P_\alpha}{ck}\right) \qquad P_g = \frac{1}{\sqrt{2}}\left(P_{\beta_+} - ck\alpha\right)$$

$$h = \frac{1}{\sqrt{2}}\left(\gamma + P_{\delta_+}\omega_o\right) \qquad P_h = \frac{1}{\sqrt{2}}\left(P_\gamma - \frac{\delta_+}{\omega_o}\right)$$

$$j = \frac{1}{\sqrt{2}}\left(\delta_+ + P_\gamma\omega_o\right) \qquad P_j = \frac{1}{\sqrt{2}}\left(P_{\delta_+} - \frac{\gamma}{\omega_o}\right).$$

The generating function for this canonical transformation is

$$S = ck\left\{fg + \alpha\beta_+ - \sqrt{2}\left(f\beta_+ + g\alpha\right)\right\}$$
$$+ \frac{1}{\omega_o}\left\{hj + \gamma\delta_+ - \sqrt{2}\left(h\delta_+ + j\gamma\right)\right\}$$

and the Hamiltonian in terms of the new coordinates α , β_+ , γ , δ_+ and the momenta canonically conjugate to these coordinates is

$$H = \tfrac{1}{2}\left(P_\alpha^2 + P_{\beta_+}^2\right) + \tfrac{1}{2}c^2k^2\left(\alpha^2 + \beta_+^2\right) + \frac{\omega_0^2}{2}\left(P_\gamma^2 + P_{\delta_+}^2\right) + \tfrac{1}{2}\left(\gamma^2 + \delta_+^2\right)$$
$$- \sqrt{\pi\beta\omega_0^2}\left[\left(P_\gamma - \frac{\delta_+}{\omega_0}\right)\left(\alpha + \frac{P_{\beta_+}}{ck}\right) + \left(P_{\delta_+} - \frac{\gamma}{\omega_0}\right)\left(\beta_+ + \frac{P_\alpha}{ck}\right)\right]$$
$$+ \pi\beta\omega_0^2\left[\left(\alpha + \frac{P_{\beta_+}}{ck}\right)^2 + \left(\beta_+ + \frac{P_\alpha}{ck}\right)^2\right].$$

Another canonical transformation is now made, defined by

$$\alpha = \frac{1}{ck}P_{\beta_-} \qquad \gamma = \omega_0 P_{\delta_-}$$
$$P_\alpha = -ck\beta_- \qquad P_\gamma = -\frac{1}{\omega_0}\delta_-$$

The generating function for this transformation is

$$S = -ck\alpha\beta_- - \frac{1}{\omega_0}\gamma\delta_-$$

The Hamiltonian in terms of these new variables is

$$H = \tfrac{1}{2}\left(P_{\beta_+}^2 + P_{\beta_-}^2\right) + \tfrac{1}{2}c^2k^2\left(\beta_+^2 + \beta_-^2\right) + \frac{\omega_0^2}{2}\left(P_{\delta_+}^2 + P_{\delta_-}^2\right)$$
$$+ \tfrac{1}{2}\left(\delta_+^2 + \delta_-^2\right) + \sqrt{\pi\beta\omega_0^2}\left[\frac{(\delta_+ + \delta_-)(P_{\beta_+} + P_{\beta_-})}{\omega_0 ck} - (P_{\delta_+} - P_{\delta_-})(\beta_+ - \beta_-)\right]$$
$$+ \pi\beta\omega_0^2\left[\left(\frac{P_{\beta_+} + P_{\beta_-}}{ck}\right)^2 + (\beta_+ - \beta_-)^2\right].$$

The normal modes of this Hamiltonian are running waves of wave-number k for β_+ coordinate and $-k$ for coordinate β_- ,

which can be verified by the solution of the Hamiltonian equations of motion. The classical field is now quantized by replacing[1] the Poisson brackets by commutator brackets. Define

$$a_+ = \frac{1}{\sqrt{2\hbar}}\left(\sqrt{ck}\,\beta_+ + \frac{i P_{\beta_+}}{\sqrt{ck}}\right) \qquad a_- = \frac{-1}{\sqrt{2\hbar}}\left(\sqrt{ck}\,\beta_- + \frac{i P_{\beta_-}}{\sqrt{ck}}\right)$$

$$a_+^* = \frac{1}{\sqrt{2\hbar}}\left(\sqrt{ck}\,\beta_+ - \frac{i P_{\beta_+}}{\sqrt{ck}}\right) \qquad a_-^* = \frac{-1}{\sqrt{2\hbar}}\left(\sqrt{ck}\,\beta_- - \frac{i P_{\beta_-}}{\sqrt{ck}}\right)$$

$$b_+ = \frac{1}{\sqrt{2\hbar}}\left(\frac{\delta_+}{\sqrt{\omega_0}} + i\sqrt{\omega_0}\,P_{\delta_+}\right) \qquad b_- = \frac{-1}{\sqrt{2\hbar}}\left(\frac{\delta_-}{\sqrt{\omega_0}} + i\sqrt{\omega_0}\,P_{\delta_-}\right)$$

$$b_+^* = \frac{1}{\sqrt{2\hbar}}\left(\frac{\delta_+}{\sqrt{\omega_0}} - i\sqrt{\omega_0}\,P_{\delta_+}\right) \qquad b_-^* = \frac{-1}{\sqrt{2\hbar}}\left(\frac{\delta_-}{\sqrt{\omega_0}} - i\sqrt{\omega_0}\,P_{\delta_-}\right)$$

The operators $a_\pm$, $a_\pm^*$, $b_\pm$, $b_\pm^*$ obey boson commutation rules. Substitution of the definitions of these operators into the Hamiltonian yields one term in the sum over k, λ of the Hamiltonian (3.9).

---

[1] L. Schiff, op. cit., p. 135.

APPENDIX B

The easiest method of extending the dispersion relation (3.17) to include more polarization modes is to attack the problem afresh from Equation (3.1). The analogue to Equation (3.1) for many polarization modes j is

$$\mathcal{L} = \frac{1}{8\pi}\left(\frac{1}{c}\frac{\partial \underline{A}}{\partial t} + \underline{\nabla}\varphi\right)^2 - \frac{1}{8\pi}\left(\underline{\nabla}\times\underline{A}\right)^2$$
$$+\sum_j\left[\frac{1}{2\omega_j^2\beta_j}\left(\frac{\partial \underline{Q}_j}{\partial t}\right)^2 - \frac{1}{2}\left(\underline{Q}_j\right)^2 + \varphi\left(\underline{\nabla}\cdot\underline{Q}_j\right) + \frac{1}{c}\underline{A}\cdot\frac{\partial \underline{Q}_j}{\partial t}\right]$$

and the equations of motion of the field variables are

$$\frac{1}{4\pi c}\frac{\partial}{\partial t}\left(\frac{1}{c}\frac{\partial \underline{A}}{\partial t} + \underline{\nabla}\varphi\right) + \frac{1}{4\pi}\left(\underline{\nabla}\times\underline{\nabla}\times\underline{A}\right) - \frac{1}{c}\sum_j\frac{\partial \underline{Q}_j}{\partial t} = 0$$

$$\frac{1}{4\pi}\underline{\nabla}\cdot\left(\frac{1}{c}\frac{\partial \underline{A}}{\partial t} + \underline{\nabla}\varphi\right) - \sum_j \underline{\nabla}\cdot\underline{Q}_j = 0$$

$$\frac{1}{\omega_j^2\beta_j}\frac{\partial^2 \underline{Q}_j}{\partial t^2} + \frac{1}{\beta_j}\underline{Q}_j + \frac{1}{c}\frac{\partial \underline{A}}{\partial t} + \underline{\nabla}\varphi = 0.$$

The plane wave solutions of these differential equations have the dispersion relation

$$\frac{c^2k^2}{\omega^2} = 1 + \sum_j \frac{4\pi\beta_j}{1-\frac{\omega^2}{\omega_j^2}}.$$

If these plane wave solutions (normal modes) are used as expansion functions for quantization, the Hamiltonian will contain no coupling between different normal modes. The quantized

harmonic oscillators have the same frequencies as the classical oscillators, so the classical and quantum-mechanical dispersion relations must be identical.

If the number of different polarization fields is small, the dispersion relation can be calculated by use of the methods of Chapter III. For the case of two polarization fields, the dispersion relation is given by the eigenvalue equation (units $\hbar = c = 1$) $A \equiv 2\pi\left(\frac{\beta_1\omega_1^2 + \beta_2\omega_2^2}{k}\right)$; $B_1 \equiv \omega_1\sqrt{\frac{\pi\beta_1\omega_1}{k}}$; $B_2 \equiv \sqrt{\frac{\pi\beta_2\omega_2}{k}}$.

$$\begin{pmatrix} k+A & -A & -iB_1 & -iB_1 & -iB_2 & -iB_2 \\ A & -k-A & -iB_1 & -iB_1 & -iB_2 & -iB_2 \\ iB_1 & -iB_1 & \omega_1 & 0 & 0 & 0 \\ -iB_1 & iB_1 & 0 & -\omega_1 & 0 & 0 \\ iB_2 & -iB_2 & 0 & 0 & \omega_2 & 0 \\ -iB_2 & B_2 & 0 & 0 & 0 & -\omega_2 \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \\ X_5 \\ X_6 \end{pmatrix} = \omega \begin{pmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \\ X_5 \\ X_6 \end{pmatrix}.$$

A little algebra verifies that the dispersion relation defined by this eigenvalue problem is correctly given by

$$\frac{k^2}{\omega^2} = 1 + \frac{4\pi\beta_1}{1-\left(\frac{\omega}{\omega_1}\right)^2} + \frac{4\pi\beta_2}{1-\left(\frac{\omega}{\omega_2}\right)^2}.$$

APPENDIX C

The damped harmonic oscillator has been the subject of several recent papers.[1] For reference the correspondence between the classical velocity-damped oscillator and a quantum-mechanical damped oscillator will be derived here in perturbation approximation.

The equation of motion of a classical velocity-damped oscillator is

$$m\ddot{x} + \gamma\dot{x} + \eta x = 0.$$

For weak damping (i.e., damping far less than critical; $\gamma \ll 2\sqrt{\eta m}$) the mean rate of energy loss of the oscillator is given by

$$\frac{\overline{dE}}{dt} = \overline{\gamma(\dot{x})^2} \approx \frac{\gamma \dot{x}^2_{max}}{2} = \frac{\overline{\gamma E}}{m}.$$

The relation $\frac{\overline{dE}}{dt} = \frac{\overline{\gamma E}}{m}$ holds independent of η for weak damping. The amplitude decay of x is given by $e^{-\frac{\gamma}{2m}t}$.

A quantum-mechanical damped harmonic oscillator can be represented by the Hamiltonian[2]

---

[1] See, for example, J. Weber, Phys. Rev. 101, 1619 (1956).

[2] The correspondence is not uniquely determined. The relation derived here would hold equally well for a coupling term in which E is replaced in the integral by $\left(\frac{p^2\eta}{m}\right)^{\frac{1}{2}}$.

$$H = \frac{p_a^2}{2m} + \frac{\eta x_a^2}{2} + \int_0^\infty \rho(E)\left[d_E^* d_E + \tfrac{1}{2}\right] dE + \frac{p_a C}{m} \int_0^\infty (d_E + d_E^*)\rho(E) dE.$$

The damped oscillator variables are here labeled with subscripts a. The absorption oscillators d_E are distributed over all energies with a density $\rho(E) = \frac{\text{constant}}{E}$. C is a coupling constant to be determined by the analysis.

Let the energy levels of the harmonic oscillator be denoted by the principal quantum number n. The unperturbed oscillator has energy levels $(n+\frac{1}{2})\hbar\omega_0$; $\omega_0 = \sqrt{\frac{\eta}{m}}$. The matrix elements of p_a between the oscillator states are

$$\langle n | p_a | n-1 \rangle = i m \omega_0 \left(\frac{n}{2}\right)^{\frac{1}{2}} \left(\frac{\hbar^2}{m\eta}\right)^{\frac{1}{4}}$$

and vanish if the states are not adjacent.

At $t=0$ let all the absorption oscillators be in their ground states and the damped oscillator be in state n. The probability per unit time of a transition of the damped oscillator to state $n-1$ is given by

$$P = \frac{\pi}{\hbar m} n |C|^2 \rho_0 .$$

The rate of loss of energy of the oscillator is, in perturbation approximation, $\hbar\omega_0 P = \frac{d\bar{E}}{dt}$. If $\bar{E}$ is defined as $\langle n \rangle \hbar\omega_0$, then

$$\frac{d\bar{E}}{dt} = \bar{E} \frac{\pi}{m\hbar} |C|^2 \rho_0 .$$

If this result is to correspond to the classical case independent of m and η, ρ_0 must be independent of energy and C given by

$$|C|^2 = \frac{\gamma \hbar}{\pi \rho_0}.$$

If it is assumed that some process continually restores the absorption oscillators to their ground states in a time short compared to the reciprocal of the transition probability but long compared to $\frac{1}{\omega_0}$, exponential decay of the expectation value of the energy of the oscillator should occur. In any event, an approximation to exponential decay of the energy of the oscillator will occur in the case $n=1$, for a Wigner-Weisskopf decay takes place here.

APPENDIX D--SYMBOLS

Symbols which have a well-established conventional meaning are generally so used throughout the paper. Exceptions to this rule and special definitions are given below for symbols used throughout the paper, with reference to the chapter and page where they are defined. The symbols $\underline{k}$, $\underline{q}$, and $\underline{\kappa}$ are reserved for wave vectors. The vector notation will be omitted for these symbols used as subscripts on operators and matrix elements. Commas are used for clarity to separate multiple subscripts when necessary.

$\underline{Q}$ polarization density III, 16.

β polarizability per unit volume at zero frequency III, 18.

$b^*(b)$ creation (annihilation) operators for polarization waves III, 21.

$\alpha^*(\alpha)$ creation (annihilation) operators for normal modes III, 22.

c_{ij} normal mode transformation matrix III, 24.

$b^*(b)$ creation (annihilation) operators for excitons IV, 48.

$c^*(c)$ creation (annihilation) operators for fermions IV, 63.

$d^*(d)$ raising (lowering) operators for atomic states IV, 47.

$d^*(d)$ creation (annihilation) operators for absorption oscillators V, 87.

BIBLIOGRAPHY

D. L. Dexter, Phys. Rev. 101, 52 (1956).

G. Dresselhaus, J. Phys. Chem. Solids 1, 4 (1956).

F. J. Dyson, Phys. Rev. 102, 1217 (1956).

J. Frenkel, Phys. Rev. 37, 17 (1931).

P. L. Hartman, J. R. Nelson and J. G. Siegfried, Phys. Rev. 105, 123 (1957).

W. Heitler, The Quantum Theory of Radiation (Oxford University Press, London, 1954).

W. R. Heller and A. Marcus, Phys. Rev. 84, 809 (1951).

F. C. Jahoda, Phys. Rev. 107, 1261 (1957).

C. Kittel, Introduction to Solid State Physics (John Wiley & Sons, Inc., New York, 1956).

S. M. Neatman, Phys. Rev. 92, 1362 (1953); 94, 327 (1954).

A. W. Overhauser, Phys. Rev. 101, 1702 (1956).

R. Peierls, Ann. Physik 13, 905 (1932).

C. I. Pekar, J. Exptl. Theoret. Phys. U.S.S.R. 33, 1022 (1957).

L. I. Schiff, Quantum Mechanics (McGraw Hill Book Company, Inc., New York, 1955.)

F. Seitz, The Modern Theory of Solids (McGraw Hill Book Company, Inc., New York, 1940).

J. S. Toll, Phys. Rev. 104, 1760 (1956).

J. Weber, Phys. Rev. 101, 1619 (1956).