THEORY OF THE LINE SHAPE FOR
OPTICAL ABSORPTION IN
NON-METALLIC SOLIDS

by

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ABSTRACT

The line shape for optical absorption by creation of an exciton is essentially proportional to the imaginary part of the Green's function for the exciton. In pure crystals, the breadths of the exciton lines are due to the interactions between the excitons and the phonon system. At sufficiently high temperatures, the nuclei may be considered infinitely massive, and the exciton moves in a static random potential caused by thermal fluctuations of the lattice. Previous attempts to understand the effects of phonon interactions on the optical absorption have usually been based on perturbation theory or on variations in which a selected infinite set of graphs in the perturbation expansion are considered. Two new approaches, not dependent on perturbation theory, are here presented, for studying the effects of static thermal fluctuations on the exciton Green's function. The first of these is a method for exactly solving some simple one-dimensional models; the second is an approximate method, applicable to three-dimensional systems, for studying the region of the low-energy tail of the absorption spectrum, a region in which perturbation techniques appear to be inapplicable.

The one-dimensional method is a procedure for finding the spectral density $A(k, E)$ of a particle in a random potential, when the potential at each point is independent of the potential at every other point on the line. The method is applied to a model of an effective mass exciton moving in a white-Gaussian-noise potential, such as may arise from thermal deformations on a continuous elastic string. It is also applied to a model of an exciton in a band of finite width, in which the exciton is confined to discrete lattice sites, and the Hamiltonian has matrix elements between nearest neighbor sites. Modifications of the procedure can be used to find the phonon Green's functions for a chain of atoms of random mass and to find various two-particle functions, such as the electrical conductivity of a system of non-interacting electrons in a random potential or the line shape for interband optical absorption, when the electron and hole do not interact.

The approximation for the low energy tail is based on the assumption that almost all of the exciton eigenstates at a given energy have approximately the same shape. It is shown that the spectral density can be approximately calculated when this shape is known, and a variational procedure is derived which gives the best possible estimate of the shape of the wavefunction. For fairly general systems, the optical absorption at frequency ω in the low energy tail has the form $A_0(\omega, T)\exp[- U_0(\omega - \omega_0 - CT)/T]$, where T is the absolute temperature, A_0 is a slowly varying function of ω and T, U_0 is a function independent of the temperature, and ω_0 and C are constants. The various functions and constants can be at least approximately calculated if the exciton band structure, elastic constants, and exciton-phonon coupling constants are known for the crystal. These calculations are performed analytically for an exactly solvable one-dimensional model, and very good agreement is found between the approximate theory and the exact asymptotic form of the spectral density.

The theory of the low energy tail is compared with the experimentally observed Urbach's rule. Although consistent with Urbach's rule, the theory does not predict Urbach's rule for simple exciton models. A full test of the theory requires detailed knowledge of band structure and phonon interactions, and cannot yet be carried out for any real crystals. Possible effects of finite nuclear masses have also been investigated.

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INTRODUCTION

The dependence of the optical absorption by materials on the wavelength of the incident light has long been a very rich source of information on the structure of matter. The greatest scientific interest has been in the number and location of peaks and discontinuities in the absorption spectra. In atomic spectra, the peaks form a series of very sharp, discrete lines, which directly tell us the energies of various excited states of the atom. Sharp threshholds for coninuum absorption likewise appear, which tell us the binding energy of electrons in the atom. In solids, the positions of peaks and threshholds are studied in order to determine the nature of the energy bands for electrons in the material. The fact that peaks and discontinuities in the optical absorption by solids are never sharp, but are broadened over a range of energies, is generally considered an unfortunate complication, which makes the extraction of precise information about the energy bands very much more difficult. Yet the shapes of these broadened peaks and threshholds themselves contain interesting and potentially useful information, and the challenge of understanding these line shapes is one which has been welcomed by theorists.

In the vicinity of the fundamental absorption edge, an important factor affecting the line shapes for optical absorption by a pure nonmetallic crystal is the coupling between electronic states and lattice vibrations. The principal techniques which have been used to date to study the effects on optical absorption of the electron-phonon coupling have been perturbation theory and variations which, in effect, sum a selected infinite set of terms in the perturbation expansion. It is the major purpose of this thesis to present several new techniques, not dependent on perturbation theory, for studying absorption line shapes in a lattice with infinitely massive nuclei. After a brief introduction to the general theory of optical absorption (Chapter I), we discuss some one-dimensional models for which the optical absorption may be calculated exactly (Chapter II). We then consider an approximate theory, applicable to three-dimensional crystals as well as to the exactly solvable one-dimensional models, which treats the region of the low-energy tail of the absorption spectrum, a region in which perturbation techniques are generally inapplicable (Chapter III). Finally, we compare our theory of the low energy tail with the experimentally observed Urbach's rule (Chapter IV). Included in this comparison is an investigation of the possible effects of finite nuclear masses.

Organization. Footnotes, tables, figures, and appendices are compiled separately at the end of each of the four chapters. Equations are numbered by section, separately for each chapter, and a reference in any chapter to an equation number refers to the same chapter, unless otherwise stated. Thus a reference found in Chapter II to Equation (1.24) would refer to Equation 24 of Section 1, Chapter II.

CHAPTER I

GENERAL THEORY OF OPTICAL ABSORPTION

Section 1. General Formulation

Let us consider an idealized experiment for measuring the optical absorption of a material. We obtain a slab of material which is infinite in the x- and y-directions, and which has a thickness d in the z-direction. We place on one side of the slab a source of monochromatic light traveling in the z-direction, and we measure the amount of light emerging from the other side which is still traveling, accurately, in the z-direction. The optical absorption constant or attenuation constant is defined as the limit, for large d, of the derivative with respect to d of the logarithm of the transmitted light intensity, for a fixed intensity of incident light.

We assume that the transverse electromagnetic field is described by a vector potential

$$\underset{\sim}{A}(\underset{\sim}{r}, t) = \underset{\sim}{A}(\underset{\sim}{r})\, e^{-i\omega t} + \text{complex conjugate} , \qquad (1.1)$$

where ω, the frequency of the light, is a positive quantity. If the coordinate system is chosen so that the material lies in the region $0 \leq z \leq d$, then the transmitted wave occurs in the region $z > d$. The transmitted wave has the form

$$\underset{\sim}{A}(\underset{\sim}{r}) = \underset{\sim}{A}_t\, e^{ikz} , \qquad (1.2)$$

where $k = \omega/c$, and c is the speed of light. In the region $z < 0$, we have both incident and reflected waves:

$$\underset{\sim}{A}(\underset{\sim}{r}) = \underset{\sim}{A}_i\, e^{ikz} + \underset{\sim}{A}_r\, e^{-ikz} . \tag{1.2a}$$

Inside the medium, $\underset{\sim}{A}(\underset{\sim}{r})$ obeys Maxwell's equations in the form

$$[\omega^2 c^{-2} + \nabla^2]\, \underset{\sim}{A}(\underset{\sim}{r}) = - 4\pi c^{-1}\, \underset{\sim}{j}(\underset{\sim}{r}) , \tag{1.3}$$

where $[\underset{\sim}{j}(\underset{\sim}{r})\, e^{-i\omega t}$ + complex conjugate] is the transverse current at position $\underset{\sim}{r}$. We assume $\underset{\sim}{A}$ sufficiently weak so that $\underset{\sim}{j}$ may be calculated from a linear response function:

$$\underset{\sim}{j}(\underset{\sim}{r}) = - c^{-1} \int \underset{\approx}{\Lambda}(\underset{\sim}{r}, \underset{\sim}{r}'; \omega)\, \underset{\sim}{A}(\underset{\sim}{r}')\, d\underset{\sim}{r}' . \tag{1.4}$$

When $\underset{\sim}{r}$ and $\underset{\sim}{r}'$ are sufficiently far from the edges of the material, $\underset{\approx}{\Lambda}$ is a function only of $(\underset{\sim}{r} - \underset{\sim}{r}')$ and can be written as

$$\underset{\approx}{\Lambda}(\underset{\sim}{r}, \underset{\sim}{r}'; \omega) = (2\pi)^{-3} \int e^{i\underset{\sim}{q}\cdot(\underset{\sim}{r}-\underset{\sim}{r}')}\, \underset{\approx}{\Lambda}(\underset{\sim}{q}, \omega)\, d\underset{\sim}{q} , \tag{1.5}$$

where the function $\underset{\approx}{\Lambda}(\underset{\sim}{q}, \omega)$ is a characteristic of the bulk material. (Actually, $\underset{\approx}{\Lambda}(\underset{\sim}{r}, \underset{\sim}{r}'; \omega)$ is invariant only under translations by a crystal lattice vector, and $\underset{\approx}{\Lambda}(\underset{\sim}{q}, \omega)$ should really be a matrix between all momenta differing from $\underset{\sim}{q}$ by a reciprocal lattice vector. These "local field corrections" cause complications which do not change the essential features of the optical absorption, and we shall ignore them here.)

We shall be interested in $\underset{\approx}{\Lambda}(\underset{\sim}{q}, \omega)$ only when $\underset{\sim}{q}$ lies along the z-axis, and shall write $\underset{\approx}{\Lambda}$ as a function of the scalar variable q. We shall assume that the material has sufficient symmetry so that $\underset{\approx}{\Lambda}$ has principal axes which are independent of q, as long as $\underset{\sim}{q}$ is in the z-direction. If we pick the polarization of $\underset{\sim}{A}$ to lie along a (transverse) principal axis, we may then treat Λ and A as scalars.

If the response function falls off sufficiently rapidly as $|\underset{\sim}{r} - \underset{\sim}{r}'|$ becomes large, (no anomolous skin effect), then $\Lambda(q, \omega)$ may be extended to complex values of q, and a possible solution of Maxwell's equations in the middle of the medium is

$$\underset{\sim}{A}(\underset{\sim}{r}) = \underset{\sim}{A}_0 \, e^{iKz} , \tag{1.6}$$

where K, a complex number, is a solution of the equation

$$\omega^2 c^{-2} - K^2 - 4\pi c^{-2} \Lambda(K, \omega) = 0. \tag{1.7}$$

The combination $1 - 4\pi\Lambda(q, \omega)/\omega^2$ is called the dielectric constant, $\epsilon(q, \omega)$, and Eq. (1.7) can be written

$$K = \pm \omega c^{-1} \epsilon(K, \omega)^{\frac{1}{2}}. \tag{1.8}$$

The response function $\Lambda(q, \omega)$ is an even function of q, and solutions to Eq. (1.7) occur in pairs, with values of K differing by the factor -1. Solutions with Re $K > 0$ correspond to waves propagating to the right, while those with Re $K < 0$ represent waves propagating to the left. Since the work done by the electromagnetic field on the medium must be non-negative, it follows that Im $\Lambda \leq 0$, and hence Im $K \cdot$ Re $K \geq 0$. (In any real medium, some dissipation occurs, and the inequality sign holds.) If the thickness d of the crystal is sufficiently large, so that multiple reflections can be neglected, (i.e., $|\text{Im } K| d \gg 1$), the vector potential will have the form (1.6) in the middle of the medium, with Re $K > 0$. If there is more than one pair of solutions of Eq. (1.7), (spatial dispersion), we can restrict ourselves to the solution with smallest $|\text{Im } K|$, provided the crystal is sufficiently thick.

To find the value of the coefficient $\underset{\sim}{A}_0$, one must solve the homogeneous boundary problem at the left-hand side of the crystal. It is sufficient for our purposes, however, to note that $\underset{\sim}{A}_o$ will be directly proportional to $\underset{\sim}{A}_i$, and for sufficiently large d, $\underset{\sim}{A}_o$ will be independent of d. Similarly, the ratio of $\underset{\sim}{A}_t$ to $\underset{\sim}{A}_o\, e^{iKd}$, which is found by solving the boundary problem at the right-hand side of the crystal, will be independent of d, when multiple reflection may be neglected. The ratio of $\underset{\sim}{A}_t$ to $\underset{\sim}{A}_i$ will thus be equal to a constant times e^{iKd}, and the ratio of the transmitted to incident intensities is proportional to $e^{-\alpha d}$, where $\alpha = 2 \operatorname{Im} K$. The constant α is the absorption constant of the material, at frequency ω. Note that to measure α one must make measurements of the transmission through two or more samples of different thickness. The optical absorption is then operationally defined by

$$\alpha = (d_2 - d_1)^{-1} \log \left(\text{Intensity transmitted through } d_1 / \text{Intensity transmitted through } d_2\right). \qquad (1.9)$$

The real part of K can also be obtained experimentally. It can be measured, in theory, by beating the transmitted signal with the incident wave in an interferometer, and measuring the change in phase as a function of d. However, it is possible to get a very good approximation to Re K, more conveniently, from a reflectivity measurement. Because the range of surface effects on the response function $\underset{\approx}{\Lambda}(\underset{\sim}{r}, \underset{\sim}{r}'; \omega)$ is generally very small compared to the wavelength of light, one can assume that the internal solution $\underset{\sim}{A}(r) = \underset{\sim}{A}_o\, e^{iKz}$ extends all the way up to the surface $z = 0$. The requirement that $\underset{\sim}{A}$ and its first derivative be continuous at the surface then determines the ratios of $\underset{\sim}{A}_i$, $\underset{\sim}{A}_r$ and $\underset{\sim}{A}_o$. The reflectivity is given by

$$R = \frac{|A_r|^2}{|A_i|^2} = \left|\frac{k - K}{k + K}\right|^2 . \qquad (1.10)$$

If the optical absorption constant, 2 Im K, is known, then (1.10) may be readily solved to obtain Re K. The ratio K/k is known as the complex index of refraction.

In order to predict the line shape for optical absorption, it is sufficient to predict the response function Λ. If one calculates the response of a homogeneous quantum mechanical system to a classical vector potential $\underset{\sim}{A}(\underset{\sim}{r}, t) = \underset{\sim}{A}\, e^{iqz-i\omega t}$ + complex conjugate, one finds according to the fluctuation-dissipation theorem,[1]

$$- \operatorname{Im} \Lambda(q, \omega) = \frac{1 - e^{-\omega/k_BT}}{2\Omega} \int e^{i\omega t} \left\langle j_q(t)\, j_{-q}(0)\right\rangle dt , \qquad (1.11)$$

where $j_q(t)$ is the current operator for wave vector q at time t in the Heisenberg picture, Ω is the volume of the crystal, k_B is Boltzmann's constant, and the expectation value indicated by the angular brackets is to be taken over a canonical ensemble at temperature T. We work in units where $\hbar = 1$. The Hamiltonian in (1.11) is the exact Hamiltonian of the material, but without the coupling to the transverse electromagnetic field. Again, we ignore the tensor character of Λ by considering the components of j_q along a suitable (transverse) symmetry direction. Because the nuclei in a solid are very much heavier than the electrons, it is generally sufficient, at optical frequencies, to consider only the electronic part of the current operator.

It is convenient to write equation (1.11) in the form

$$- \operatorname{Im} \Lambda(q, \omega) = \frac{1 - e^{-\omega/k_BT}}{2\Omega} \sum_{a,b} \frac{e^{-E_a/k_BT}}{Z} \left|(a|j_q|b)\right|^2 2\pi\delta(\omega - E_b + E_a), \qquad (1.12)$$

where a and b are exact eigenstates of the Hamiltonian with energies E_a and E_b, and Z is the partition function defined by $Z = \Sigma_a \, e^{-E_a/k_BT}$. Usually in optical experiments, we have $\omega/k_BT \gg 1$; thus in (1.11) and (1.12), the quantity $e^{-\omega/k_BT}$ may be neglected. In order to calculate approximately the imaginary part of Λ, one must first identify the states which lie an energy ω above the thermally occupied states, and then one must estimate the matrix elements of the current operator between the relevant states. When Im Λ has been calculated for all ω, the real part of the response function may be determined from the Kramers-Kronig relation

$$\mathrm{Re}\ \Lambda(q, \omega) = \frac{ne^2}{m} + \int_0^\infty \frac{\omega' \ \mathrm{Im}\ \Lambda(q, \omega')}{\omega'^2 - \omega^2} \frac{d\omega'}{\pi}, \tag{1.13}$$

where n is the number of electrons per unit volume, e is the electronic charge, and m is the electronic mass. In (1.13) the principal value of the integral is to be taken.

The main concern of the theorist is to predict the imaginary part of Λ. The theorist will often work very hard to develop an approximation which will give good values of Im Λ in a small region of frequencies. In order to obtain the real part of Λ in the same frequency range, he would have to calculate Im Λ, at least roughly, for all values of ω. Rather than do this, the theorist would often prefer to compare his predicted values of Im Λ directly with experiment. This can be done if reflectivity, as well as optical absorption, has been measured. In terms of Re K and α, the experimantally observed value of Im Λ may be expressed, using (1.7) as

$$\mathrm{Im}\ \Lambda(K, \omega) = - c^2(4\pi)^{-1} \alpha \ \mathrm{Re}\ K. \tag{1.14}$$

When Λ is small, the dielectric constant is close to 1, and Eq. (1.8) gives

$$\alpha \approx 4\pi \omega^{-1} c^{-1} |\mathrm{Im}\ \Lambda| . \qquad (1.15)$$

In this case, the optical absorption is simply proportional to Im Λ, and it is unnecessary to know Re Λ or Re K. When Re K is large, however, it may play an important role in the absorption spectrum. For example, when the real part of the dielectric constant is negative, a finite attenuation constant α will be observed, even for infinitessimal values of Im Λ.

One complication still exists in comparing theory with experiment. The experimental value of $\Lambda(q, \omega)$ is obtained for a complex value of q, whereas in theoretical calculations one normally works with real q. In most cases, however, very little change results from dropping the imaginary part of K in the argument of Λ in Eq. (1.14). In a nonmetal, changes in $\Lambda(q, \omega)$ usually occur only when q is changed by an amount comparable to a reciprocal lattice vector; the imaginary part of K is always very much smaller than the size of the Brillouin zone, regardless of the frequency of the incident light. At optical frequencies, the real part of K is also much smaller than a reciprocal lattice vecotr, and it is generally correct in practice to approximate $\Lambda(q, \omega)$ by $\Lambda(0, \omega)$, where $\Lambda(0, \omega)$ is the limit of $\Lambda(q, \omega)$ as $q \rightarrow 0$. In the limit of $q \rightarrow 0$, the current operator j_q becomes the total momentum operator for the electrons

$$j_o = \frac{e}{m} P . \qquad (1.16)$$

It is not necessarily correct, however, to substitute the limit (1.15) in (1.11) or (1.12) to obtain $\Lambda(0, \omega)$. Because of the infinite range of the

Coulomb interaction, and because we have eliminated the transverse electromagnetic field from the Hamiltonian, there is a discontinuity at $\underset{\sim}{q} = \underset{\sim}{0}$ between the longitudinal and transverse current correlation functions. The correlation function for $\underset{\sim}{j}_0$ is thus undefined in the infinite medium. In models where the effects of the long-range Coulomb interaction are neglected, the discontinuity between longitudinal and transverse disappears, and one can then use the operator $\underset{\sim}{j}_0$ without ambiguity.

The theory of optical absorption outlined above is semi-classical, in that we have treated the electromagnetic field as a classical field, while using quantum mechanics to determine the response function. A completely quantum mechanical treatment, using the techniques of quantum field theory, can also be given, and leads to results very similar to the semi-classical treatment. The reason for this similarity is that Dyson's equation for the photon propagator is essentially identical to equations (1.3) and (1.4) for $\underset{\sim}{A}(\underset{\sim}{r})$. The only difference between the correct quantum mechanical formula for the optical absorption and the semiclassical result is a slight change in the equation for Im $\Lambda(q, \omega)$, Eq. (1.11). Instead of using the current-current correlation function calculated in the absence of interactions with the electromagnetic field, one must use the irreducible part of the correlation function for the complete Hamiltonian, i.e., the sum of all Feynman diagrams for the correlation function which cannot be separated into two disconnected parts by breaking a single photon line. The sum of all diagrams with no internal photon lines is just the correlation function in the semiclassical calculation. The effect of diagrams with one or more internal photon lines is two-fold. First, those diagrams with no real photon containing intermediate states lead to slight shifts in energies due to magnetic interactions between electrons, and can be neglected in most cases. Second, there are diagrams with real photon-containing intermediate states, which can lead to a qualitative change in the absorption. The simplest class of such diagrams may be indicated as

(1.17)

where the dotted line represents a photon, the wavy line a phonon, and the triangles represent the complete vertex functions for the process. Such a diagram represents the process of Raman or Brillouin scattering of light, and leads to optical attentuation even at frequencies where the semiclassical theory predicts no absorption. This scattering is generally very small at optical frequencies, however, because the number of photon states which can satisfy conservation of energy is very small.

A diagram very similar to (1.17) is obtained when light is scattered by a static inhomogeneity in the crystal. In this case the wavy line in (1.17) does not carry any energy and is merely used to indicate that momentum has been transferred to the inhomogeneity. In a carefully grown crystal this scattering will also be very small.

Other diagrams which appear in the irreducible part of the current correlation function are diagrams in which the intermediate state has several phonons and/or several photons. Also one has diagrams with several real photon-containing intermediate states, corresponding to multiple scattering of the photon. Clearly all of these may be neglected.

Except for a brief discussion in Chapter IV, Section 3, the remainder of this thesis will be concerned with the problem of calculating the imaginary part of Λ in the semiclassical approximation, i.e., the contribution of diagrams with no internal photons.

Section 2. Crystal Models

The simplest model one can consider for a solid consists of a set of non-interacting electrons moving in a periodic potential caused by fixed ions of infinite mass. If the crystal is a non-conductor, the ground state will have an energy gap, E_g, between a filled valence band and an empty conduction band. Because in most cases of interest, the energy gap is much greater than $k_B T$, very few electrons will be excited in the thermal ensemble, and it is correct to assume in equation (1.12) that $T = 0$. Thus, the only initial state we consider is the one in which the crystal is in its ground state.

The current operator j_q connects the ground state with excited states in which a single electron of momentum $\underset{\sim}{k}$ is removed from the valence band and added to the conduction band with wave-vector $\underset{\sim}{k} - \underset{\sim}{q}$. For optical absorption, $q \approx 0$, and $\underset{\sim}{k} - \underset{\sim}{q} \approx \underset{\sim}{k}$. The minimum energy of these excited states is called the direct band gap, E_d; it is the minimum difference between the conduction and valence band energies of the same wave-vector. The function $\mathrm{Im}\,\Lambda(0, \omega)$, and hence, the optical absorption, will be zero for all $\omega < E_d$, and will be non-zero for a continuum of energies above E_d. If, as is frequently the case, the minimum energy in the conduction band does not occur at the same wave-vector as the maximum in the valence band, the direct gap E_d will be larger than the indirect gap E_g. Above the direct energy gap, Im Λ will be a smoothly varying function of the frequency ω, except at points where the density of states with total momentum $\underset{\sim}{0}$ has a Van Hove singularity. Such singularities occur when the sum of the particle and hole energies has a minimum, maximum, or saddle point as a function of relative wave-vector. Observations of the corresponding singularities in the optical absorption have been important tools in the experimental determination of the band structure of solids.

The prediction of optical absorption for the one-electron model we have discussed is within the range of computer techniques. If the periodic potential is known, the eigenstates and energies may be calculated by solving the Schrödinger equation in a single unit cell, with the modified periodic boundary conditions appropriate to the given wave vector. Once the wave functions are known, the matrix elements of the current operator are easily calculated, and Im Λ thus obtained. Ideally, the periodic potential which is used should be obtained self-consistently; in addition to the Hartree terms it should include a non-local exchange potential, which, in turn, should include effects due to electronic polarizability. In band calculations which have been done so far, however, it has generally been the practice to use simpler, local potentials to approximate the ideal potential.

The optical absorption in the non-interacting electron model would still differ qualitatively from the absorption of a real crystal, no matter how well the periodic potential were chosen. The energy eigenstates of the real system are not simple products of a hole wave-function and an electron wave-function. An important term which should be included in the

Hamiltonian is the Coulomb interaction between the electron and hole. For each value of the total momentum there will then be a discrete series of positronium-like bound states of the electron and hole, lying below a continuum of unbound states. The bound states are called excitons, and play an important role in the optical absorption.

The inclusion of electron-electron interactions does not destroy conservation of wave-vector. The current operator j_{-q} couples the ground state to states of total wave-vector $\underset{\sim}{q}$; hence Im $\Lambda(q, \omega)$ now consists of a set of δ-functions at the energies of the excitons of wave-vector $\underset{\sim}{q}$, followed by a continuum, beginning at the energy of the direct band gap, E_d. (The δ-functions in Im Λ will actually give rise to optical attenuation bands, because by the Kramers-Kronig relations, the real part of the dielectric constant will always be negative for a small region above the energy of the δ-function. This effect will not lower the threshhold for absorption, however, as Re ϵ will always be positive below the first δ-function.)

Calculation of the exciton wave-functions and energies, and thus of the strengths and positions of the δ-functions in Im Λ have generally been done with drastic simplifying assumptions appropriate to the limits of either "tight" or "weak" binding. Yet one can imagine that with some improvement in mathematical and computer techniques, it would be feasible to calculate quite accurate exciton functions. The many-body Hamiltonian would be restricted to the subspace in which one electron and one hole are present, with total momentum $\underset{\sim}{q}$. The wave-function is thus a function of the relative momentum of the electron and hole, and of two discrete indices designating the electron and hole bands. The complete Coulomb interaction Hamiltonian should be written in terms of electron and hole creation and annihilation operators, and all terms should be dropped except those which involve the product of one hole annihilation operator, one hole creation operator, one electron annihilation operator, and one electron creation operator. Physically, the terms which are kept are of two types. First, there are terms in which the electron is scattered from one electron-state to another and the hole from one hole-state to another; second, there are terms in which the electron is scattered into the vacant hole state at one lattice site, while an electron is lifted from a filled state to an empty one at a different site. The first type of term is the one primarily responsible for the exciton's binding energy, while the second is the source of the dipole-dipole coupling responsible for exciton mobility in the tight-binding limit.

When the dipole-dipole term is large, it can cause the exciton effective mass to be quite different from the sum of the electron and hole masses. The dipole-dipole term causes a splitting between the energies of the transverse and longitudinal excitons at $\underset{\sim}{q} \approx \underset{\sim}{0}$, causing in turn the splitting between the transverse and longitudinal current correlation functions mentioned earlier. The transverse exciton, which is the one which couples to the transverse electromagnetic field in a crystal of high symmetry, always lies lower than the longitudinal exciton.

In order to correctly obtain a good estimate of the exciton energies, it is important to include some many-body corrections to the exciton calculation just described. One should use, instead of the bare

Coulomb interaction for the electron and hole, an interaction screened by an appropriate dielectric constant. Using the screened interaction presumably includes the most important effects of intermediate states in which two or more electron-hole pairs are excited. The problem of accurately calculating this dielectric constant, which may have to include terms non-linear in the interaction, is one of the major obstacles to good exciton binding energy calculations at the present time.

The calculations for the exciton states can also be carried out for electron-hole continuum states. The electron-hole interaction, of course, cannot change the energy of the continuum states, but the change in wave-function can produce major changes in the current matrix elements, and hence in the optical absorption. It is believed that resonances in this matrix element due to "meta-stable excitons" can cause subsidiary peaks in the optical absorption, just below the peaks associated with various Van Hove singularities in the density of states.[2]

When ω exceeds twice the minimum energy necessary to produce a single exciton or particle-hole pair, calculations restricted to states in which one real electron and one real hole exist will no longer be valid. This is because of the possibility of transitions to states in which two particles and two holes occur. This difficulty shows up in the two-body calculation because the dielectric constant necessary to screen the electron-hole interaction becomes complex. In fact, the same difficulty occurs in the calculation of the single particle energies -- at high energies the dielectric constant used in the self-consistent potential becomes complex, and a one electron state can decay into a state in which two electrons and one hole are excited. Since we will be primarily concerned with states near the energy gap, we need not worry about these complications.

The calculations we have discussed so far have all assumed electrons which move in a perfectly periodic lattice. The inclusion of the fact that the ions are not fixed in a periodic array causes great complications, and qualitatively changes the absorption spectrum. Because the energies of long wavelength accoustic phonons are arbitrarily small, it is no longer correct to assume, at finite temperatures, that the initial state of the crystal is the ground state. One can assume that the initial states in equation (1.12) are those in which the "electronic system" is in its ground state, but the phonon states are thermally populated. If the ionic mass is sufficiently great, or the temperature sufficiently high, the ions may be treated as static classical particles. The positions of the nuclei are then just parameters in the electronic Hamiltonian, and the average over phonon states becomes an average over nuclear positions, weighted according to the rules of classical statistical mechanics. (See Chapter III, Eqs. (1.3) and (1.4).)

The first result of the destruction of the periodicity of the lattice is the destructions of wave-vector conservation with its associated selection rule. Thus, whereas in the perfect lattice, the operator j_q couples the ground state to a single state in each exciton band, in a random lattice j_q couples the ground state to all the energy eigenstates of the exciton band. The δ-functions in Λ associated with excitons in the perfect lattice are now broadened into absorption bands. When the minimum energy of the lowest exciton band does not occur at wave-vector zero, the destruction of the wave-vector selection rule results in a lowering of the minimum energy for optical absorption. Similarly, if the direct band gap for electron-hole continuum states is larger than the indirect band gap, elimination of the wave-vector selection rule reduces the threshhold for the production of an unbound electron and hole.

There are additional effects of the lattice fluctuations which cause small amounts of optical absorption even at energies well below the minimum exciton energy of the perfect lattice. If the periodic lattice is uniformly distorted, it is clear that the energy gap and the exciton energy minimum will be changed. If the deformation is of the proper magnitude and direction, the exciton energy minimum can be greatly reduced. In a real crystal, at finite temperatures, there will always be some regions of the crystal which will be sufficiently distorted, because of thermal fluctuations, to cause absorption at an arbitrary energy below the threshhold for the perfect lattice. The study of the low energy tail of the absorption spectrum will be the subject of Chapters III and IV of this thesis.

The quantitative calculation of the effects of a non-periodic lattice on optical absorption is in general very difficult. One usually makes the assumption that the Hamiltonian can be written as a sum of three terms: a phonon Hamiltonian, an electronic Hamiltonian, and an interaction term.

The phonon Hamiltonian is expanded as

$$H_{ph} = \sum_{\underset{\sim}{k}\eta} \omega_{\eta}(\underset{\sim}{k})\, b^{+}_{\underset{\sim}{k}\eta}\, b_{\underset{\sim}{k}\eta} + \text{higher terms}, \tag{2.1}$$

where the first term is just the Hamiltonian of a perfect harmonic lattice; the "higher terms" are anharmonic terms involving three or more phonon annihilation or creation operators, which we shall keep in some of our later work. The index η is a polarization index, and $\underset{\sim}{k}$ is the momentum of the phonon.

The electronic Hamiltonian is assumed to be of the form:

$$H_{el} = \sum_{\underset{\sim}{k}\mu} \epsilon_{\mu}(\underset{\sim}{k})\, a^{+}_{\underset{\sim}{k}\mu}\, a_{\underset{\sim}{k}\mu} + \text{higher terms,} \tag{2.2}$$

where $a^{+}_{\underset{\sim}{k}\mu}$ is the creation operator for an exciton or an electron-hole continuum state with total wave-vector $\underset{\sim}{k}$, and $\epsilon_{\mu}(\underset{\sim}{k})$ is the energy of this excitation calculated for the perfect lattice. "Higher terms" includes the interaction between two or more electronic excitations. Since we are only interested in states with a single electronic excitation, of energy close to the energy gap, we shall neglect the higher terms in (2.2).

The interaction Hamiltonian may be written

$$H_{int} = \sum_{\substack{\underset{\sim}{k}\underset{\sim}{k}' \\ \eta\mu\mu'}} \left(c^{\eta\mu'\mu}_{\underset{\sim}{k}\underset{\sim}{k}'}\; b^{+}_{\underset{\sim}{k}\eta}\; a^{+}_{\underset{\sim}{k}'\mu'}\; a_{\underset{\sim}{k}+\underset{\sim}{k}',\mu} + \text{Hermitian conjugate}\right) + \text{higher terms.} \tag{2.3}$$

In (2.3), the first term describes scattering of an electronic excitation of momentum $\underset{\sim}{k} + \underset{\sim}{k}'$ into another electronic excitation of wave-vector $\underset{\sim}{k}'$, with emission of a phonon of wave-vector $\underset{\sim}{k}$. The Hermitian conjugate of this describes a similar process with phonon absorption. The higher terms are of several kinds. There are terms describing the scattering of an electronic excitation with the production or annihilation of two or more phonons: this is a non-linear electron phonon interaction, and may be important under some conditions. We shall keep these terms in some of our later work. There are terms which involve one creation or destruction operator for an electronic excitation and one or more phonon operators. Because of the great difference in energies between the electronic excitations and phonons, at least one of the two states connected by these terms will be very far off the energy shell. Such terms will only cause slight renormalizations of energies and interactions, and may be neglected. Among the "higher terms" there are also terms involving three or more electronic operators and one or more phonon operators. Like the higher terms in (2.2), these may be neglected when we are at energies close to the energy gap.

The numerical values of the coefficients in the various terms of (2.1) and (2.3) are not uniquely determined, even in theory. This is because the creation operators themselves have not been unambiguously defined. One requires that the phonon operators obey boson commutation relations, and it is usual to require the same of exciton operators. (In fact, since we are not interested in states where several electronic excitations are present, it is not necessary to specify whether the excitons are bosons or fermions.) We require that the $a^{+}_{\underset{\sim}{k}\mu}$ commute with all the phonon operators. Beyond these requirements there are few *a priori* restrictions on the operators.

The phonon operators are *usually* defined from the point of view of the Born-Oppenheimer separation. The general phonon state consists of an arbitrary function $\psi(R)$ of the nuclear coordinates, multiplied by a fixed function $\varphi_o(R, r)$ of the nuclear and electronic coordinates, where for each nuclear configuration R, $\varphi_o(R, r)$ is the ground state solution of the electronic Hamiltonian in the potential field of the nuclei. (We use the symbols R and r to represent the coordinates of all the nuclei and electrons respectively.) The phonon operators change the functions $\psi(R)$ without changing the function $\varphi_o(R, r)$.

The creation operators for the electronic excitations, operating on a general phonon state, are assumed to change the function $\varphi_o(R, r)$ without changing the function $\psi(R)$. Thus we have $a^+_{\underset{\sim}{k}\mu}\psi(R)\,\varphi_o(R,r) \equiv \psi(R)\,\varphi_{\underset{\sim}{k}\mu}(R, r)$. When the coordinates of the nuclei are at the equilibrium position, we know that the effect of $a^+_{\underset{\sim}{k}\mu}$ is to raise the ground state of the electronic system to an exact energy eigenstate of wave-vector $\underset{\sim}{k}$. The effect on $\varphi_o(R, r)$ for any other configuration R is not yet defined. The principal restrictions are that $\varphi_{\underset{\sim}{k}\mu}(R, r)$ should be orthogonal to the ground state and all other excited states for each fixed R, and that it be normalized to unity for each fixed R. In other words, we require:

$$\int \varphi_o{}^*(R, r)\, \varphi_{\underset{\sim}{k}\mu}(R, r)\, dr = 0, \tag{2.4}$$

$$\int \varphi_{\underset{\sim}{k}'\mu'}{}^*(R, r)\, \varphi_{\underset{\sim}{k}\mu}(R, r)\, dr = \delta_{\underset{\sim}{k}\underset{\sim}{k}'}\,\delta_{\mu\mu'} . \tag{2.5}$$

The association of a wave-vector $\underset{\sim}{k}$ with the operator $a^+_{\underset{\sim}{k}}$ requires that

$$\mathcal{T}_{\underset{\sim}{\ell}}\, \varphi_{\underset{\sim}{k}\mu}(R, r) = e^{-i\underset{\sim}{k}\cdot\underset{\sim}{\ell}}\, a^+_{\underset{\sim}{k}\mu}\,\mathcal{T}_{\underset{\sim}{\ell}}\, \varphi_o(R, r) , \tag{2.6}$$

where $\mathcal{T}_{\underset{\sim}{\ell}}$ is the operator which translates the entire system by a lattice vector $\underset{\sim}{\ell}$. It is also natural to require that the function $\varphi_{\underset{\sim}{k}\mu}(R, r)$ be continuous in the variables R. The states $\varphi_{\underset{\sim}{k}\mu}(R, r)$ will <u>not</u> be eigenstates of the electronic Hamiltonian when the nuclei are not at their equilibrium configuration.

Once the operators $a^+_{\underset{\sim}{k}}$ are defined, the operators $a_{\underset{\sim}{k}}$ are defined on the spaces of zero and one electronic excitation by the requirement that $a_{\underset{\sim}{k}}$ operating on any pure phonon state gives zero, and $a_{\underset{\sim}{k}\mu} \varphi_{\underset{\sim}{k}'\mu'}(R,r) = \delta_{\underset{\sim}{k}\underset{\sim}{k}'} \delta_{\mu\mu'} \varphi_o(R, r)$. The choice of definition for the raising operators $a^+_{\underset{\sim}{k}}$ is guided by the desire to make the coefficients in H_{int} as small as possible. It is also necessary to choose the raising operators in a sufficiently simple manner such that some approximate calculation of the coefficients is possible. A sensible procedure is to express the operators $a^+_{\underset{\sim}{k}}$ for the periodic lattice in terms of the single electron creation and annihilation operators, $\psi^+(\underset{\sim}{x})$ and $\psi(\underset{\sim}{x})$. When the nuclei are displaced from equilibrium, we define a continuous coordinate transformation $\underset{\sim}{x} \rightarrow \underset{\sim}{x} + \Delta \underset{\sim}{x}$ by interpolating between the discrete lattice points in some manner. This coordinate transformation will define a canonical transformation on the $\psi^+(\underset{\sim}{x})$ and $\psi(\underset{\sim}{x})$, and hence on the $a^+_{\underset{\sim}{k}\mu}$. Because the function $\varphi_o(R, r)$ at the displaced nuclear position R is <u>not</u> obtained from the periodic ground state by this same canonical transformation, the functions $a^+_{\underset{\sim}{k}\mu} \varphi_o(R, r)$ will not in general satisfy the orthogonality and normalization conditions (2.4) and (2.5). These properties may be restored by taking linear combinations of the non-orthogonal functions. The orthogonalization can be done as follows: Let the matrix M(R) have the elements

$$M_{\underset{\sim}{k}\mu,\underset{\sim}{k}'\mu'}(R) \equiv \int \varphi^o_{\underset{\sim}{k}\mu}(R, r)\, \varphi^o_{\underset{\sim}{k}'\mu'}(R, r)^* \, dr \, , \qquad (2.7)$$

where $\varphi^o_{\underset{\sim}{k}\mu}$ and $\varphi^o_{\underset{\sim}{k}'\mu'}$ are the non-orthogonal functions $a^+_{\underset{\sim}{k}\mu} \varphi_o(R, r)$ and $a^+_{\underset{\sim}{k}'\mu'} \varphi_o(R, r)$. The matrix M(R) will be a positive-definite Hermitian matrix. The correct orthogonalized functions $\varphi_{\underset{\sim}{k}\mu}(R, r)$ are then given by

$$\varphi_{\underset{\sim}{k}\mu}(R,\ r) = \sum_{\underset{\sim}{k}'\mu'} [M(R)^{-\frac{1}{2}}]_{\underset{\sim}{k}\mu,\underset{\sim}{k}'\mu'}\ \varphi^{o}_{\underset{\sim}{k}'\mu'}(R,\ r)\ . \tag{2.8}$$

If R is sufficiently close to the equilibrium positions, M(R) will differ from the unit matrix I by a small matrix m(R). The matrix $M(R)^{-\frac{1}{2}}$ can then be expanded as

$$M(R)^{-\frac{1}{2}} = I - \frac{1}{2}\,m(R) + m(R)^{2}/8 - \dots\ , \tag{2.9}$$

It is clear the $M(R)^{-\frac{1}{2}}$ goes continuously into the unit matrix as R approaches the equilibrium configuration.

Once the operators $b^{+}_{\underset{\sim}{k}\eta}$ and $a^{+}_{\underset{\sim}{k}\mu}$ are defined, the coefficients in H_{int} may be found by taking matrix elements of the Hamiltonian among the states with specified phonons and electronic excitations excited. The current operator, like the Hamiltonian, may be expanded in terms of the creation and destruction operators for phonons and electronic excitations. For optical absorption near the energy gap, we need only keep terms which connect states having one electronic excitation with those having zero electronic excitations:

$$j_{-q} \approx \sum_{\mu} (\xi^{\mu}_{\underset{\sim}{q}}\ a^{+}_{\underset{\sim}{q}\mu} + \xi^{\mu *}_{-\underset{\sim}{q}}\ a_{-\underset{\sim}{q}\mu}) + \sum_{\mu\underset{\sim}{k}\eta} [\xi^{\mu\eta}_{\underset{\sim}{q}\underset{\sim}{k}}\ a^{+}_{\underset{\sim}{k}-\underset{\sim}{q},\mu}\ (b^{+}_{\underset{\sim}{k}\eta} + b_{-k\eta})$$

$$+ \xi^{\mu\eta}_{\underset{\sim}{q}\underset{\sim}{k}}\ a_{-\underset{\sim}{k}+\underset{\sim}{q},\mu}\ (b^{+}_{\underset{\sim}{k}\eta} + b_{-\underset{\sim}{k}\eta})] + \dots\ , \tag{2.10}$$

The coefficients ξ may be calculated by taking matrix elements of the current between the appropriate states. The first set of terms above have the form of the current operator in the perfect lattice. The higher terms involving phonon operators arise from the dependence of the matrix elements of the electronic current operator on the lattice configuration R; they occur because the definitions of the exciton creation operators depend on the lattice configuration.

In practice we know neither the exact function $\varphi_0(R, r)$ nor the structure of the exact excitations in the perfect lattice, which are both necessary to perform the calculation of the coefficients in the Hamiltonian and current-operator expansion. An ambitious attempt to evaluate these coefficients might involve approximations to the electronic excitations of the perfect lattice such as those described earlier, and some self-consistent calculations of the change in the electronic ground state φ_0 for small displacements of the nuclei from equilibrium. The problems arising in such an attempt will not concern us here. We shall assume that such an attempt has been made and that the coefficients are known -- the problems we shall investigate in this thesis concern the question of how to use these coefficients.

It should be pointed out that some information about these coefficients is directly observable in experiments on the pressure dependence of the position of absorption lines. If measurements are made at low temperatures where the effects of phonon broadening are small, the peak of the exciton absorption band is roughly at the position of the $\underset{\sim}{k} = \underset{\sim}{0}$ exciton line in the perfect lattice. Thus it is possible to find the linear shift in the energy of the $\underset{\sim}{k} = \underset{\sim}{0}$ exciton when the crystal is uniformly strained. If we assume that the linear change in exciton energy only depends on the change in volume of the crystal, then we may write

$$\delta \epsilon_\mu(\underset{\sim}{0}) = V_\mu \, \delta v/v \tag{2.11}$$

where $\delta v/v$ is the fractional change in volume, and V_μ is called the deformation potential coefficient. If we form an exciton wave packet of states close to $\underset{\sim}{k} = \underset{\sim}{0}$, and place it in a crystal with a weak, long-wavelength density fluctuation, it is physically clear that the energy of the packet will be shifted by $V_\mu \ \delta v/v$ where $\delta v/v$ is now the fractional change in volume in the neighborhood of the exciton wave packet, provided the interaction between exciton and lattice is not too long range. (Transverse and longitudinal exciton packets may be considered separately by forming needle-shaped and coin-shaped wave-packets, respectively, with axes parallel to the polarization in both cases.) The condition of "not-too-long-range exciton-lattice interaction" is satisfied even in a piezoelectric crystal because the exciton carries no charge. The fractional change in volume at point $\underset{\sim}{r}$, due to a long-wavelength fluctuation is given in terms of phonon operators by

$$\delta \ v(\underset{\sim}{r})/v \ = \sum_{\underset{\sim}{k}} i|k|\,(2\rho\Omega\omega_{\underset{\sim}{k}\lambda})^{-\frac{1}{2}} \, e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}} \, (b_{\underset{\sim}{k}\lambda} + b^{+}_{-\underset{\sim}{k}\lambda}) \ , \tag{2.12}$$

where ρ is the density of the crystal and λ designates the longitudinal acoustic phonon mode. On the other hand, if the phonon-exciton Hamiltonian is given by (2.3), and the exciton band is non-degenerate, the shift in the wave-packet-energy, linear in the phonon amplitues, just comes from the terms $c^{\lambda\mu\mu}_{\underset{\sim}{k}\underset{\sim}{k}'}$ which are diagonal in the exciton band μ. Hence it follows that the coefficients c, for the longitudinal acoustic modes, have the form

$$c^{\lambda\mu\mu}_{\underset{\sim}{k}\underset{\sim}{k}'} \ = \ i \ V_\mu |k|\,(2\rho\Omega \ \omega_{\underset{\sim}{k}\lambda})^{-\frac{1}{2}} \ , \qquad \text{for } \underset{\sim}{k},\underset{\sim}{k}' \to 0. \tag{2.13}$$

It is sometimes assumed, in simple models, that the deformation potential coupling (2.13) holds throughout the Brillouin zone.

It is necessary in the derivation we have given of the deformation potential coupling, that the off-diagonal elements ($\mu \neq \mu'$) not become infinitely large compared to the diagonal coupling constants, as $k \rightarrow 0$. The off-diagonal elements will be well behaved whenever one chooses a definition of the operators $a^{+}_{\underset{\sim}{k}\mu}$ which causes the electrons to follow the lattice when the lattice is simply displaced; the interaction for a long-wavelength fluctuation will then be proportional to "strain" not "displacement". The definition of $a^{+}_{\underset{\sim}{k}\mu}$ that we have described above satisfies this criterion.

If the crystal is not isotropic, or if the exciton band is non-degenerate, measurement of the pressure-dependence of the $\underset{\sim}{k} = \underset{\sim}{0}$ exciton energy only determines the long wavelength behavior of an average of the coefficients c over direction and polarizations. A more complete discussion of deformation potential theory, which includes the cases of degenerate bands and of shearing strains, is given by Lax,[3] together with references to the earlier literature. Lax's presentation, like most work in the field, deals with the interaction of the lattice and a single electron, treated from the non-interacting-electron point of view.

Section 3. Perturbation Methods

One of the most widely used approaches for predicting line shapes for optical absorption has been perturbation theory and variations in which infinite sets of Feynman graphs are summed. In these works it has been usual to assume either that the electron-hole interaction is very weak, so that the electron and hole may be treated as independent, or to deal with optical absorption below the particle-hole continuum, and assume that only bound exciton states need be considered. In the present paper, we shall concentrate on this latter situation.

It has also been usual to neglect the dependence of the current operator on the phonon displacements, and simply assume that

$$j_{-q} = \sum_{\mu} (\xi_{\underset{\sim}{q}\mu} \, a^{+}_{\underset{\sim}{q}\mu} + \xi^{*}_{-\underset{\sim}{q}\mu} \, a_{-\underset{\sim}{q}\mu}) \; . \qquad (3.1)$$

In a system invariant under time reversal, it then follows that

$$- \operatorname{Im} \Lambda(q, \omega) = \sum_{\mu\mu'} \xi_{\underset{\sim}{q}\mu} \, \xi^{*}_{\underset{\sim}{q}\mu'} \, A_{\mu\mu'}(\underset{\sim}{q}, \omega) \; , \qquad (3.2)$$

where $A_{\mu\mu'}(\underset{\sim}{q}, \omega)$ is $-1/\pi$ times the anti-Hermitian part of the Green's function for the exciton:

$$A_{\mu\mu'}(\underset{\sim}{q}, \omega) = \frac{-1}{\pi i} \, [G_{\mu\mu'}(\underset{\sim}{q}, \omega) - G_{\mu'\mu}{}^{*}(\underset{\sim}{q}, \omega)] \; . \qquad (3.3)$$

The Green's function, in turn, is defined by

$$G_{\mu\mu'}(\underset{\sim}{q}, \omega) = \int e^{i\omega t} \, G_{\mu\mu'}(\underset{\sim}{q}, t) \, dt \; , \qquad (3.4)$$

where

$$G_{\mu\mu'}(\underset{\sim}{q}, t) = i \, \left\langle T[a_{\underset{\sim}{q}\mu}(t) \, a_{\underset{\sim}{q}\mu'}(0)] \right\rangle \; . \qquad (3.5)$$

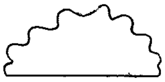
In Eq. (3.5), T is the time ordering symbol. We assume here, as throughout this thesis, that the temperature is very much smaller than the minimum energy E_o of the exciton band, and thus the exciton Green's function may be treated as a zero-temperature function.[4] In the absence of the exciton-phonon interaction, $G_{\mu\mu'}(\underset{\sim}{q}, \omega)$ would be given by

$$G^{o}{}_{\mu\mu'}(\underset{\sim}{q}, \omega) = \delta_{\mu\mu'} \, \frac{1}{\omega - \epsilon_{\mu}(\underset{\sim}{q}) + i \, 0^{+}} \; . \qquad (3.6)$$

Dyson's equation for the exciton propagator is

$$G(\underset{\sim}{q},\ \omega)^{-1} = G^{o}(\underset{\sim}{q},\ \omega)^{-1} - \Sigma(\underset{\sim}{q},\ \omega)\ , \tag{3.7}$$

where Σ, the self-energy matrix, is the sum of all irreducible Feynman diagrams in the expansion of G. The simplest approximation to Σ is that which keeps just the lowest diagram



$$, \tag{3.8}$$

where the solid line represents a bare exciton propagator G^{o}, and the wavy line represents a phonon propagator. If we keep only the harmonic term in the lattice Hamiltonian, and the linear term in the exciton-phonon interaction, this diagram may be evaluated as

$$\begin{aligned}\Sigma_{\mu\mu'}(\underset{\sim}{q},\ \omega) = \sum_{\eta\mu''\mu'''} \frac{\Omega}{(2\pi)^3}\int d\underset{\sim}{k}\ \ [n(\omega_{\underset{\sim}{k}\eta}) + 1]\ c^{\eta\mu''\mu}_{\underset{\sim}{k}\ \underset{\sim}{k}-q}{}^{*} \\ \times G^{o}_{\mu''\ \mu'''}(\underset{\sim}{q} - \underset{\sim}{k},\ \omega - \omega_{\underset{\sim}{k}\eta})\ c^{\eta\mu'''\mu'}_{\underset{\sim}{k}\ \underset{\sim}{k}-q} + n(\omega_{\underset{\sim}{k}\eta})\ c^{\eta\mu\mu''}_{\underset{\sim}{k}\ \underset{\sim}{q}} \\ \times G^{o}_{\mu''\mu'''}(\underset{\sim}{q} - \underset{\sim}{k},\ \omega + \omega_{\underset{\sim}{k}\eta})\ c^{\eta\mu'\mu''}_{\underset{\sim}{k}\ \underset{\sim}{q}}{}^{*}\ ,\end{aligned} \tag{3.9}$$

where $n(\omega)$ is the boson occupation number

$$n(\omega) = [\exp(\omega/k_B T) - 1]^{-1}\ . \tag{3.10}$$

In most cases, in inorganic solids, the phonon energies are much smaller than the widths of the exciton bands, and the term $\pm\ \omega_{\underset{\sim}{k}\eta}$ may be dropped in the arguments of the propagators, G^{o}.

The approximation described above may be called the one-phonon procedure, because the intermediate states have one phonon more or less than the initial state. Toyozawa[5,6] and Suna[4] have studied the line shape for optical absorption for a number of models using this procedure. The one-phonon approximation is expected to be valid whenever the self-energies are small compared to the energies over which the density of intermediate states exhibits an appreciable fractional change. At energies where the unperturbed density of states is non-zero and non-singular, this condition will hold for sufficiently weak exciton-phonon coupling constants. The approximation will not be valid at and below the lower edge of the unperturbed exciton bands.

An improvement over the one-phonon approximation is a self-consistent Green's function approximation, in which one replaces G^o, in Eq. (3.10) for the self-energy, by the complete Green's function G. Since G is itself expressible in terms of Σ, the result is an integral equation for Σ. The solution of this integral equation is equivalent to the summation of an infinite set of graphs for the self-energy, and it includes some of the effects due to multiphonon intermediate states. We shall call this self-consistent Green's function approximation the "$\Gamma = 1$ approximation", according to the usage of Suna.[4] Unfortunately, the conditions for validity of the $\Gamma = 1$ approximation are much the same as those for the validity of the $\Gamma = 1$ approximation. The $\Gamma = 1$ approach, however, does give qualitatively more reasonable pictures of the exciton Green's function. The self-consistent approximation also is an improvement over the one-phonon approach in that it properly treates such effects as the renormalization of exciton energies due to interaction with short wavelength phonons or due to coupling to higher exciton bands. The $\Gamma = 1$ approximation has been used by Suna to study some simple one-dimensional exciton bands interacting with phonons of finite frequency. A similar approach has been used by Toyozawa[7] for the three-dimensional model with zero-frequency phonons. In studying this model, Toyozawa has also employed a method which approximately includes the contributions of many other diagrams to the self-energy, and has found significant changes from results of the $\Gamma = 1$ approximation.

The weaknesses of the one-phonon and $\Gamma = 1$ approximations are best illustrated by the example of a one-dimensional model which we shall solve exactly in Chapter II. We consider a one-dimensional model consisting of a single exciton band in the effective mass approximation, such that

$$\epsilon(k) = \frac{1}{2} k^2 . \tag{3.11}$$

We assume that the "effective coupling constant" between the excitons and phonons, $c_{kk'}[2n(\omega_k) + 1]^{\frac{1}{2}}$, is a constant, independent of k and k', given by

$$[2n(\omega_k) + 1]c_{kk'}{}^2 = D/2L , \tag{3.12}$$

where L is the length of the system, and D is a constant. We consider the limit where the phonon frequencies are all zero. Note that this model describes equally well the case of optical phonons of constant frequency and constant matrix element or the case of local deformation-potential-coupling to Debye-model acoustic phonons, provided that the nuclei may be considered to be infinitely massive. When the phonon energies are taken to be zero, in an exciton-phonon model, the model is completely equivalent to that of a particle in a random potential. In the one-dimensional model just defined, the random potential may be described as white-Gaussian-noise.

The self-energy for the one-dimensional model is independent of k in the one-phonon approximation, and is given by

$$\Sigma(k, \omega) = \Sigma(\omega) = -2^{-3/2} D(-\omega)^{-\frac{1}{2}} . \tag{3.13}$$

The self-energy is real for all $\omega < 0$ and is pure imaginary for all $\omega > 0$.

The spectral density $A(k, \omega)$, which determines the optical absorption, is given by

$$A(k, \omega) \equiv - \frac{1}{\pi} \operatorname{Im} G(k, \omega) = - \frac{1}{\pi} \operatorname{Im} \frac{1}{\omega - \frac{1}{2} k^2 - \Sigma(\omega) + i0^+} . \qquad (3.14)$$

In the one-phonon approximation, the spectral density is non-zero for all $\omega > 0$, and approaches zero like $\omega^{\frac{1}{2}}$ as $\omega \to 0^+$. In addition, it has a delta-function peak at $\omega = \nu_k$, where ν_k is the solution of the equation

$$\nu_k - \frac{1}{2} k^2 + 2^{-3/2}(-\nu_k)^{-\frac{1}{2}} D = 0. \qquad (3.15)$$

As k changes from 0 to ∞, ν_k increases monotonically from $- 2D^{2/3}$ to 0.

In the $\Gamma = 1$ approximation, Σ is still independent of k, and is given by

$$\Sigma(\omega) = - 2^{-3/2} D [\Sigma(\omega) - \omega]^{-\frac{1}{2}} . \qquad (3.16)$$

The self-energy is real for all ω less than $\omega_0 = - \frac{3}{4} 2^{1/3} D^{2/3}$ ($\approx - 0.9449 D^{2/3}$) and is complex for all ω larger than this value. The spectral density, again given by (3.14), is non-zero if and only if $\omega > \omega_0$; the spectral density approaches zero like $(\omega - \omega_0)^{\frac{1}{2}}$ as ω approaches ω_0 from above. The spurious δ-function peak of the one-phonon approximation is now absent.

Note that in both the one-phonon and $\Gamma = 1$ approximations, there is a definite minimum frequency below which no optical absorption occurs. Such a cutoff was also found by Toyozawa in his three-dimensional model, both in the $\Gamma = 1$ approximation, and in the higher approximation he considered. Thus it appears that, at least when phonon frequencies are small, these methods are useless for describing the very interesting low energy tail of the absorption spectrum.

The exact spectral density for the one-dimensional model is compared with the $\Gamma = 1$ approximation in Figure 2, Chapter II.[8]

REFERENCES FOR CHAPTER I

1. M. Lax, J. Phys. Chem. Solids 25, 487 (1964).
2. J. C. Phillips, Phys. Rev. 136, A1705 (1964).
3. M. Lax, Symmetry Principles in Solid State Physics (to be published) Chap. 23, Sect. H.
4. A. Suna, Phys. Rev. 135, A111 (1964); Ph.D. thesis, Princeton University (1963).
5. Y. Toyozawa, Progr. Theor. Phys. 20, 53 (1958).
6. Y. Toyozawa, Technical Report, Ser. A, No. 79, Institute for Solid State Physics, University of Tokyo (1963).
7. Y. Toyozawa, Progr. Theor. Phys. 27, 89 (1962).
8. An extensive review of recent research on the effects of exciton-phonon interactions on the line shape for optical absorption may be found in R. S. Knox, Theory of Excitons, Solid State Physics, Supplement 5 (Academic Press, New York, 1963) Sect. 10.

CHAPTER II

GREEN'S FUNCTIONS FOR A PARTICLE IN A ONE-DIMENSIONAL RANDOM POTENTIAL

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Green's Functions for a Particle in a One-Dimensional Random Potential[†]

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ABSTRACT

A method has been found for exactly calculating the spectral density, A(k,E), for a particle in a one-dimensional random potential, when the potential at each point is statistically independent of the potential at all other points. Generalizations of this method can also be used to find the phonon Green's functions for a chain of atoms of random mass, or to find various two-particle functions, such as the electrical conductivity of a system of non-interacting electrons in a random potential. Two functions of the position, x, on the line are defined, which depend on the particular potential configuration and on the parameters k and E. The spectral density is expressed in terms of the probability distribution of these functions when x is at the right-hand end of the line. The distribution is known at the left-hand end, and the values of the functions, as x moves from left to right, form a Markoff process. One can therefore obtain the spectral density by solving the equation of motion for the probability distribution. Further simplification is possible because it

is sufficient to know the first two moments of the joint distribution with respect to one variable, and because in the limit of an infinite line, only the asymptotic form of these moments is necessary. The spectral density requires the solution of a pair of differential or integral equations in one variable, while two-particle functions involve similar equations in two variables. Calculations have been carried out for the spectral density of a Schrödinger particle in a "white Gaussian noise" potential and of a particle confined to fixed lattice sites in a random thermal deformation potential.

INTRODUCTION

Many problems which are difficult or impossible to solve in three dimensions turn out to be readily solvable in one dimension. One class of problems which has been studied successfully in one dimension is the calculation of the density of energy eigenstates of a particle moving in a potential which is not known exactly, but which obeys a statistical distribution such that the potential at one point is independent of the potential at all other points.[1-4] Another, closely related, problem which has been solved is the density of normal modes, as a function of frequency, for a chain of several kinds of atoms occuring in random order.[2,5,6] For many purposes, however, one is interested not in the density of states, but in a more complicated function, such as the spectral density associated with a state of a given wave vector, or in two-particle Green's functions of various kinds. In the present paper a method is presented for exact solution of one-dimensional models for a number of these problems.

The single-particle spectral density, $A(k,E)$, is of particular interest when the particle is an exciton in a lattice distorted by thermal fluctuations. Under proper circumstances, the line shape for the optical absorption due to an exciton in a non-degenerate band is given by the spectral density of the zero-momentum exciton state.[7,8] For <u>electrons</u> in an imperfect lattice, the one-particle

Green's function is of less direct interest, but it is still useful for understanding the nature of the energy eigenstates. A slightly generalized form of A(k,E), for the phonon modes of a disordered lattice, is of interest for the inelastic scattering of neutrons and for infrared absorption by the lattice. Among the problems which require knowledge of two-particle Green's functions are the conductivity of electrons in an imperfect lattice and the optical absorption due to interband transitions in a non-metal. The methods of the present paper are restricted to cases of non-interacting particles.

The essential features of the methods of this paper are as follows. We consider the problem of finding the spectral density, A(k,E), for a particle in a random potential on the line segment $0 \leq x \leq L$. One first defines certain mathematical quantities z and U_1, which are functions of the position, x, on the line, as well as of k and E, and of the particular potential configuration. The spectral density may be written as an average, over the potential configurations in the ensemble, of a certain function of the values of z and U_1 at the position $x = L$; hence A(k,E) is determined by the probability distribution of the values of z and U_1 at the right-hand end of the line. The functions z and U_1 are defined in such a way that for $x = 0$ they are independent of the potential configuration, and at any other position x, they depend only on the potential to the left of x. Furthermore, they depend on the potential in such a way, that if the potential has the property that its value at each point on the line is independent of the value at all other points, then the values of z and U_1 constitute a Markoff process as x goes from 0 to L. Consequently, one can write down an "equation of motion" for the joint probability distribution of z and U_1, which one must then integrate from x = 0 to x = L in order to find the distribution at x = L. An important mathematical simplification is possible because the nature of the equation of motion enables one to work with the zeroth, first, and second moments with respect to U_1 of the joint distribution, for each value of z, rather than the distribution itself. When one is interested in the case of very large L, it is only necessary to find the asymptotic form, for large x, of these moments, and further simplification results.

The calculation of two-particle functions is similar in principle to the calculation of A(k,E), but the variable z is replaced by two variables, z and z′.

In Section 1, A(k,E) is found for a Schrödinger particle in a potential whose fluctuations, as a function of position, may be described as "white Gaussian noise". Such a potential can arise as the potential due to a random array of point scatterers in the limit of infinite density of scatterers, or as a deformation potential due to thermal fluctuations of a continuous, classical, harmonic elastic string. The particle may be an electron or an exciton in the effective mass approximation. The total density of states for this model can be found by the method of Frisch and Lloyd$^{1)}$, and as shown in Appendix B of the present paper, can be expressed analytically in terms of Airy functions. The spectral density, A(k,E), is expressed, for each value of k and E, in terms of the solution of an ordinary differential equation, and has been computed numerically for several values of k and a range of values of E. The exact values of the spectral density are compared with the results of a self-consistent Green's function approximation in which one sums a selected set of diagrams in the perturbation series. The asymptotic forms for A(k,E) are found analytically for fixed k, with $E \rightarrow \pm \infty$, and for fixed E, with $k \rightarrow \infty$. At the end of Section 1, the generalization of the procedure for finding A(k,E) to handle Schrödinger particles in other random potentials is briefly discussed.

In Section 2, we discuss applications of the method to a model of an exciton or an electron in an energy band of finite width, in a lattice perturbed by thermal fluctuations. Here the position of the particle is restricted to a discrete set of lattice sites, and the Hamiltonian has terms which connect nearest neighbor sites, as well as terms diagonal in the position of the particle. The spectral density for the problem is given in terms of the solutions of a pair of integral equations in one variable. These have been solved numerically for several values of the parameters involved, and have been plotted to show the transition from the case of infinite band width (Section 1) to the case of zero band width.

In Section 3, we discuss the phonon spectral density for a chain of random mass, with a harmonic interaction between nearest neighbors. The equations derived are similar to those of Section 2.

Finally, in Section 4, we illustrate applications to two-particle Green's functions by deriving the equations for the frequency dependent conductivity of a system of non-interacting electrons in the white Gaussian noise potential of Section 1, and by briefly discussing a model for inter-band optical transitions in a non-metal. The two-particle functions are expressed in terms of a pair of partial differential equations in two variables. No numerical examples have been calculated for Sections 3 and 4.

1. SCHRÖDINGER PARTICLES

White Gaussian noise potential. We wish to find the spectral density for a particle on the line segment $0 \leq x \leq L$, obeying the Hamiltonian

$$H = \frac{-\hbar^2}{2m^*} \frac{d^2}{dx^2} + V(x) \quad , \tag{1.1}$$

where V is a random potential described by a Gaussian statistical distribution with the expectation values

$$\langle V(x)\rangle = 0 \quad , \tag{1.2}$$

$$\langle V(x)V(x')\rangle = \frac{1}{2} D\ \delta(x-x') \quad , \tag{1.3}$$

where D is a constant and δ is the Dirac δ-function. The wave functions are assumed to satisfy boundary conditions of the form

$$\frac{d\psi}{dx}(0) = z_0\ \psi(0) \quad , \tag{1.4}$$

$$\frac{d\psi}{dx}(L) = z_L\ \psi(L) \quad , \tag{1.5}$$

where z_0 and z_L are arbitrary real constants.

The potential V is described as white Gaussian noise because its Fourier amplitudes have a Gaussian distribution with standard deviations independent of the frequency, and with no correlations between the amplitudes at different frequencies. Because a Gaussian distribution of any number of variables is completely described by its first and second moments, equation (1.3) implies that the potential at any point is completely independent of the potentials at all other points.

The white Gaussian noise potential may arise from a deformation potential on an infinitely massive continuous string. Let the deformation potential be given by

$$V(x) = V_0\ dR(x)/dx \quad , \tag{1.6}$$

where R(x) is the displacement from equilibrium of the point x on the string. We assume that the string obeys Hooke's law exactly with elastic modulus B. Then according to classical statistical mechanics, the potential V has a Gaussian white noise distribution with the constant D given, at temperature T, by

$$D = 2V_0^2 k_B T/B \,, \tag{1.7}$$

where k_B is Boltzmann's constant.

An alternate interpretation of V is the potential arising, in the high density limit, from the model used by Frisch and Lloyd1) for an impurity band -- a set of δ-function potentials of fixed magnitude, distributed at random on the line. In the high density limit, the fluctuations about the average potential have a Gaussian white noise distribution with

$$D = 2nv_0^2 \,, \tag{1.8}$$

where v_0 is the coefficient of the δ-function potential and n is the number of scatterers per unit length.

The spectral density for a one-dimensional Schrödinger particle in a random potential is defined by

$$A(k,E) \equiv \frac{1}{L}\langle \Sigma_i \, |\int_0^L e^{ikx} \psi_i(x)\, dx|^2 \, \delta(E-E_i)\rangle \,, \tag{1.9}$$

where E_i and ψ_i are the energy and wave function of the i^{th}

eigenstate of the Hamiltonian. (Throughout this paper we use angular brackets $\langle \dots \rangle$ to indicate an average over the statistical ensemble.) The total density of states at energy E is defined by

$$\rho(E) = L^{-1} \langle \Sigma_i \ \delta(E-E_i) \rangle \quad . \qquad (1.10)$$

The spectral density is normalized so that

$$\int_{-\infty}^{\infty} A(k,E) \ dE = 1 \quad , \qquad (1.11)$$

$$(2\pi)^{-1} \int_{-\infty}^{\infty} A(k,E) \ dk = \rho(E) \quad . \qquad (1.12)$$

The spectral density is equal to - $1/\pi$ times the imaginary part of the Green's function $G(k,E)$ for the particle at energy E and wave vector k.[9)]

In the problem we are considering, it is always possible to choose units of length, time, and mass, such that $\hbar = m^* = D = 1$; in the remainder of this section we shall assume this has been done. To obtain results in any other system of units, it is necessary to substitute for E, in the expressions given below, the energy divided by the unit of energy, $\varepsilon_0 = (D^2 \ m^* \ \hbar^{-2})^{\frac{1}{3}}$, and to substitute for k and L^{-1}, the wave vector and inverse crystal size divided by the unit of reciprocal length, $\kappa_0 = (D \ m^{*2} \ \hbar^{-4})^{\frac{1}{3}}$. In addition, the expressions for the spectral density must be multiplied by the overall factor ε_0^{-1}, while the total density of states must be multiplied by $\varepsilon_0^{-1} \ \kappa_0$.

Procedure. For each potential configuration in the ensemble of possible configurations, we define the function $\varphi(x;E)$ to be the unique solution of the second order differential equation

$$-\frac{1}{2}\frac{\partial^2}{\partial x^2}\varphi + V(x)\,\varphi = E\varphi \quad , \qquad (1.13)$$

with the initial conditions

$$\varphi(0;E) = 1 \quad , \qquad (1.14)$$

$$\frac{\partial\varphi}{\partial x}(0;E) = z_0\,\varphi(0;E) \quad . \qquad (1.15)$$

Note that although φ obeys the Schrödinger equation for energy E, it will not be an energy eigenstate unless it also obeys the boundary condition $\frac{\partial\varphi}{\partial x}(L;E) = z_L\,\varphi(L;E)$. Furthermore, φ will not, in general, be properly normalized on the interval $0 \leq x \leq L$. We also define the four functions

$$z(x;E) \equiv \frac{\partial\varphi}{\partial x}(x;E)/\varphi(x;E) \quad , \qquad (1.16)$$

$$U_1(x;E) \equiv \Big[\int_0^x e^{ikx'}\,\varphi(x';E)\,dx'\Big]/e^{ikx}\,\varphi(x;E) \quad , \qquad (1.17)$$

$$U_2(x;E) \equiv \Big[\int_0^x \varphi(x';E)^2\,dx'\Big]/\varphi(x;E)^2 \quad , \qquad (1.18)$$

$$U_3(x;E) \equiv \frac{\partial z}{\partial E}(x;E) \quad . \qquad (1.19)$$

From (1.16) and (1.13) we find that $z(x;E)$ obeys the "equation of motion"

$$\frac{\partial z}{\partial x} = \left[\varphi \frac{\partial^2\varphi}{\partial x^2} - \left(\frac{\partial\varphi}{\partial x}\right)^2\right] \Big/ \varphi^2$$

$$= - z^2 - 2E + 2V(x) \quad . \tag{1.20}$$

Similarly, U_1 and U_2 obey

$$\frac{\partial U_1}{\partial x} = 1 - zU_1 - ikU_1 \quad , \tag{1.21}$$

$$\frac{\partial U_2}{\partial x} = 1 - 2zU_2 \quad . \tag{1.22}$$

Differentiating both sides of Eq. (1.20) with respect to E, we find

$$\frac{\partial U_3}{\partial x} = - 2 - 2zU_3 \quad . \tag{1.23}$$

At $x = 0$ we have the initial conditions $z = z_0$ and $U_1 = U_2 = U_3 = 0$. If x_n is a point such that $\varphi(x_n;E) = 0$, then the quantities z, U_1, U_2, and U_3 all become infinite at $x = x_n$. However, the four quantities $(x-x_n)z$, $(x-x_n)U_1$, $(x-x_n)^2U_2$, and $(x-x_n)^2U_3$ are continuous in the neighborhood of x_n. With these conditions, the four differential equations (1.20)-(1.23) uniquely determine z, U_1, U_2, and U_3 for all x. Comparison of equations (1.22) and (1.23) establishes that, for all x,

$$U_3(x;E) = - 2U_2(x;E) \quad . \tag{1.24}$$

Since U_2 is greater than zero, for $x > 0$, it follows that U_3 is less than zero.

For each potential configuration, the energy, E_i, of the i^{th} eigenstate, is the i^{th} value of E which satisfies the equation $z(L;E) = z_L$. Hence,

$$\Sigma_i \ \delta(E-E_i) = \delta[z_L - z(L;E)] \left| \frac{\partial z}{\partial E} (L,E) \right| . \qquad (1.25)$$

It follows that

$$A(k,E) = \frac{1}{L} \left\langle \frac{|\int_0^L \varphi(x;E) \ e^{ikx} \ dx \ |^2}{\int_0^L \varphi(x;E)^2 \ dx} \ \Sigma_i \ \delta(E-E_i) \right\rangle$$

$$= \frac{1}{L} \left\langle \frac{| \ U_1(L;E) \ |^2}{U_2(L;E)} \ | \ U_3(L;E) \ | \ \ \delta[z_L - z(L;E)] \right\rangle$$

$$= 2L^{-1} \langle \ | \ U_1(L;E) \ |^2 \ \delta[z - z(L;E)] \rangle \ . \qquad (1.26)$$

Let us restrict ourselves, temporarily, to the case of $k = 0$, in order to avoid complications due to the presence of complex numbers. The joint probability distribution of z and U_1, at the point x, is defined by

$$P(z,U_1;x) \equiv \langle \ \delta[z - z(x;E)] \ \delta[U_1 - U_1(x;E)] \rangle \ . \qquad (1.27)$$

The spectral density is given by

$$A(0,E) = 2L^{-1} \int_{-\infty}^{\infty} U_1^{\ 2} \ P(z_L,U_1;L) \ dU_1 \ . \qquad (1.28)$$

The spectral density would be determined if one knew the probability distribution of z and U_1 at $x = L$. The distribution at $x = 0$ is known:

$$P(z,U_1;0) = \delta(z-z_0) \ \delta(U_1) \ . \qquad (1.29)$$

If we can find and solve an "equation of motion" for the probability distribution, as x moves from left to right on the line, we will be able to obtain the spectral density. If the potential V(x) were absent in equation (1.20) the probability distribution would obey the simple "flow" equation

$$\frac{\partial P}{\partial x} = - \frac{\partial}{\partial z} \left(\frac{\partial z}{\partial x} P\right) - \frac{\partial}{\partial U_1} \left(\frac{\partial U_1}{\partial x} P\right)$$

$$= \left[\frac{\partial}{\partial z} (z^2+2E) + \frac{\partial}{\partial U_1} (zU_1-1)\right] P \quad .$$

The random potential V(x) causes a "random walk" of the quantity z, with $\langle [z(x+dx;E) - z(x;E)]^2 \rangle = 2dx$. This adds a diffusion term $\partial^2 P/\partial z^2$ to the equation of motion:

$$\frac{\partial P}{\partial x} = \left[\frac{\partial^2}{\partial z^2} + \frac{\partial}{\partial z} (z^2+2E) + \frac{\partial}{\partial U_1} (zU_1-1)\right] P \quad . \qquad (1.30)$$

Equation (1.30) has precisely the form of the Fokker-Planck equation, and is exact when V(x) has the form of white Gaussian noise.10)

The distribution of z and U_1 obeys boundary conditions at infinity which are determined by the behavior of z and U_1 at the zeros of φ. Together with these boundary conditions, equations (1.29) and (1.30) determine $P(z,U_1;x)$ for all x. The solution of a partial differential equation such as (1.30) involves formidable numerical computations, however, and it is fortunate that several simplifications can be made.

We define the three functions $P_s(z;x)$, $(s=0,1,2)$, by

$$P_s(z;x) \equiv \langle U_1(x;E)^s \, \delta[z - z(x;E)] \rangle$$

$$= \int_{-\infty}^{\infty} P(z,U_1;x) \, U_1{}^s \, dU_1 \quad . \qquad (1.31)$$

The function $P_0(z;x)$ is just the probability distribution of $z(x;E)$, while P_1 and P_2 are the first and second moments with respect to U_1 of the joint distribution of z and U_1. These functions obey the equations of motion

$$\frac{\partial P_0}{\partial x} = \left[\frac{\partial^2}{\partial z^2} + \frac{\partial}{\partial z} (z^2+2E)\right] P_0 \quad , \qquad (1.32)$$

$$\frac{\partial P_1}{\partial x} = \left[\frac{\partial^2}{\partial z^2} + \frac{\partial}{\partial z} (z^2+2E) - z\right] P_1 + P_0 \quad , \qquad (1.33)$$

$$\frac{\partial P_2}{\partial x} = \left[\frac{\partial^2}{\partial z^2} + (z^2+2E) \frac{\partial}{\partial z}\right] P_2 + 2P_1 \quad , \qquad (1.34)$$

with the boundary conditions

$$\lim_{z\to +\infty} z^{2-s} P_s = \lim_{z\to -\infty} z^{2-s} P_s \quad . \qquad (1.35)$$

Equation (1.35) is derived from the properties of z and U_1 at the nodes of φ, where z crosses from $-\infty$ to ∞.

At the point $x = 0$, we have

$$P_0(z;0) = \delta(z-z_0) \quad , \qquad (1.36)$$

$$P_1(z;0) = P_2(z;0) = 0 \quad . \qquad (1.37)$$

The differential equations (1.32)-(1.34), together with the boundary conditions, determine P_s, for all x, and are much easier to solve numerically than the equation of motion for $P(z,U_1;x)$. The spectral density is given by

$$A(k,E) = 2L^{-1}\, P_2(z_L;L) \quad . \tag{1.38}$$

When k does not equal zero, certain changes must be made. The definition of P_2 must be modified to

$$P_2(z;x) = \langle\, |U_1(x;E)|^2\, \delta[z - z(x;E)] \rangle \quad . \tag{1.39}$$

Equations (1.33) and (1.34) are replaced by

$$\frac{\partial P_1}{\partial x} = \left[\frac{\partial^2}{\partial z^2} + \frac{\partial}{\partial z}\,(z^2+2E) - z - ik\right] P_1 + P_0 \quad , \tag{1.40}$$

$$\frac{\partial P_2}{\partial x} = \left[\frac{\partial^2}{\partial z^2} + (z^2+2E)\,\frac{\partial}{\partial z}\right] P_2 + 2 \text{ Real } P_1 \tag{1.41}$$

The rest of equations (1.31)-(1.38) still apply.

If we are interested in the properties of macroscopic systems, we only need to find the spectral density in the limit L → ∞; this makes still further simplification possible. In Appendix A, we give physical arguments to show that for large x, the P_s have asymptotic forms

$$P_0(z;x) \sim p_0(z) \quad , \tag{1.42}$$

$$P_1(z;x) \sim p_1(z) \quad , \tag{1.43}$$

$$P_2(z;x) \sim Cx + f(z) \quad , \tag{1.44}$$

where p_0, p_1, f, and the constant C are independent of x. The spectral density is given, for large L, by

$$A(k,E) = 2C \quad . \tag{1.45}$$

It is independent of the length L and independent of the boundary conditions z_0 and z_L imposed on the particle wave functions.

The functions p_0 and p_1 obey equations (1.32) and (1.40), respectively, with the left-hand sides set equal to zero:

$$\left[\frac{\partial^2}{\partial z^2} + \frac{\partial}{\partial z}\,(z^2+2E)\right] p_0 = 0 \quad , \tag{1.46}$$

$$\left[\frac{\partial^2}{\partial z^2} + \frac{\partial}{\partial z}\,(z^2+2E) - z - ik\right] p_1 + p_0 = 0 \quad . \tag{1.47}$$

The boundary conditions of (1.35) still apply, and p_0 satisfies the normalization

$$\int_{-\infty}^{\infty} p_0(z)\,dz = 1 \quad , \tag{1.48}$$

which is imposed by the fact that $P_0(z;x)$ is a probability distribution. If one substitutes (1.43) and (1.44) in Eq. (1.41), multiplies both sides of the equation by $p_0(-z)$, and integrates with respect to z, one obtains

$$A(k,E) = 4\int_{-\infty}^{\infty} p_0(-z)\ \mathrm{Real}\ p_1(z)\,dz \quad . \tag{1.49}$$

The simple form of (1.49) arises from the fact that the differential operator on the left-hand side of (1.46) is the adjoint, except for a change of the sign of z, of the operator on the right-hand side of (1.41).

Numerical calculations. Equations (1.46)-(1.49) reduce the problem of finding the spectral density to the solution of two ordinary differential equations and one numerical quadrature, tasks which are easily handled by an electronic computer. The results of numerical computations of A(k,E) are plotted, for several values of k, in Fig. 1. In Fig. 2, the values of A(k,E) are compared with the approximate values obtained by the "$\Gamma = 1$ approximation" of Suna,11) or equivalently, by "approximation number 3" of Klauder.12) These are self-consistent Green's function approximations, which, in effect, sum an infinite set of Feynman diagrams in the perturbation theory expansion of the Green's function, G(k,E), as indicated in Fig. 3. The resulting equations for G are

$$G(k,E) = [E - \tfrac{1}{2} k^2 - \Sigma(E)]^{-1} \quad , \qquad (1.50)$$

$$\Sigma(E) = - 2^{-3/2} [\Sigma(E) - E]^{-\frac{1}{2}} \quad , \qquad (1.51)$$

The approximate method, as expected, gives good agreement with the exact results for positive energies, but is not very accurate for negative energies. The low-energy tail of the spectral density is entirely absent, in the self-consistent approximation, as (1.51) leads to Green's functions which are real at energies less than $- \frac{3}{4} \sqrt[3]{2}$ ($\approx$ - .9449).

Density of states. The total density of states, $\rho(E)$, is somewhat easier to find than A(k,E); for an infinite line it may be found directly from the function $p_0(z)$. By using the fact that the number of energy eigenstates with energy less than E, in any particular potential configuration, is equal to the number of nodes in the function $\varphi(x;E)$, within a possible error of ± 1, Frisch and Lloyd$^{1)}$ show that

$$\lim_{z\to \pm\infty} z^2 p_0(z) = N(E) \quad , \tag{1.52}$$

where N(E) is the cumulative density of states defined by

$$N(E) \equiv \int_{-\infty}^{E} \rho(E') \, dE' \quad . \tag{1.53}$$

The function $\rho(E)$ is obtained from N(E) by differentiation. A plot of N(E) for a white Gaussian noise potential may be found in reference 1, Fig. 6.

The function $\rho(E)$ can also be expressed in terms of the function $p_0(z)$ at the single energy E, by use of the methods of the present paper. It is easily seen that

$$\rho(E) = L^{-1} \langle \, | U_3(L;E) | \, \delta[z_L - z(L;E)] \rangle \quad . \tag{1.54}$$

If one studies the equation of motion for the function $\langle U_3(x;E) \, \delta[z - z(x;E)] \rangle$ in the same manner that we studied the equation of motion for $P_2(z;x)$, one finds that for large L,

$$\rho(E) = 2\int_{-\infty}^{\infty} p_0(-z) \, p_0(z) \, dz \quad . \tag{1.55}$$

Analytic results. It is interesting to see what properties of the eigenstates of the Gaussian white noise potential can be derived analytically from equations (1.46)-(1.49). The general solution of the differential equation (1.46) can be written in integral form. The solution which is bounded as $z \to -\infty$ is

$$p_0(z) = C\ s(z) \quad , \tag{1.56}$$

where

$$s(z) \equiv \exp(-\tfrac{1}{3} z^3 - 2Ez) \int_{-\infty}^{z} \exp(\tfrac{1}{3} u^3 + 2Eu)\ du \quad . \tag{1.57}$$

The constant C is determined by the normalization condition, Eq. (1.48). This gives

$$C = \left[\int_{-\infty}^{\infty} s(z)\ dz\right]^{-1} \quad . \tag{1.58}$$

When (z^2+2E) is large compared to 1, s(z) may be expanded as

$$s(z) \sim (z^2+2E)^{-1} + 2z(z^2+2E)^{-3} + \ldots \tag{1.59}$$

It follows that

$$\lim_{z \to \pm\infty} z^2\ s(z) = 1 \quad , \tag{1.60}$$

and from (1.52) we see that the constant C is just the cumulative density of states, N(E). Hence, substituting (1.57) in (1.58), we find after changing variables and performing one integration,

$$N(E) = \left[\int_{0}^{\infty} \pi^{\frac{1}{2}}\ u^{-\frac{1}{2}} \exp(-\tfrac{1}{12} u^3 - 2Eu)\ du\right]^{-1} \quad , \tag{1.61}$$

same time the expansion for p_0. We find

$$p_1(z) \sim -N(E)\left[\frac{z}{2E(z^2+2E)} + \frac{z^2-4E}{3E(z^2+2E)^3} + \dots\right] . \qquad (1.65)$$

Substitution of the expansions for p_0 and p_1 in (1.49) gives the asymptotic form for the spectral density:

$$A(0,E) \sim 2^{-3/2}\,\pi^{-1}\,E^{-5/2} \quad , \qquad \text{for } E \gg 0 \quad . \qquad (1.66)$$

This is in agreement with the results of perturbation theory.

The form of $A(0,E)$ when $E \ll 0$ is considerably harder to obtain. One may proceed by first finding two independent solutions, in the limit $E \ll 0$, of the homogeneous equation

$$\left[\frac{d^2}{dz^2} + \frac{d}{dz}\,(z^2+2E) - z\right] f(z) = 0 \quad . \qquad (1.67)$$

From the two solutions of the differential equation one can construct the Green's function for the differential operator on the right hand side, with the boundary condition

$$\lim_{z\to+\infty} z\,f(z) = \lim_{z\to-\infty} z\,f(z) \quad . \qquad (1.68)$$

Applying the Green's function to the known function $p_0(z)$, one obtains the function $p_1(z)$, and thence, the asymptotic form of $A(0,E)$.

The form of the solutions of (1.67) can best be understood by writing which is a result obtained by Frisch and Lloyd. In Appendix B we show, by working with the Fourier transform of p_0, that the cumulative density of states can also be expressed as

$$N(E) = \pi^{-2} \{[Ai(-2E)]^2 + [Bi(-2E)]^2\}^{-1} \quad , \qquad (1.62)$$

where Ai and Bi are the well known Airy functions.$^{13)}$

From either (1.61) or (1.62) we may establish the asymptotic forms:

$$N(E) \sim (2E)^{\frac{1}{2}} \pi^{-1} \quad , \qquad \text{for } E \gg 0 \ , \quad (1.63)$$

$$N(E) \sim |2E|^{\frac{1}{2}} \pi^{-1} \exp(-\tfrac{4}{3}|2E|^{3/2}) \quad , \qquad \text{for } E \ll 0 \ . \quad (1.64)$$

Equation (1.63) is just the result one would obtain in the absence of the random potential, and is the result one expects from perturbation theory. Equation (1.64), however, cannot be obtained by such simple methods.

In order to find A(k,E), it is necessary to know $p_1(z)$ as well as p_0. Unfortunately, no explicit solution of Eq. (1.47) has been found. It has been possible, however, to find simple analytic expressions for the asymptotic forms of the spectral density, when one of the variables k and E remains fixed, and the other approaches infinity. Let us first consider the asymptotic forms of A(0,E) when E approaches $\pm\infty$. When $E \gg 0$, p_0 can be expanded in the form of Eq. (1.59). We may obtain a similar asymptotic expansion for $p_1(z)$ by treating the diffusion term in (1.47) as a small perturbation, and expanding p_1 in powers of this perturbation, using at the

$$f(z) \equiv \exp(-\tfrac{1}{6} z^3 - Ez)\, u(z) \quad . \tag{1.69}$$

Equation (1.66) then assumes the more familiar form,

$$\left[-\frac{d^2}{dz^2} + \frac{1}{4}(z^2+2E)^2\right] u(z) = 0 \quad , \tag{1.70}$$

which is the Schrödinger equation for a particle in a certain quartic potential. For $E \ll 0$, $u(z)$ may be approximated by the W.K.B. method. The points $z = \pm|2E|^{\frac{1}{2}}$ are second order classical turning points, and the appropriate connecting functions must be used in the vicinity of these points.14) The result of these calculations is that the spectral density has the asymptotic form:

$$A(0,E) \sim 2\pi\,|2E|^{\frac{1}{2}} \exp(-\tfrac{4}{3}|2E|^{3/2}), \qquad \text{for } E \ll 0. \tag{1.71}$$

Although the asymptotic forms for $A(k,E)$ given by (1.66) and (1.71) were derived for $k = 0$, it is not difficult to verify that the same results hold for $k \neq 0$, provided that k is held constant while $|E|$ becomes sufficiently large. The asymptotic form, when $E \to -\infty$ and $k/|E|^{\frac{1}{2}}$ approaches a finite, non-zero constant, is also of interest. It may be obtained by a procedure very similar to that leading to Eq. (1.71) for the case of $k = 0$. The result is that $A(k,E) \sim A(0,E)\,\text{sech}^2(\pi k/|8E|^{\frac{1}{2}})$.

The asymptotic form, when $k \to \infty$ while E is held fixed, can be found by expanding the solution of Eq. (1.47) for $p_1(z)$ in powers of k^{-1}. The fourth term in the expansion is the first which contributes to the integral (1.49) for $A(k,E)$, and using the relation (1.55), it can be shown that for sufficiently large k,

$$A(k,E) \sim 2\, k^{-4}\, \rho(E) \quad . \tag{1.72}$$

The asymptotic form of the spectral density, for large k, may also be obtained by perturbation-theoretic arguments.

Other potentials. The essential property of the equations of motion for z and U_1 which permitted us to write down an equation of motion for the joint probability distribution $P(z,U_1;x)$ was that the quantities $z(x;E)$ and $U_1(x;E)$ form a Markoff process as x moves from left to right along the line. If, instead of the Gaussian white noise potential we had used a model such as Frisch and Lloyd's, of δ-function potentials scattered, independently, at random on the line, the Markoff property would still hold and the procedures of this section could be carried out. If the "impurity" potentials have non-zero range, however, $z(x;E)$ and $U_1(x;E)$ are not a Markoff process. On the other hand, if one considers any model in which various kinds of "impurity" potentials of finite spatial extent occur in random sequence on a line, with a given distribution of possible distances between successive impurity potentials, and zero probability of overlap between two potentials, one can obtain a discrete Markoff process by considering the values of z and U_1 at the right-hand side of each impurity potential.

The condition which enabled us to work with the functions $P_s(z;x)$, instead of the joint distribution of z and U_1, was that the equation of motion for U_1 was linear in

U_1. This condition also applies to the more general model of the preceding paragraph. It follows that the spectral density of such a system is accessible to the general methods of this paper. The mathematical details of such a calculation are very similar to the procedures to be discussed in Sections 2 and 3 of this paper, and we shall not examine them further.

2. DISCRETE PARTICLES

<u>The model</u>. As another application of the general method we calculate the spectral density for a model of a particle in an energy band in a discrete lattice. We may imagine the particle to be a conduction electron or a tightly bound exciton in a chain of N identical atoms of infinite mass, the random part of the particle Hamiltonian arising from thermal fluctuations in the distances between neighboring atoms. The electronic state of the system is described by giving the probability amplitude $\psi(m)$ for finding the particle at each lattice site, $1 \leq m \leq N$. We assume that the particle Hamiltonian, H, is of the form

$$H\psi(m) \equiv K_m\psi(m) + M_{m-1}\psi(m) + M_m\psi(m+1), \qquad \text{for } 2 \leq m \leq N-1 \quad . \tag{2.1}$$

The diagonal matrix element, K_m, is assumed to depend linearly on h_m and h_{m-1}, the deviations from equilibrium of the distances between atom m and its nearest neighbors, atom m + 1 and atom m - 1, respectively. The off-diagonal element M_m is assumed to be a linear function of the distance between atoms m and m + 1. Thus we may write

$$K_m \equiv E_0 + \alpha h_m + \alpha h_{m-1} \quad , \tag{2.2}$$

$$M_m \equiv M + \beta h_m \quad . \tag{2.3}$$

We assume all quantities in (2.2) and (2.3) to be real.

If the atoms of the lattice are connected with springs between nearest neighbors only, we know from classical statistical mechanics that the distributions of the various h_m are statistically independent. If the springs are perfectly harmonic, then the distribution of each h_m is a Gaussian distribution with mean zero and variance $k_B Ta/B$, where T is the temperature, a is the equilibrium interatomic distance, and B is the elastic modulus of the chain.

The spectral density is defined as

$$A(q,E) \equiv N^{-1} \left\langle \sum_i \left| \sum_{m=1}^{N} e^{-iqm} \, \psi_i(m) \right|^2 \delta(E-E_i) \right\rangle \quad , \tag{2.4}$$

where E_i and ψ_i are the i^{th} eigenvalue and eigenfunction of the Hamiltonian, the eigenfunction being normalized by

$$\sum_{m=1}^{N} | \psi_i(m) |^2 = 1 \ . \tag{2.5}$$

To completely specify the Hamiltonian, (2.1), we must specify the values of $H\psi(m)$ at the end points m = 1 and m = N. For a perfect lattice ($h_m \equiv 0$), it is convenient to assume periodic boundary conditions. In that case the eigenstates of the Hamiltonian are periodic waves,

$$\psi_q(m) = N^{-\frac{1}{2}} e^{iqm} \quad , \tag{2.6}$$

for $q = 0, \pm 2\pi N^{-1}, \pm 4\pi N^{-1}$, etc., with energies

$$E_q = E_0 + 2M \cos q \quad . \tag{2.7}$$

For our present purposes, we shall not use periodic boundary conditions, but shall specify the boundary conditions by defining quantities $\psi(0)$, $\psi(N+1)$, h_0 and h_N to be substituted in equation (2.1) at the endpoints. We define

$$\psi(0) \equiv y_0 M^{-1} \psi(1) \quad , \tag{2.8}$$

$$h_0 \equiv 0 \quad , \tag{2.9}$$

$$\psi(N+1) \equiv (M+\beta h_N)(y_N-\alpha h_N)^{-1} \psi(N) \quad , \tag{2.10}$$

where y_0 and y_N are real fixed constants. We shall not fix the quantity h_N, however, but shall consider a statistical ensemble of crystals, in which h_N is a random variable which is statistically independent of the other h_m and has the same probability distribution as each of the h_m. When the number of atoms is large, of course, the spectral density will be independent of the choice of boundary condition.

The relation between the discrete Hamiltonian of the present section and the Schrödinger Hamiltonian of Section 1 may be seen if one assumes that the wave functions of interest are slowly varying functions of m. The finite difference operator H can then be approximated by a differential operator, which, for the case of a perfect lattice, is the Schrödinger Hamiltonian for a free particle with effective mass $m^* = -2\hbar^2/Ma^2$. For the imperfect lattice, we have the additional terms αh_m and βh_m of equations (2.2) and (2.3). The first of these leads to a deformation potential, while the second leads to a combination deformation potential and local change of effective mass. If the wave functions are sufficiently slowly varying, and the perturbation sufficiently weak, the local change of effective mass will be negligible compared to the deformation potential. The value of the deformation potential coefficient V_0, as defined by Eq. (1.6) is given for the present model by

$$V_0 = (2\alpha+2\beta)a \quad . \tag{2.11}$$

In the limit of slowly varying wave functions the effect of the deformation potential is the same as that of a Gaussian white noise potential, with coefficient D given, as for the continuous string, by

$$D = 2V_0 k_B T/B \quad . \tag{2.12}$$

Although the equations for A(q,E) given below are derived for general values of the parameters, numerical computations have been carried out only for the case of β and q equal to zero. To facilitate comparison with the results of Section 1, the units of length, time, and mass were again chosen such that $\hbar = m^* = D = 1$, with D defined by (2.12) and (2.11). Also to facilitate comparisons, the origin of the energy scale was chosen to be the edge of the unperturbed energy band, so that $E_0 + 2M = 0$. The dimensionless parameter which controls the shape of the spectral density is the lattice constant a, expressed in terms of the unit of length, $\kappa_0^{-1} = (Dm^{*2}\hbar^{-4})^{-\frac{1}{3}}$.

The function A(0,E) is plotted, for several values of the lattice parameter a, in Fig. 4. The value a = 0 corresponds to the continuous model of Section 1. The limit $a \gg \kappa_0^{-1}$ corresponds to an energy band width $(|4M| = 2\hbar^2 |m^*|^{-1}a^{-2})$ which is small compared with the root-mean-square deformation potential. In such a system, the eigenstates are localized at a single lattice site, m, and the energy is shifted by the deformation potential at that site, $\alpha(h_m + h_{m-1})$. This leads to a spectral density, independent of the wave-number q, which is a Gaussian distribution with variance equal to D/4a.15,16) When a is not large compared to κ_0^{-1}, the spectral density still has the Gaussian form, $\text{const.}\exp(-2(E-E_0)^2 a/D)$, whenever the magnitude of $(E-E_0)$ is large compared to the band width. Note that the center of this Gaussian is the center of the unperturbed band. In Fig. 4, the curve corresponding to a = 8 is almost undistinguishable from a Gaussian.

Procedure. For each energy, and each lattice configuration, we define a function $\varphi(m)$, such that $\varphi(0) = 1$, $\varphi(m)$ obeys the homogeneous "initial condition" (2.8), and φ obeys the difference equation

$$M_m\ \varphi(m+1) + M_{m-1}\ \varphi(m-1) + (K_m - E)\ \varphi(m) = 0 \quad . \qquad (2.13)$$

We define

$$y(m) \equiv (M+\beta h_{m-1})\ \varphi(m-1)/\varphi(m) + \alpha h_{m-1} \quad . \qquad (2.14)$$

The "initial condition" (2.8) implies that

$$y(1) = y_0 \quad . \qquad (2.15)$$

The final condition (2.10) means that E is an eigenvalue of the Hamiltonian, if and only if

$$y(N+1) = y_N \quad . \qquad (2.16)$$

We also define

$$U_1(m) \equiv \sum_{m'=1}^{m-1} e^{-iqm'}\ \varphi(m')/e^{-iqm}\ \varphi(m) \quad , \qquad (2.17)$$

$$U_2(m) \equiv \sum_{m'=1}^{m-1} \varphi(m')^2/\varphi(m)^2 \quad , \qquad (2.18)$$

$$U_3(m) \equiv \frac{\partial}{\partial E}\ y(m) \quad . \qquad (2.19)$$

The functions y and U obey the equations

$$y(m+1) = \alpha h_m - (M+\beta h_m)^2\ [y(m) + \alpha h_m - E + E_0]^{-1} \quad , \qquad (2.20)$$

$$U_1(m+1) = e^{iq}\ [U_1(m) + 1][y(m+1) - \alpha h_m]\ (M+\beta h_m)^{-1} \quad , \qquad (2.21)$$

$$U_2(m+1) = [U_2(m) + 1][y(m+1) - \alpha h_m]^2\ (M+\beta h_m)^{-2} \quad , \qquad (2.22)$$

$$U_3(m+1) = [U_3(m) - 1][y(m+1) - \alpha h_m]^2\ (M+\beta h_m)^{-2} \quad . \qquad (2.23)$$

The three functions $U(m)$ are equal to zero when $m = 1$. Hence, comparing (2.22) and (2.23) we see that for all m,

$$U_2(m) = -U_3(m) \quad . \tag{2.24}$$

The spectral density is then given by

$$\begin{aligned} A(q,E) &= N^{-1}\left\langle \frac{|U_1(N+1)|^2}{U_2(N+1)} \, |U_3(N+1)| \, \delta[y_N - y(N+1)]\right\rangle \\ &= N^{-1}\left\langle |U_1(N+1)|^2 \, \delta[y_N - y(N+1)]\right\rangle \quad . \end{aligned} \tag{2.25}$$

We define the functions $P_s(y;m)$ as

$$\begin{aligned} P_s(y;m) &= \langle U_1(m)^s \, \delta[y - y(m)]\rangle, \quad \text{for } s = 0,1 \\ &= \langle |U_1(m)|^2 \, \delta[y - y(m)]\rangle, \quad \text{for } s = 2 \ . \end{aligned} \tag{2.26}$$

These obey equations of motion of the form

$$P_0(y;m+1) = \int_{-\infty}^{\infty} F_0(y,y') \, P_0(y';m) \, dy' \ , \tag{2.27}$$

$$P_1(y;m+1) = e^{iq}\int_{-\infty}^{\infty} F_1(y,y')[P_1(y';m) + P_0(y';m)] \, dy' \ , \tag{2.28}$$

$$P_2(y;m+1) = \int_{-\infty}^{\infty} F_2(y,y')[P_2(y';m) + 2\mathrm{Real}\ P_1(y';m) + P_0(y';m)] \, dy' \ . \tag{2.29}$$

The kernels $F_s(y,y')$ are given, in terms of the probability distribution $p(h)$ obeyed by each of the h_m, by the equation

$$F_s(y,y') = \int \left(\frac{y-\alpha h}{M+\beta h}\right)^s \delta\left[y - \alpha h - \frac{(M+\beta h)^2}{y' - \alpha h - E + E_0}\right] p(h) \, dh \ . \tag{2.30}$$

The behavior of $P_s(y;m)$ for large m may be studied by a procedure very similar to the analysis of the corresponding quantities for the white Gaussian noise potential given in Appendix A. We use the fact that the integral operator on the right-hand side of (2.29) is related by a change of variables to the adjoint of the operator in (2.27), a fact which follows from the relation

$$F_2(y,y') = F_0(E-E_0-y', E-E_0-y) \quad . \qquad (2.31)$$

The functions $P_0(y;m)$ and $P_1(y;m)$ approach functions $p_0(y)$ and $p_1(y)$, independent of m, when m becomes large. These limiting functions may be determined by substituting p_0 and p_1 for P_0 and P_1 on both sides of (2.27) and (2.28), and using the fact that p_0, as a probability distribution, is normalized to have area 1. When m is large, the function $P_2(y;m)$ has the asymptotic form, constant·m + f(y). The resulting spectral density, for large N, is independent of N and y_N, and is given by

$$A(q,E) = \int_{-\infty}^{\infty} p_0(E-E_0-y)[2 \text{ Real } p_1(y) + p_0(y)] \, dy \quad . \qquad (2.32)$$

Thus, the problem of finding the spectral density is reduced to the solution of two one-dimensional integral equations, for p_0 and p_1, and one quadrature.

3. PHONON GREEN'S FUNCTIONS

The similarity between problems involving normal modes of phonons and those involving electronic eigenstates has been emphasized by Schmidt.$^{2)}$ It is not surprising, therefore, that the methods of the previous sections may be used to find phonon Green's functions for certain one-dimensional models. We shall consider here a model in which N atoms on a line are connected to their nearest neighbors by identical harmonic springs with spring constant K. The mass of each atom may be any one of the values M_1, M_2, ...; the probability that mass of the m^{th} atom, μ_m, has the value M_r is w_r, and is independent of all the other masses on the line. The functions we are interested in are correlation functions of the form

$$D(q,\omega) = \int_{-\infty}^{\infty} e^{i\omega t} \langle\langle X_q(t)\, X_q^+(0)\rangle\rangle \, dt \quad , \tag{3.1}$$

where we have used the double angular bracket $\langle\langle \ldots \rangle\rangle$ to indicate the quantum mechanical expectation value for a variable, averaged over the thermal distribution of phonon occupation numbers, as well as over the possible sequences of the different masses. The variables X_q are defined as

$$X_q = N^{-\frac{1}{2}} \sum_{m=1}^{N} e^{-iqm} \lambda_m R_m \quad , \tag{3.2}$$

where R_m is the displacement of the m^{th} atom from equilibrium and λ_m is a real or complex number which depends on the particular type of atom at the m^{th} site. For example, in applications to the one-phonon inelastic scattering of neutrons,17) λ_m would be the scattering length of the m^{th} atom. To each value of the mass, M_r, there is a corresponding value Λ_r, so that $\lambda_m = \Lambda_r$ whenever $\mu_m = M_r$. The operator R_m may be expanded in terms of the normal coordinates Q_i of the crystal as

$$R_m = \Sigma_i \; u_i(m) \; Q_i \quad , \tag{3.3}$$

where $u_i(m)$ is the eigenfunction for the i^{th} normal mode. The function $D(q,\omega)$ may then be expressed as

$$D(q,\omega) = \pi\hbar \, |\omega|^{-1} \, n(\omega) \; A(q, |\omega|) \quad , \tag{3.4}$$

where

$$\begin{aligned} n(\omega) &\equiv [\exp(\hbar\omega/k_BT) - 1]^{-1} + 1, \qquad \text{for } \omega > 0, \\ &\equiv [\exp(\hbar|\omega|/k_BT) - 1]^{-1}, \qquad \text{for } \omega < 0, \end{aligned} \tag{3.5}$$

and the spectral density $A(q,\omega)$ is defined by

$$A(q,\omega) = N^{-1} \left\langle \sum_i \left| \sum_{m=1}^{N} e^{iqm} \, \lambda_m u_i(m) \right|^2 \delta(\omega - \omega_i) \right\rangle , \tag{3.6}$$

where ω_i is the frequency of the i^{th} mode. The eigenfunctions $u_i(m)$ obey the equations

$$Ku_i(m+1) + Ku_i(m-1) - (2K - \mu_m \omega_i^{\,2}) \, u_i(m) = 0 \quad , \tag{3.7}$$

$$\sum_{m=1}^{N} \mu_m u_i(m)^2 = 1 \quad . \tag{3.8}$$

The u_i must obey appropriate homogeneous boundary conditions at the ends of the line, which we shall not specify here.

In order to simplify slightly the equations which follow, we assume that units have been chosen such that the spring constant, K, equals 1.

In the analogy with the procedures of Sections 1 and 2, we define for each frequency $\omega > 0$, and for each of the possible sequences of masses, a function $\varphi(m)$, which has a fixed value at $m = 0$, which obeys the homogeneous boundary condition at the left-hand end of the chain, and which obeys the difference equation of (3.7) with ω and φ substituted for ω_i and u_i. Let us also define

$$y(m) = \varphi(m-1)/\varphi(m) \quad , \tag{3.9}$$

$$U_1(m) = \sum_{m'=1}^{m-1} \lambda_{m'} \, e^{-iqm'} \varphi(m')/e^{-iqm} \varphi(m) \quad , \tag{3.10}$$

$$U_2(m) = \sum_{m'=1}^{m-1} \mu_{m'} \, \varphi(m')^2/\varphi(m)^2 \quad , \tag{3.11}$$

$$U_3(m) = \frac{\partial}{\partial\omega} y(m) \quad . \tag{3.12}$$

These obey the equations,

$$y(m+1) = [2 - \mu_m\omega^2 - y(m)]^{-1} \quad , \tag{3.13}$$

$$U_1(m+1) = e^{iq} \, y(m+1) \, [U_1(m) + \lambda_m] \quad , \tag{3.14}$$

$$U_2(m+1) = y(m+1)^2 \, [U_2(m) + \mu_m] \quad , \tag{3.15}$$

$$U_3(m+1) = y(m+1)^2 \, [U_3(m) + 2\mu_m\omega] \quad . \tag{3.16}$$

From the last two equations we see that

$$U_3(m) = 2\omega U_2(m) \quad . \tag{3.17}$$

If we define $P_s(y;m)$ precisely as in Eq. (2.26), then

$$A(q,\omega) = 2\omega N^{-1} P_2(y_N;N) \quad , \tag{3.18}$$

where we have assumed a boundary condition on the right-hand end of the chain of form $y(N+1) = y_N$. The equations of motion for the P_s are

$$P_0(y;m+1) = y^{-2} \Sigma_r w_r P_0(2-M_r\omega^2-y^{-1};m) \quad , \tag{3.19}$$

$$P_1(y;m+1) = e^{iq}y^{-1} \Sigma_r w_r [P_1(2-M_r\omega^2-y^{-1};m) + \Lambda_r P_0(2-M_r\omega^2-y^{-1};m)] \quad , \tag{3.20}$$

$$\begin{aligned} P_2(y;m+1) = \Sigma_r w_r \{ & P_2(2-M_r\omega^2-y^{-1};m) + 2 \text{ Real}[\Lambda_r P_1(2-M_r\omega^2-y^{-1};m)] \\ & + |\Lambda_r|^2 P_0(2-M_r\omega^2-y^{-1};m)\} \quad . \end{aligned} \tag{3.21}$$

If the functions $P_0(y;m)$ and $P_1(y;m)$ approach continuous limits, $p_0(y)$ and $p_1(y)$, as $m \to \infty$, then these limits can be found by substituting p_s for P_s on both sides of equations (3.19) and (3.20). If furthermore, the function $P_2(y;m)$ has the asymptotic form const$\cdot$m + f(y), as $m \to \infty$, then we may find the spectral density by multiplying both sides of equation (3.21) by $\Sigma_{r'} w_{r'} p_0(2-M_{r'}\omega^2-y)$ and integrating with respect to y. By changing the variable of integration on the right-hand side from y to $Y = 2 - M_r - y^{-1}$, and using the difference equation satisfied by p_0, we find (in the limit $N \to \infty$),

$$A(q,\omega) = 2\omega \int_{-\infty}^{\infty} \Sigma_r w_r p_0(2-M_r-Y) \{2 \text{ Real}[\Lambda_r p_1(Y)] + |\Lambda_r|^2 p_0(Y)\} \, dY \ . \tag{3.22}$$

Unfortunately, the functions $P_s(y;m)$ do not necessarily approach continuous limits as $m \to \infty$, even if one starts with a continuous function for $P_0(y;0)$. Schmidt[2)] showed that, at least in certain cases, $p_0(y)$, if it exists at all, is highly discontinuous, the values of $p_0(y)$ being infinite at a dense set of points. Even if the limit $p_0(y)$ does exist, in these cases, it is not clear that the limit $p_1(y)$ will exist, or that the integral on the right-hand side of (3.22) will exist. In fact, there is reason for believing that $A(q,\omega)$ itself is infinite at a dense set of points, in certain regions of the line $0 < \omega < \infty$, while the integral $\int_0^\omega A(q,\omega')\,d\omega'$ is a continuous function of ω. Numerical computations of $A(q,\omega)$ in these regions of bad behavior is clearly out of the question.

The reason for this difficulty is that we have chosen a discrete set of masses M_r. If we had chosen a continuous distribution of possible masses, so that the sums in equations (3.19)-(3.22) were changed to integrals, then all the limits would have existed and the functions p_s would be continuous. Physically, we expect to be able to approximate a discrete distribution as closely as we desire by a continuous distribution which is sharply peaked about the values of the discrete distribution. If $A(q,\omega)$ is discontinuous for the discrete distribution, we would not expect to be able to calculate it in this manner; but the quantities of real physical interest are averages of the spectral density over a finite spread of ω, such as $(\Delta\omega)^{-1}\int_\omega^{\omega+\Delta\omega} A(q,\omega')\,d\omega'$, and we do expect that, for fixed $\Delta\omega$, such quantities can be calculated as accurately as desired by choosing a continuous distribution sufficiently close to the discrete distribution.

4. TWO-PARTICLE FUNCTIONS

Electrical Conductivity. The methods of the previous sections can be generalized to two particle functions, such as the frequency dependent electrical conductivity of a system of non-interacting electrons in a random potential. The real part of the conductivity, at frequency ω, for a collection of non-interacting, spinless particles of charge e and mass m, is given by$^{18)}$

$$\text{Real } \sigma(\omega) = \frac{\pi e^2}{m^2}\int_{-\infty}^{\infty} \frac{f(\hbar\nu) - f[\hbar(\nu+\omega)]}{\hbar\omega} F(\nu,\nu+\omega)\, d\nu \ , \qquad (4.1)$$

where f is the Fermi function,

$$f(E) \equiv \{\exp[(E-\mu)/k_BT] + 1\}^{-1} \ , \qquad (4.2)$$

and F is defined by

$$F(\nu,\nu') \equiv L^{-1}\left\langle \sum_{ij} |(i\,|\,p\,|\,j)|^2 \,\delta(\nu - \frac{E_i}{\hbar})\,\delta(\nu' - \frac{E_j}{\hbar})\right\rangle . \qquad (4.3)$$

In Eq. (4.3), L is the length of the system, $(i\,|\,p\,|\,j)$ is the matrix element of the momentum operator between the eigenstates i and j of the one-particle Hamiltonian, and E_i and E_j are the energies of the eigenstates; the quantity μ in equation (4.2) is the chemical potential of the electron system. If the real part of the conductivity is known, the imaginary part may be calculated by use of the Kramers-Kronig relations.

As an example, we shall derive the expressions for F when the random potential is the white Gaussian noise potential of Section 1. We again choose units such that $\hbar = m = D = 1$. We define the functions $\varphi(x;E)$ and $z(x;E)$ as in Section 1. We also define a new function

$$W(x;E,E') \equiv \frac{\int_0^x \varphi(x';E) \frac{\partial}{\partial x'} \varphi(x';E')\, dx'}{\varphi(x;E)\, \varphi(x;E')} \quad . \tag{4.4}$$

The equation of motion for W is

$$\frac{\partial W}{\partial x} = z(x;E') - [z(x;E') + z(x;E)]\, W \quad . \tag{4.5}$$

Functions $P_s(z,z';x)$ are defined, for $s = 0,1,2$, by

$$P_s(z,z';x) \equiv \langle W(x;E,E')^s\, \delta[z - z(x;E)]\, \delta[z' - z(x;E')]\rangle \quad . \tag{4.6}$$

The equations of motion for these functions are

$$\frac{\partial P_s}{\partial x} = \left[\frac{\partial^2}{\partial z^2} + 2\frac{\partial^2}{\partial z \partial z'} + \frac{\partial^2}{\partial z'^2} + (z^2+2E)\frac{\partial}{\partial z} + (z'^2+2E')\frac{\partial}{\partial z'} + (2-s)(z+z')\right] P_s + szP_{s-1} \quad . \tag{4.7}$$

(Note that the "diffusion term", $\frac{\partial^2}{\partial z^2} + 2\frac{\partial^2}{\partial z \partial z'} + \frac{\partial^2}{\partial z'^2}$, represents random walk in the $(z+z')$ direction only; the random potential in the equation of motion for $z(x;E)$ is the same as that in the equation for $z(x;E')$.) The boundary conditions at infinity on the functions P_s are

$$\lim_{z\to +\infty} z^{2-s} P_s = \lim_{z\to -\infty} z^{2-s} P_s \ ,$$

$$\lim_{z'\to +\infty} z'^{2-s} P_s = \lim_{z'\to -\infty} z'^{2-s} P_s \ . \qquad (4.8)$$

If E does not equal E′, then P_0 and P_1 approach limits $p_0(z,z')$ and $p_1(z,z')$, independent of x, as x approaches infinity. The limiting functions are determined by the differential equations (4.7), with the left-hand sides set equal to zero, together with the boundary conditions (4.8) and the normalization condition $\iint p_0(z,z')\, dzdz' = 1$. The function P_2 has the asymptotic form, $\text{const}\cdot x + f(z,z')$, and we find that in the limit of very large L,

$$F(E,E') = 4L^{-1} P_2(z_L, z_L; L)$$

$$= 8 \iint p_0(-z,-z')\, p_1(z,z')\, zdzdz' \ . \qquad (4.9)$$

For the case where E = E′, these methods cannot be used directly, because p_0 and p_1 do not then approach a well-behaved limit as $x \to \infty$. The zero-frequency conductivity must therefore be obtained by studying the limit of $\sigma(\omega)$ as $\omega \to 0$.

Interband optical transitions. As a final example of the properties which can be calculated using the methods of this paper, we mention the line shape for optical absorption by interband electronic transitions, under the assumption that the electron and hole do not interact. We consider a model in which the electron and hole are treated in the effective mass approximation, and the random potential is white Gaussian noise arising from a deformation potential on a classical continuous string. The effective mass, m^*, and the deformation potential coefficient, V_0, may be different for the electron and hole. We assume that the interband part of the momentum operator, which is responsible for the interband transitions, has the form

$$p_{\text{interband}} = \text{const}\cdot\int [a_h^{\dagger}(x)\, a_e^{\dagger}(x) + a_e(x)\, a_h(x)]\, dx\ , \qquad (4.10)$$

where $a_h^{\dagger}$, a_h, $a_e^{\dagger}$, and a_e are the creation and annihilation operators for a hole and an electron, respectively. The optical absorption for this model is proportional to

$$\alpha(\omega) \equiv \int G(\nu,\omega-\nu)\, d\nu\ , \qquad (4.11)$$

where G is defined, in terms of $\varphi_i^{\,h}$ and $E_i^{\,h}$, the wave function and energy of the i^{th} hole eigenstate, and $\varphi_j^{\,e}$ and $E_j^{\,e}$, the wave function and energy of the j^{th} electron state, by

$$G(\nu,\nu') \equiv L^{-1}\left\langle \sum_{ij} \left[\int_0^L \varphi_i^{\,h}(x)\, \varphi_j^{\,e}(x)\, dx\right]^2 \delta\!\left(\nu - \frac{E_i^{\,h}}{\hbar}\right) \delta\!\left(\nu' - \frac{E_j^{\,e}}{\hbar}\right)\right\rangle . \qquad (4.12)$$

The procedures for calculating $G(\nu,\nu')$ are very similar to the methods used in calculating the function $F(\nu,\nu')$ of Eq. (4.3), and we shall not discuss them further, here.

ACKNOWLEDGMENTS

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APPENDIX A. ASYMPTOTIC BEHAVIOR OF $P_s(z;x)$

We wish to study the behavior, for large x, of the functions $P_s(z;x)$ for the Gaussian white noise potential of Section 1. The function P_0 is the probability distribution of $z(x;E)$, and we shall give a physical argument that this probability must approach a limiting distribution as $x \to \infty$. It is perhaps easiest to first project the line, $-\infty \leq z(x;E) \leq \infty$ onto the unit circle, $0 \leq \theta(x) < 2\pi$ by

$$\theta(x) = 2 \arctan z(x;E) \quad . \tag{A1}$$

The equation of motion (1.20) for z can be translated into an equation of motion for $\theta(x)$, which may be described, like the equation for z, as a "flow" plus a "random walk". The flow velocity for θ is continuous at all points on the unit circle, including the point $\theta = \pi$, corresponding to $z = \infty$. The magnitude of the random walk vanishes at the point $\theta = \pi$, but the flow velocity at this point is not zero. At all other points on the circle, the random walk is non-zero. It is physically clear that no matter what the value is of $\theta(x)$, there will be a finite and non-vanishing probability density for $\theta(x+\Delta x)$ to be at any point on the circle, for any $\Delta x > 0$. More explicitly, we claim that for any $\Delta x > 0$, the conditional probability density, $p(\theta'|\,\theta'',\Delta x)$, for $\theta(x+\Delta x)$ to have value θ', when $\theta(x) = \theta''$, is bounded above for all θ' and θ'', and that there exists a lower bound $m > 0$ such that

$$p(\theta'|\theta'',\Delta x) \geq m, \qquad \text{for all } \theta',\theta'' \quad . \tag{A2}$$

These conditions are more than sufficient to insure that the probability density of $\theta(x)$, and hence that of $z(x;E)$, approaches a limit exponentially fast as $x \to \infty$. It would have been sufficient for convergence, that the above conditions hold for one particular $\Delta x > 0$. Also it would have been sufficient that (A2) hold for all θ'', whenever θ' lies in a specified non-zero segment of the circle.[19)]

The function $P_1(z;x)$ obeys the differential equation (1.40) with the boundary condition (1.35). Since the inhomogeneous term in (1.40), $P_0(z;x)$, approaches a limit exponentially fast, the function P_1 will approach a limit if all solutions of the homogeneous equation,

$$\frac{\partial}{\partial x} f(z;x) = \left[\frac{\partial^2}{\partial z^2} + (z^2+2E)\frac{\partial}{\partial z} + z - ik\right] f(z;x) \ , \tag{A3}$$

with the boundary condition

$$\lim_{z\to+\infty} zf = \lim_{z\to-\infty} zf \quad , \tag{A4}$$

decay to zero as $x \to \infty$. Let us define the function $U_4(x;E)$ by

$$U_4(x;E) \equiv c/e^{ikx}\, \varphi(x;E) \ , \tag{A5}$$

where c is some constant. By examining the equation of motion for U_4, one can readily see that the functions $f(z;x)$ are just the expectation values $\langle U_4(x;E)\ \delta[z - z(x;E)]\rangle$, where the average is to be taken not only over all potential configurations, but over a distribution of initial conditions z_0 and constants c, chosen so as to give the correct values for f(z,0). Using the same reasoning as that used in equation (1.26), we see that

$$\langle U_4(L;E)\ \delta[z_L - z(L;E)]\rangle = \frac{1}{2}\, e^{-ikL} \langle c \sum_i \psi_i(0)\ \psi_i(L)\ \delta(E-E_i)\rangle\ , \tag{A6}$$

where the ψ_i are the normalized eigenstates of the Hamiltonian, with the boundary condition z_L. Borland$^{20)}$ has shown that the eigenstates in a one-dimensional disordered potential are highly localized in space, decaying exponentially on either side of the point at which they are maximum. It follows that the product $\psi_i(0)\ \psi_i(L)$ will be very small for large L, and unless the density of states is infinite at energy E, the function $f(z_L;L)$ must be very small, for large L. Since z_L is an arbitrary constant, it follows that all solutions of (A3) and (A4) decay to zero as $x \to \infty$.

Finally we consider $P_2(x;z)$. If the spectral density is to be independent of L, and of the boundary condition z_L, it follows that,

$$x^{-1}\ P_2(z;x) = C + R(z,x)\ , \tag{A7}$$

where C is a constant, and the remainder, R(z,x), vanishes as $x \to \infty$. If we make the further assumption that $\frac{x\partial R}{\partial x}(z,x)$ goes to zero for large x, then one can use the reasoning preceding (1.49) to evaluate C, and thus determine the spectral density.

It is also possible to study the limiting form of P_2 more directly from the equation of motion (1.41), without use of the physical interpretation of P_2. The function P_2 may be written as

$$P_2(z;x) = 2\int_{-\infty}^{\infty} dz' \int_0^x dx'\ G(z,x-x';z')\ \text{Real}\ P_1(z';x')\ , \tag{A8}$$

where the Green's function $G(z,x;z')$ is the solution of the homogeneous equation

$$\frac{\partial}{\partial x} G(z,x;z') = \left[\frac{\partial^2}{\partial z^2} + (z^2+2E)\frac{\partial}{\partial z}\right] G(z,x;z')\ , \tag{A9}$$

for x greater than zero, with the boundary conditions

$$\lim_{z\to+\infty} G(z,x;z') = \lim_{z\to-\infty} G(z,x;z')\ , \tag{A10}$$

$$G(z,0;z') = \delta(z-z')\ . \tag{A11}$$

We know that $P_1(z';x')$ approaches a limit as $x \to \infty$; in order to find the asymptotic behavior of P_2 from (A8) we must also study the behavior of G. Let $H(z',x;z)$ be the solution of the adjoint equations:

$$\frac{\partial H}{\partial x} = \left[\frac{\partial^2}{\partial z'^2} - \frac{\partial}{\partial z'}(z'^2+2E)\right] H, \qquad \text{for } x > 0\ , \tag{A12}$$

$$\lim_{z'\to+\infty} z'^2 H = \lim_{z'\to-\infty} z'^2 H\ , \tag{A13}$$

$$H(z',0;z) = \delta(z-z') \quad . \tag{A14}$$

If we multiply both sides of (A12) by $G(z',x''-x;z'')$ and integrate with respect to z' and x, over the region $-\infty < z' < \infty$ and $0 \leq x \leq x''$, then we find, after integration by parts,[21)]

$$G(z,x'';z'') = H(z'',x'';z) \quad . \tag{A15}$$

Note that Eq. (A12) is identical to the equation of motion, (1.32), for P_0, except for the sign of z'. Hence, from our discussion of the limiting form of P_0, it follows that $G(z,x;z')$ approaches the limit $p_0(-z')$, independent of the value of z, as $x \to \infty$, and that this approach is exponentially fast. From this it follows that $P_2(z;x)$ has the form (const$\cdot x + f(z)$ + terms which go to zero as $x \to \infty$), and the spectral density, for large L, may be found from Eq. (1.49).

APPENDIX B. DENSITY OF STATES FOR THE WHITE GAUSSIAN NOISE POTENTIAL IN TERMS OF AIRY FUNCTIONS

Equation (1.46) for the probability distribution $p_0(z)$, in the case of a white Gaussian noise potential, may be integrated once with respect to z, giving

$$[\frac{d}{dz} + (z^2+2E)]\ p_0(z) = \text{const.} \tag{B1}$$

From (1.60) and the discussion following it, we see that the constant in (B1) is just the cumulative density of states, N(E). Taking the Fourier transform of (B1), we have

$$(-\frac{d^2}{dq^2} + iq + 2E)\ p(q) = 2\pi N(E)\ \delta(q)\quad , \tag{B2}$$

where p(q) is the Fourier transform of $p_0(z)$. As a Fourier transform of a probability distribution, p(q) must be equal to 1 when q equals zero, p(q) must approach zero when $q \to \pm \infty$, and p(q) must equal $p(-q)^*$. This last requirement, together with (B2), implies that

$$-\lim_{q \to 0^+} \text{Real}\ dp(q)/dq = \pi N(E)\quad . \tag{B3}$$

If g(q) is any solution of the homogeneous part of equation (B2), such that $g(q) \to 0$ as $q \to +\infty$, then it follows that $-\pi^{-1}$ Real $[g'(0)/g(0)] = N(E)$. If we write $g(q) \equiv G(t)$, where $t = -iq - 2E$, we have

$$N(E) = -\pi^{-1}\ \text{Imag}\ [G'(-2E)/G(-2E)]\quad . \tag{B4}$$

The function $G(t)$ must approach zero as $t \to -i\infty$, and G must obey Airy's differential equation,

$$G''(t) = t\,G(t) \quad . \tag{B5}$$

The general solution of (B5) is $G(t) = a\,\mathrm{Ai}(t) + b\,\mathrm{Bi}(t)$, where Ai and Bi are the Airy integrals, defined and tabulated for real values of t in reference (13). The Airy integrals may be expressed in terms of Bessel's functions of 1/3 order, and have an analytic continuation to the entire complex plane. From the well-known asymptotic properties of the Bessel's functions,22) it follows that when $|t| \to \infty$, the Airy functions have the asymptotic form,

$$\mathrm{Ai}(-t) \sim \pi^{-\frac{1}{2}}\, t^{-\frac{1}{4}} \sin\left(\tfrac{1}{4}\pi + \tfrac{2}{3}t^{3/2}\right) , \tag{B6}$$

$$\mathrm{Bi}(-t) \sim \pi^{-\frac{1}{2}}\, t^{-\frac{1}{4}} \cos\left(\tfrac{1}{4}\pi + \tfrac{2}{3}t^{3/2}\right) , \tag{B7}$$

in the sector $-\frac{2}{3}\pi < \arg t < \frac{2}{3}\pi$. The condition $G(t) \to 0$, as $t \to -i\infty$, thus implies

$$G(t) = a[\mathrm{Ai}(t) - i\,\mathrm{Bi}(t)] \quad . \tag{B8}$$

Since the Wronskian, $\mathrm{Ai}'(t)\,\mathrm{Bi}(t) - \mathrm{Bi}'(t)\,\mathrm{Ai}(t)$, equals $-1/\pi$ for all t, we have, finally,

$$N(E) = \pi^{-2}\left\{[\mathrm{Ai}(-2E)]^2 + [\mathrm{Bi}(-2E)]^2\right\}^{-1} \quad . \tag{B9}$$

FOOTNOTES

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1. H. L. Frisch and S. P. Lloyd, Phys. Rev. 120, 1175 (1960).
2. H. Schmidt, Phys. Rev. 105, 425 (1957).
3. M. Lax and J. C. Phillips, Phys. Rev. 110, 41 (1958).
4. R. E. Borland, Proc. Phys. Soc. (London) 77, 705 (1961).
5. F. J. Dyson, Phys. Rev. 92, 1331 (1953).
6. R. L. Agacy, Proc. Phys. Soc. (London) 83, 581 (1964); R. E. Borland, Proc. Phys. Soc. (London) 83, 1027 (1964).
7. J. J. Hopfield, Phys. Chem. Solids 22, 63 (1961).
8. Y. Toyozawa, Prog. Theoret. Phys. (Kyoto) 20, 53 (1958).
9. D. Pines, The Many-Body Problem (W. A. Benjamin, Inc., New York, 1961) p. 31.
10. For a derivation of the Fokker-Planck equation, see M. C. Wang and G. E. Uhlenbeck, Revs. Mod. Phys. 17, 323 (1945).
11. A. Suna, Phys. Rev. 135, A111 (1964).
12. J. R. Klauder, Ann. Phys. (N.Y.) 14, 43 (1961).
13. J. C. P. Miller, The Airy Integral, British Association for the Advancement of Science Mathematics Tables, Part-Volume B (University Press, Cambridge, England, 1946).
14. L. I. Schiff, Quantum Mechanics (McGraw Hill Book Co., Inc., New York, 1955) pp. 184-192.

15. The Gaussian shape for the spectral density in the limit of zero band width is derived in Reference 8 by summation of the perturbation theory expansion for the Green's function.

16. When the band width is zero, it is possible to calculate the spectral density exactly, even when phonon energies are not zero. See: J. J. Hopfield, in *International Conference on the Physics of Semiconductors, Exeter, 1962* (The Institute of Physics and the Physical Society, London 1962) p. 75; M. Lax, J. Chem. Phys. *20*, 1752 (1952).

17. See C. Kittel, *Quantum Theory of Solids* (John Wiley and Sons, Inc., New York, 1963) Chap. 19.

18. See H. Nakano, Prog. Theoret. Phys. (Kyoto) *15*, 77 (1956).

19. *cf*. the discussion in Reference 1, Appendix 2.

20. R. E. Borland, Proc. Roy. Soc. (London) *A274*, 529 (1963).

21. *cf*. B. Friedman, *Principles and Techniques of Applied Mathematics* (John Wiley and Sons, Inc., New York, 1956) p. 174.

22. E. Jahnke, F. Emde, and F. Lösch, *Tables of Higher Functions* (B. G. Teubner Verlagsgesellschaft, Stuttgart, 1960) 6th ed., p. 147.

FIGURE CAPTIONS

Figure 1. Spectral density, A(k,E), for white Gaussian noise potential. Energy is measured in units of $\varepsilon_o = (D^2 m^* \hbar^{-2})^{\frac{1}{3}}$, wave number in units of $\kappa_o = (Dm^{*2} \hbar^{-4})^{\frac{1}{3}}$. The spectral density is normalized so that the area under the curve is 1.

Figure 2. Comparison of exact values of A(k,E) with results of self-consistent Green's function approximation, for white Gaussian noise potential. (a) - Wave number $k = 0$. (b) - Wave number $k = 1$. On this scale, the exact and approximate curves for the spectral density would be almost indistinguishable for $k = 2$. Units are the same as in Fig. 1.

Figure 3. Self-consistent Green's function approximation. Heavy solid line denotes complete Green's function for particle; light solid line denotes unperturbed Green's function for particle; dotted line denotes a phonon (Reference 11) or connects repeated scattering from same impurity (Reference 12).

Figure 4. The spectral density, A(0,E), for the discrete model, for several values of the lattice constant a. The energy E is measured in units of $\varepsilon_o = (D^2 m^* \hbar^{-2})^{\frac{1}{3}}$; the lattice constant in units of $\kappa_o^{-1} = (Dm^{*2} \hbar^{-4})^{-\frac{1}{3}}$. The zero of energy is the energy of the $k = 0$ state in the unperturbed lattice.

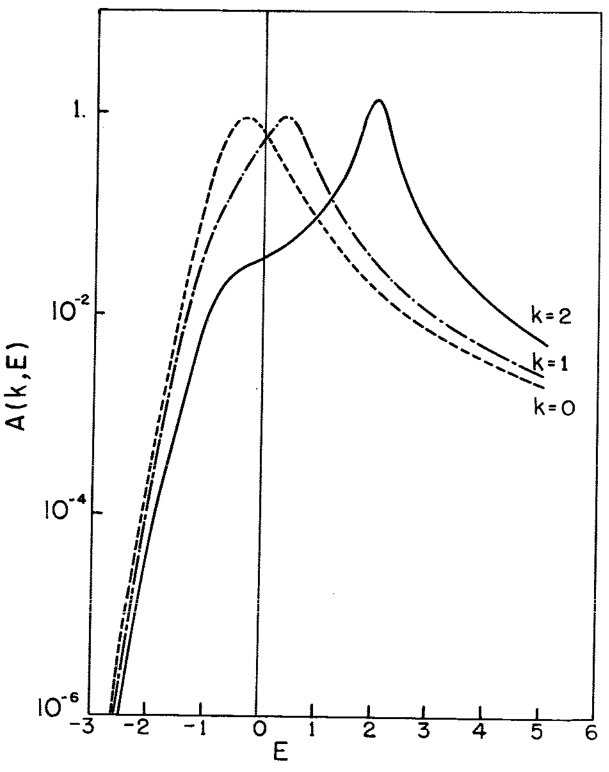

FIGURE 1

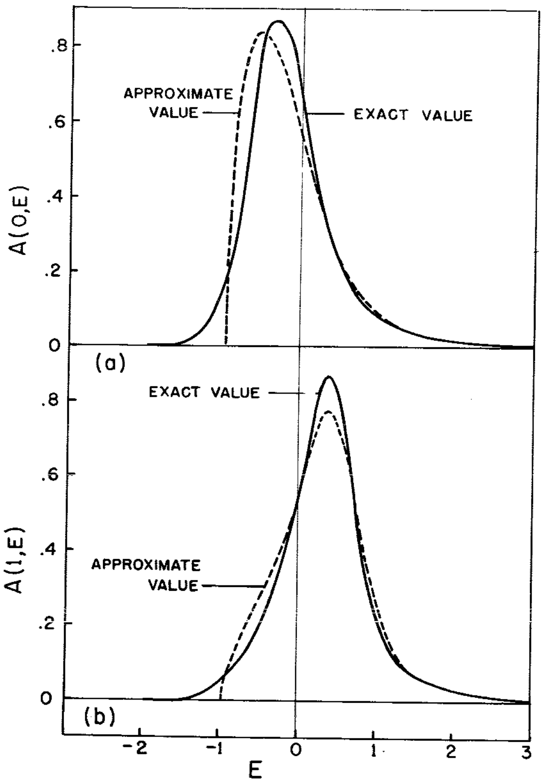

FIGURE 2

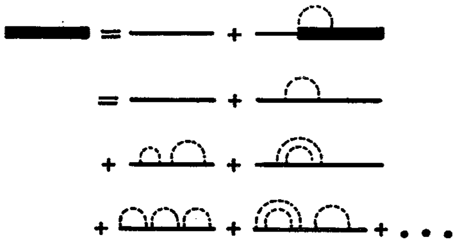

FIGURE 3

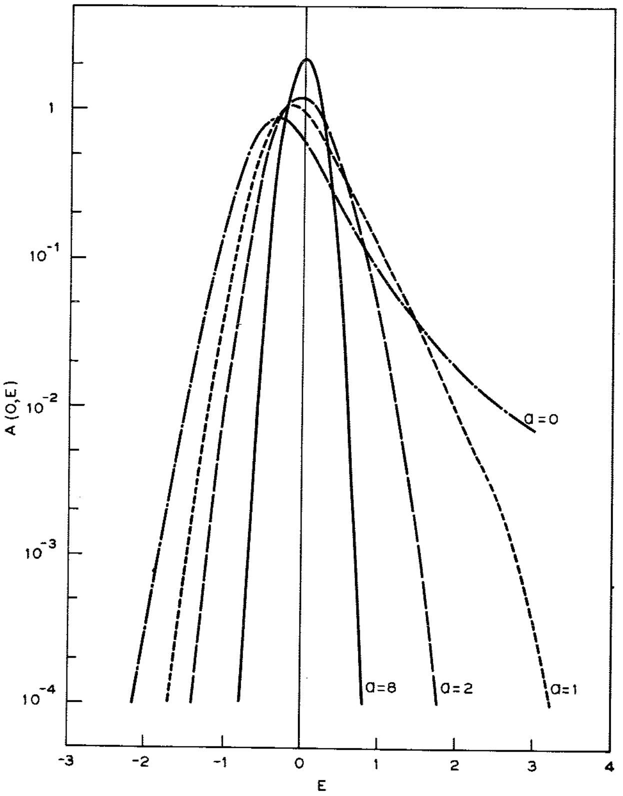

FIGURE 4

CHAPTER III

THEORY OF THE LOW ENERGY TAIL

Section 1. The Density of States

In this chapter we present a general method for approximating the low energy tail of $A(\underset{\sim}{k}, E)$ for an exciton interacting with phonons of zero frequency. As we have remarked before, the problem, in this case, is that of finding the spectral density for a particle in a random potential. This chapter represents an adaptation to the exciton-phonon problem of techniques recently developed by the author, in collaboration with Dr. M. Lax of the Bell Telephone Laboratories, for studying the density of electronic states in the low energy tail of a high density impurity band.[1]

The Hamiltonian for the exciton is assumed to have the form

$$H = \mathcal{T} + V(\underset{\sim}{x}) . \tag{1.1}$$

The operator $\mathcal{T}$, the "kinetic energy" of the exciton, is the energy of the exciton in the perfect lattice, and is a function only of the exciton momentum. The random potential $V(\underset{\sim}{x})$ is diagonal in the exciton position, and depends on the particular lattice configuration. (The following discussion will in fact be equally applicable to the case of a non-local random potential, but we have assumed a local potential in order to simplify our equations.) We shall denote the minimum eigenvalue of $\mathcal{T}$ by the symbol E_o. We assume that the average value of $V(\underset{\sim}{x})$ is zero; this is no restriction because we may always include the average value of V in the kinetic energy.

The exciton spectral density is given by

$$A(\underset{\sim}{k}, E) = \frac{1}{\Omega}\left\langle \Sigma_i |\psi_i(\underset{\sim}{k})|^2 \, \delta(E - E_i) \right\rangle , \tag{1.2}$$

where Ω is the volume of the crystal, E_i is the energy of the i^{th} eigenstate of H, and $\psi_i(\underset{\sim}{k})$ is the $\underset{\sim}{k}^{th}$ Fourier coefficient of the corresponding wave function, $\psi_i(\underset{\sim}{k}) = \int e^{-i\underset{\sim}{k}\cdot\underset{\sim}{x}}\, \psi_i(\underset{\sim}{x})\, d\underset{\sim}{x}$. The angular brackets indicate a thermal average over lattice configurations, which may be defined by

$$\langle \xi \rangle \equiv Z^{-1} \int \xi \exp[- U(Q)/k_B T]\, dQ \;, \qquad (1.3)$$

where U(Q) is the potential energy of the lattice configuration Q (with no exciton present), and Z is the partition function,

$$Z = \int \exp[- U(Q)/k_B T]\, dQ \;. \qquad (1.4)$$

The indicated integrations in (1.3) and (1.4) are multiple integrals over all the lattice degrees of freedom.

The spectral density is closely related to the total density of states, $\rho(E)$, defined by

$$\rho(E) \equiv \frac{1}{\Omega} \langle \Sigma_i\, \delta(E - E_i) \rangle \;. \qquad (1.5)$$

When the energy E is sufficiently far below E_o, the density of states $\rho(E)$ decreases very rapidly with decreasing E. Because the average value of $|\psi_i(\underset{\sim}{k})|^2$ is a relatively slowly varying function of the energy, we expect that the behavior of $A(\underset{\sim}{k}, E)$ will be principally determined by the behavior of the density of states, and our first task will be to determine the approximate form of $\rho(E)$.

The approximations we will make will be valid only in the low energy tail. For the time being we shall not be precise about the meaning of the low energy tail -- that is, we shall not specify just how far below E_o one must be. We <u>do</u> state that the energy must be sufficiently low so that the ratio $\rho(E)/\rho(E_o)$ must be much smaller than 1. This means that $|E - E_o|$

must be large compared to the energy easily obtainable from the potential fluctuations. Note that the low energy tail may be reached in two ways, by keeping the fluctuations fixed and letting $E - E_0 \to -\infty$, or by holding $E - E_0$ fixed at a given negative value and letting the fluctuations become small, (i.e., $T \to 0^\circ$ K).

If the exciton band were perfectly flat, so that the kinetic energy term $\mathcal{T}$ were simply a constant, E_0, the density of states would be very simple. The energy eigenfunctions would be localized at a single lattice site, and the energy of the state would be E_0 plus the value of $V(\underset{\sim}{x})$ at that site. The density of states $\rho(E)$ would then be equal to the number of lattice sites per unit volume, multiplied by the probability density for the value of $V(\underset{\sim}{x})$, at any one lattice site, to take on the value $E - E_0$.

As soon as the kinetic energy operator is non-trivial, however, the eigenstates are no longer localized at a single site; the potential energy is not the value of $V(\underset{\sim}{x})$ at a single site but the average of $V(\underset{\sim}{x})$ over several adjacent sites. As a result, the only potential fluctuations which can produce a low energy eigenstate are those which have a wavelength larger than the "width" of a "typical wave-function". This means that the number of low-energy eigenstates is greatly reduced. The method described below for estimating the density of states in the low energy tail is a method for making the best possible estimate of the "width" of a typical wave-function, at a given energy, and then using this information to calculate the probability of occurrence of a potential fluctuation of the necessary magnitude over a region the size of the wave-function.

The crucial assumption we make is that at a given energy E in the low energy tail, almost all of the energy eigenfunctions have approximately the same shape. Specifically let us assume that whenever $E_i \approx E$, we find

$$\psi_i(\underset{\sim}{x}) \approx f(\underset{\sim}{x} - \underset{\sim}{x}_o) \quad , \tag{1.6}$$

where f is a fixed function, and $\underset{\sim}{x}_o$ is a position variable which may be anywhere in the crystal and will be different for each eigenstate. It is no restriction to assume that f has its maximum when its argument is zero. States in the low energy tail will generally be highly localized in a region of low potential, and it is clear that f must be rapidly decreasing when its argument becomes large. We also require that $f(\underset{\sim}{x})$ obey the normalization condition imposed on the wave-function ψ_i.

For the present, let us assume that the function f is known -- we shall discuss later the best method for finding this function. Let us use the right-hand side of (1.6) in a variational estimate of the energy E_i. The variational estimate, for a particular choice of $\underset{\sim}{x}_o$, is defined by

$$E(\underset{\sim}{x}_o) \equiv \int f(\underset{\sim}{x} - \underset{\sim}{x}_o)\, H\, f(\underset{\sim}{x} - \underset{\sim}{x}_o)\, d\underset{\sim}{x} \quad .$$

The variational energy can be written as the sum of two terms

$$E(\underset{\sim}{x}_o) = \boldsymbol{\theta} + V_s(\underset{\sim}{x}_o) \quad , \tag{1.7}$$

where

$$\begin{aligned} \boldsymbol{\theta} &= \int f(\underset{\sim}{x} - \underset{\sim}{x}_o)\, \mathcal{T}\, f(\underset{\sim}{x} - \underset{\sim}{x}_o)\, d\underset{\sim}{x} \;, \\ V_s(\underset{\sim}{x}_o) &= \int f(\underset{\sim}{x} - \underset{\sim}{x}_o)^2\, V(\underset{\sim}{x})\, d\underset{\sim}{x} \quad . \end{aligned} \tag{1.8}$$

Note that the kinetic energy $\boldsymbol{\theta}$ is independent of the choice of $\underset{\sim}{x}_o$, because the operator $\mathcal{T}$ is translationally invariant. The potential energy $V_s(\underset{\sim}{x}_o)$ is an average of the potential $V(\underset{\sim}{x})$ in a region about $\underset{\sim}{x} = \underset{\sim}{x}_o$. As $\underset{\sim}{x}_o$ is permitted to vary throughout the crystal, $V_s(\underset{\sim}{x}_o)$ will fluctuate about an average value of zero, and at various places in the crystal, $V_s(x_o)$ will exhibit an unusually large negative fluctuation. These places correspond to regions of very low $V(\underset{\sim}{x})$, and hence to places where we expect to find a low energy eigenstate $\psi_i(\underset{\sim}{x})$. We know that a variational estimate of the ground state energy of a system always overestimates this energy. Hence we expect that $E(\underset{\sim}{x}_o)$, in a region of negative fluctuation, will always be larger than the true energy E_i of the local low energy eigenstate. The best estimate of the energy E_i is thus obtained by choosing $\underset{\sim}{x}_o$ so that $E(\underset{\sim}{x}_o)$ is as small as possible, i.e., so that $E(\underset{\sim}{x}_o)$ is a local minimum. In general, $E(\underset{\sim}{x}_o)$ at this minimum may be considereably larger than E_i; however, if the assumption (1.6) holds, we expect $E(\underset{\sim}{x}_o)$ to be a good approximation to E_i whenever $E_i \approx E$. It may also be seen that, in general, if $E(\underset{\sim}{x}_o)$ is close to E, then E_i will be close to E, and hence $E(\underset{\sim}{x}_o)$ will again be a good approximation to E_i. (This last statement follows from the fact that the density of states is rapidly falling with decreasing energy, and thus almost all of the eigenstates with energy less than E have energy close to E.)

It may be objected that the variational principle rigorously tells us that $E(\underset{\sim}{x}_o)$ is greater than E_i only if ψ_i is the ground state of the exciton for the whole crystal. In order for $E(\underset{\sim}{x}_o)$ to be smaller than E_i, however, the trial function $f(\underset{\sim}{x} - \underset{\sim}{x}_o)$ must mix in another wave function ψ_j whose energy is lower than E_i. In the low energy tail, where the density of states is very small, energy eigenstates are very few and far between, and the possibility of simultaneous overlap between $f(\underset{\sim}{x} - \underset{\sim}{x}_o)$ and two different eigenstates is quite negligible.

If, as we claim, there is a close one-to-one correspondence between local minima in $E(\underset{\sim}{x}_o)$ and the energies of eigenstates in the vicinity of E, then the number of eigenstates with energy E is approximately equal to the number of local minima in $E(\underset{\sim}{x}_o)$ with value E. Thus we have the following approximation to the density of states:

$$\rho_f(E) \;=\; \frac{1}{\Omega dE}\left\langle \begin{array}{l} \text{Number of local minima in } E(\underset{\sim}{x}_o) \\ \text{such that at the minimum} \\ \quad E \leq E(\underset{\sim}{x}_o) \leq E + dE. \end{array} \right\rangle . \qquad (1.9)$$

We have placed the subscript f on the density of states to remind us that the validity of the estimate will depend on the correct choice of f.

Until now, we have used the words "local minimum" loosely to mean the minimum value of $E(\underset{\sim}{x}_o)$ in some region. For purposes of computation we wish to define a local minimum as any point where $\underset{\sim}{\nabla} E(\underset{\sim}{x}_o)$ equals zero and the second derivatives are positive. (We assume here a model of the exciton band in which the position $\underset{\sim}{x}$ is a continuous variable. The modifications necessary, when the position variable is treated as discrete, will be discussed at the end of section 3.) If two points with vanishing first derivatives occur very close together, then the use of this new definition may destroy the one-to-one correspondence between local minima and eigenstates, because the same eigenstate may be counted twice. It may be shown, however, that in the low energy tail, the probability of occurrence of two points close together, with $\underset{\sim}{\nabla} E(\underset{\sim}{x}_o) = 0$ and $E(\underset{\sim}{x}_o) \leq E$ at each point, is extremely small. Furthermore, if there is only one such point in a region, it must be a local minimum, so that the second derivaties are automatically positive. Hence, we may substitute for the words "local minimum in $E(\underset{\sim}{x}_o)$", in Eq. (1.9), the words "point where $\underset{\sim}{\nabla} E(\underset{\sim}{x}_o) = 0$".

Let us now consider the problem of finding the best trial function f. We know that regardless of the choice of f, the variational estimates of the energies of the eigenstates will be high. In the low energy tail, where the density of states is rapidly falling, any approximation which systematically overestimates the energies of all the eigenstates is bound to underestimate the density of states. Thus we claim that in the low energy tail, no matter what the choice of f, $\rho_f(E)$ will be smaller than the true density of states, $\rho(E)$. Clearly the best choice of f, for any given energy E, is that which maximizes $\rho_f(E)$. We call the density of states obtained by this optimum choice "$\rho_1(E)$"; i.e., we have

$$\rho_1(E) = \max_f \rho_f(E) . \tag{1.10}$$

Section 2. The Spectral Density

Thus far we have discussed only the total density of states, $\rho(E)$. In order to calculate the optical absorption, one needs to know the spectral density, $A(\underset{\sim}{k}, E)$. The spectral density is, by definition, the product of the density of states $\rho(E)$ times the expectation value of the absolute square of the $\underset{\sim}{k}^{th}$ Fourier component of the wave functions at the given energy. If our assumption is correct, that almost all the wave-functions at energy E have the approximate form $f(\underset{\sim}{x} - \underset{\sim}{x}_o)$, then the absolute square of their Fourier transforms must be approximately $|f(\underset{\sim}{k})|^2$. Thus we claim that in the low energy tail,

$$A(\underset{\sim}{k}, E) \approx |f(\underset{\sim}{k})|^2 \rho(E) , \tag{2.1}$$

where f is the function which maximizes $\rho_f(E)$. To compute $A(\underset{\sim}{k}, E)$ when we do not know the exact density of states, $\rho(E)$, we use the approximate density of states, $\rho_1(E)$.

Section 3. Method of Calculation -- Linear Systems

In general, the calculation of $\rho_1(E)$ must be carried out approximately on a computer. The value of $\rho_f(E)$ must be computed for a number of different trial functions, and the largest value so obtained chosen as the approximate density of states. In the important case of a linear system (i.e., harmonic phonons and linear phonon-exciton interaction) important simplifications exist. In this case the potential $V(x)$ obeys Gaussian statistics, and ρ_f has a simple explicit expression in terms of integrals involving f. These integrals can often be performed explicitly for simple trial functions, and a good estimate of ρ_1 may be obtainable by hand. Alternatively, the optimization may be performed by computer, and the approximation $\rho_1(E)$ obtained, in the Gaussian case, with very high accuracy.

In any case, one must first convert Eq. (1.9) into a more convenient expression for ρ_f. The method we use is essentially a generalization to three dimensions of a method used by Rice in random noise problems.[2] Equation (1.9)may be written

$$\rho_f(E) = \frac{1}{\Omega} \int d\underset{\sim}{y} \left\langle \Sigma_j \, \delta(\underset{\sim}{y} - \underset{\sim}{y}_j) \, \delta[E - \boldsymbol{\theta} - V_s(\underset{\sim}{y})] \right\rangle , \tag{3.1}$$

where $\{y_j\}$ is the set of all points satisfying

$$\underset{\sim}{\nabla} V_s(\underset{\sim}{V}_j) = 0 \, . \tag{3.2}$$

When the indicated average over all potential configurations has been taken, the quantity in brackets in (3.1) becomes independent of $\underset{\sim}{y}$, and the integration over $\underset{\sim}{y}$ merely yields a factor of Ω. Thus we may write

$$\rho_f(E) = \left\langle \Sigma_j \, \delta(\underset{\sim}{y} - \underset{\sim}{y}_j) \, \delta[E - \boldsymbol{\theta} - V_s(\underset{\sim}{y})] \right\rangle \quad , \tag{3.3}$$

where $\underset{\sim}{y}$ is any point in the crystal. We next make a transformation from the variable $\underset{\sim}{y}$ to the variable $\underset{\sim}{\nabla} V_s(\underset{\sim}{y})$ by writing

$$\Sigma_j \, \delta(y - y_j) = \delta[\underset{\sim}{\nabla} V_s(\underset{\sim}{y})] \, |\det \underset{\sim}{\nabla}\underset{\sim}{\nabla} V_s(y)| \, . \tag{3.4}$$

The determinant of the second derivatives in (3.4) arises as the Jacobian of the transformation. Equation (3.3) can now be written

$$\rho_f(E) = \left\langle \delta[E - \boldsymbol{\theta} - V_s(\underset{\sim}{y})] \, \delta[\underset{\sim}{\nabla} V_s(\underset{\sim}{y})] \det \underset{\sim}{\nabla}\underset{\sim}{\nabla} V_s(\underset{\sim}{y}) \right\rangle \, . \tag{3.5}$$

In (3.5) we have dropped the absolute value sign from the determinant because, as mentioned earlier, almost all the critical points of $V_s(y)$ with $V_s(y) = E - \boldsymbol{\theta}$ have positive second derivatives. The quantity $\rho_f(E)$ is then determined by the 10-variable joint probability distribution of V_s and its first and second derivatives at a single point.

We now restrict ourselves to linear systems, where the random potential obeys Gaussian statistics. The potential energy of the lattice is expressed in terms of the phonon displacements $Q_{\underset{\sim}{k}\eta}$ and the elastic constant $\alpha_{\underset{\sim}{k}\eta}$, where $\underset{\sim}{k}$ is the wave vector of the phonon mode and η is a polarization index. We have

$$U(Q) = \frac{1}{2} \sum_{\underset{\sim}{k}\eta} \alpha_{\underset{\sim}{k}\eta} \, |Q_{\underset{\sim}{k}\eta}|^2 \, . \tag{3.6}$$

The coordinates $Q_{\underset{\sim}{k}\eta}$ are not linearly independent because $Q_{\underset{\sim}{k}\eta} \equiv Q_{-\underset{\sim}{k}\eta}{}^*$. The displacements have a Gaussian distribution with $\langle Q_{\underset{\sim}{k}\eta} \, Q_{\underset{\sim}{k}'\eta'}{}^* \rangle = \delta_{\underset{\sim}{k}\underset{\sim}{k}'} \, \delta_{\eta\eta'} \, k_B T/\alpha_{\underset{\sim}{k}\eta}$. The exciton-phonon potential is expressed as

$$V(\underset{\sim}{x}) = \sum_{\underset{\sim}{k}\eta} \lambda_{\underset{\sim}{k}\eta} \, e^{i\underset{\sim}{k}\cdot\underset{\sim}{x}} \, Q_{\underset{\sim}{k}\eta} \, , \tag{3.7}$$

where we have the condition that $\lambda_{\underset{\sim}{k}\eta} \equiv \lambda_{-\underset{\sim}{k}\eta}{}^{*}$. (In the case of a lattice with one atom per unit cell, the correspondence between the symbols λ, α, and Q, and the symbols of Chapter I is quite simple. We have

$$Q_{\underset{\sim}{k}\eta} = (b_{\underset{\sim}{k}\eta} + b^{+}_{-\underset{\sim}{k}\eta})\,(2\rho\Omega\,\omega_{\underset{\sim}{k}\eta})^{-\frac{1}{2}} ,$$

$$\lambda_{\underset{\sim}{k}\eta} = (2\rho\Omega\,\omega_{\underset{\sim}{k}\eta})^{\frac{1}{2}}\, c^{\eta}_{\underset{\sim}{k}\underset{\sim}{k}'} , \text{ (independent of } \underset{\sim}{k}'\text{)},$$

$$\alpha_{\underset{\sim}{k}\eta} = \rho\Omega\,\omega_{\underset{\sim}{k}\eta}{}^{2} .$$

When there are two or more atoms per unit cell the relations are similar but somewhat more complicated.)

The random potential $V(\underset{\sim}{x})$ obeys Gaussian statistics with

$$\langle V(\underset{\sim}{x})\rangle = 0 ,$$

$$\langle V(\underset{\sim}{x})\,V(\underset{\sim}{x}')\rangle = T\,W(\underset{\sim}{x} - \underset{\sim}{x}') , \qquad (3.8)$$

where

$$W(x) = \sum_{\underset{\sim}{k}\eta} e^{i\underset{\sim}{k}\cdot\underset{\sim}{x}}\,|\lambda_{\underset{\sim}{k}\eta}|^{2}\,\alpha^{-1}_{\underset{\sim}{k}\eta}\, k_B . \qquad (3.9)$$

Similarly, the function $V_s(y)$, being a linear combination of the Gaussian variables $V(x)$, obeys Gaussian statistics with

$$\langle V_s(\underset{\sim}{y})\rangle = 0 ,$$

$$\langle V_s(\underset{\sim}{y})\,V_s(\underset{\sim}{y}')\rangle = T\,G(\underset{\sim}{y} - \underset{\sim}{y}') , \qquad (3.10)$$

where

$$G(\underset{\sim}{y} - \underset{\sim}{y}') = \int f(\underset{\sim}{x} - \underset{\sim}{y})^{2}\, f(\underset{\sim}{x}' - \underset{\sim}{y}')^{2}\, W(\underset{\sim}{x} - \underset{\sim}{x}')\, d\underset{\sim}{x}d\underset{\sim}{x}'. \qquad (3.11)$$

The autocorrelation function $G(\underset{\sim}{y})$ completely determines the statistics of V_s and its derivatives. Let us first compute the four-variable joint distribution function of $V_s(\underset{\sim}{y})$ and its first derivatives at a single point. The variance of V_s is given by

$$\left\langle V_s(\underset{\sim}{y})^2 \right\rangle = T\, G(0) \equiv T\, \sigma_o^2 . \tag{3.12}$$

The covariance of V_s with its first derivatives is given by

$$\left\langle V_s(\underset{\sim}{y})\, \underset{\sim}{\nabla} V_s(\underset{\sim}{y}) \right\rangle = T\, \underset{\sim}{\nabla}_{y'}\, G(\underset{\sim}{y} - \underset{\sim}{y}')\big|_{\underset{\sim}{y}'=\underset{\sim}{y}} . \tag{3.13}$$

Because the function G, by definition, is an even function of its argument, the right-hand side of (3.13) vanishes identically. Finally, the correlations of the derivatives among themselves are given by

$$\left\langle [\underset{\sim}{\nabla} V_s(\underset{\sim}{y})]\, [\underset{\sim}{\nabla} V_s(\underset{\sim}{y})] \right\rangle = - T\, \underset{\sim}{\nabla}\, \underset{\sim}{\nabla} G(0) . \tag{3.14}$$

It is convenient to choose the coordinate axes such that the matrix of second derivatives of G is diagonal, with the form

$$\underset{\sim}{\nabla}\, \underset{\sim}{\nabla} G(0) = - \begin{pmatrix} \sigma_1^2 & 0 & 0 \\ 0 & \sigma_2^2 & 0 \\ 0 & 0 & \sigma_3^2 \end{pmatrix} . \tag{3.15}$$

In this case, the three components of $\underset{\sim}{\nabla} V_s(\underset{\sim}{y})$ are uncorrelated, and the joint distribution function P_4 of V_s and its derivatives is simply the product of four Gaussians:

$$P_4(\lambda, \underset{\sim}{\Lambda}) \equiv \left\langle \delta[\lambda - V_s(y)]\, \delta[\underset{\sim}{\Lambda} - \underset{\sim}{\nabla} V_s(y)] \right\rangle$$

$$= \frac{1}{(2\pi)^2\, T^2\, \sigma_o \sigma_1 \sigma_2 \sigma_3} \exp\left[- \frac{\lambda^2}{2T\sigma_o^2} - \frac{\Lambda_1^2}{2T\sigma_1^2} - \frac{\Lambda_2^2}{2T\sigma_2^2} - \frac{\Lambda_3^2}{2T\sigma_3^2} \right] . \tag{3.16}$$

The density of states $\rho_f(E)$, according to (3.5), is equal to the product of the probability density $P_4(E - \theta, \underset{\sim}{0})$ and the conditional expectation value of the determinant of second derivatives, given that $V_s(\underset{\sim}{y}) = E - \theta$ and $\underset{\sim}{\nabla} V_s(\underset{\sim}{y}) = 0$. Each of the second derivatives may be written as the sum of a term proportional to $V_s(\underset{\sim}{y})$ and a term uncorrelated with $V_s(\underset{\sim}{y})$; that is

$$\underset{\sim}{\nabla}\underset{\sim}{\nabla} V_s(\underset{\sim}{y}) = V_s(\underset{\sim}{y}) \underset{\approx}{M} + \underset{\approx}{X} \quad , \tag{3.17}$$

where $\underset{\approx}{M}$ is a constant matrix, and $\underset{\approx}{X}$ is a matrix of variables, uncorrelated with $V_s(\underset{\sim}{y})$, which have mean zero and variances proportional to the temperature T. The matrix $\underset{\approx}{M}$ is given by

$$\underset{\approx}{M} = \frac{\left\langle V_s(\underset{\sim}{y}) \underset{\sim}{\nabla}\underset{\sim}{\nabla} V_s(\underset{\sim}{y}) \right\rangle}{\left\langle V_s(\underset{\sim}{y})^2 \right\rangle} = - \frac{\underset{\sim}{\nabla}\underset{\sim}{\nabla} G(0)}{G(0)} \quad . \tag{3.17a}$$

Note that $\underset{\approx}{M}$ is independent of T. Thus, when $V_s(\underset{\sim}{y}) = E - \theta$, the second derivatives are equal to $(E - \theta)\underset{\approx}{M}$ plus terms which disappear as $T \to 0$. The determinant of the second derivatives is therefore equal to $(\theta - E)^3 \sigma_1^2 \sigma_2^2 \sigma_3^2 / \sigma_0^6$ plus terms which are negligible in the low energy tail. This reasoning also confirms our earlier claim that almost all critical points of V_s are minima when $V_s \leq E - \theta$.

Our final result for ρ_f is

$$\rho_f(E) = \frac{\sigma_1 \sigma_2 \sigma_3 (\theta - E)^3}{(2\pi)^2 T^2 \sigma_0^7} \exp\left[- \frac{(\theta - E)^2}{2T \sigma_0^2} \right] . \tag{3.18}$$

We must now choose f so as to maximize (3.18). When $T \to 0$, it is clear that the exponential factor will become extremely sensitive to the choice of f, while the other factors are much more slowly varying. Hence, the best choice of f is that which maximizes the exponential factor in (3.18), or equivalently, that which minimizes the expression

$$\frac{(\theta - E)^2}{\sigma_0^2} = \frac{[E - \int f(\underset{\sim}{x})\, \mathcal{T} f(\underset{\sim}{x})\, d\underset{\sim}{x}]^2}{\int f(\underset{\sim}{x})^2\, f(\underset{\sim}{x}')^2\, W(\underset{\sim}{x} - \underset{\sim}{x}')\, d\underset{\sim}{x} d\underset{\sim}{x}'} . \qquad (3.19)$$

Note that in the low-energy tail the choice of f is independent of T. Hence the factors σ_0, σ_1, σ_2, σ_3 and θ will also be chosen independent of T, and the temperature dependence of $\rho_1(E)$ will be just the explicit T-dependence of (3.18):

$$\rho_1(E) = A(E)\, T^{-2} \exp[-B(E)/T] . \qquad (3.20)$$

The physical significance of choosing f so as to minimize (3.19) may be explained as follows: The function $W(\underset{\sim}{x} - \underset{\sim}{x}')$ is the autocorrelation function of the random potential $V(\underset{\sim}{x})$ and is generally very small for distances larger than a few lattice constants. When $f(\underset{\sim}{x})$ is spread out over distances large compared to the correlation distance of $V(\underset{\sim}{x})$, the probability of finding a large fluctuation in V over the entire volume of the wave-function becomes small. The variance of V_s which appears in the denominator of (3.19), is inversely proportional to the cube of the width of the function f when this width becomes large, and the value of (3.19) becomes very large as the width becomes large. On the other hand, if one attempts to make $f(\underset{\sim}{x})$ very narrow, the kinetic energy θ in the numerator becomes very large and (3.19) again becomes large. (If the kinetic energy is proportional to k^2, the numerator of (3.19) is proportional to the inverse fourth power of the width of f, for narrow f.) The perfect f is a compromise between these two extemes.

The problem of minimizing (3.19) can be reduced to the solution of a non-linear integral equation. Let us multiply the quantity E in (3.19) by the normalization integral $\int f(\underset{\sim}{x})^2 d\underset{\sim}{x}$ in order to make the expression homogeneous in f. Expression (3.19) is then independent of the normalization of f, and may be minimized by holding the denominator fixed at any constant value, and varying f to minimize the numerator. Introducing a Lagrange multiplier μ, we find by the methods of variational calculus

$$\mathcal{T} f(\underset{\sim}{x}) - \mu\, f(\underset{\sim}{x}) \int f(\underset{\sim}{x}')^2\, W(\underset{\sim}{x} - \underset{\sim}{x}')\, d\underset{\sim}{x}' = E\, f(\underset{\sim}{x}) . \tag{3.21}$$

This equation looks like the Hartree equation for a particle bound in its own self-consistent field, with an interaction $- \mu\, W(x - x')$, the only difference being that in the present case we have specified E and consider μ as the eigenvalue to be found. Equation (3.21) can be solved on a computer using the techniques developed by Hartree[3] for solving his self-consistent equations. Essentially, one assumes a potential, solves the Schroedinger equation for the wave-function of a particle in that potential, and then uses this wave-function to guess a better shape for the self-consistent potential. Hartree has found a number of tricks for making this process converge rapidly.

An alternative procedure for minimizing (3.19) is simply to introduce a trial function with several parameters and to minimize with respect to these parameters. If $\mathcal{T}$ and W are sufficiently simple, the necessary integrals can be done explicitly for a well chosen trial function, and a minimization with respect to a small number of parameters may even be carried out by hand.

That a minimum value for (3.19) exists is pretty clear. We know that (3.19) is always greater than zero and that it becomes large if f is either too spread out in space or too confined. It also becomes large if f is not smooth. It is very hard to imagine any situation other than that (3.19) achieves its greatest-lower-bound for some well-behaved, smooth f.

The question of the uniqueness of the optimizing function f is a more difficult one to answer. To be more specific, let us assume that $\mathcal{T}$ and W are spherically symmetric. There will then always be a spherically symmetric solution of the Hartree equation (3.21), because (3.21) is the same equation which occurs if one wishes to find the <u>spherically symmetric function</u> which minimizes (3.19). On the other hand, the Hartree equation is non-linear, and we must worry about the possibility of a "lower" solution with "broken symmetry", i.e., a solution which is not rotationally invariant. If the "lowest" solution is not rotationally invariant, then there is not one optimum choice of f but a continuous family of solutions, obtained by arbitrary rotations of any one solution. (Actually, we already have one broken symmetry: Equation (3.21) is translationally invariant, but we know that the best choice of f must be localized in space. The translational degeneracy of the solution has been removed by specifying that $f(\underset{\sim}{x})$ have its maximum at $\underset{\sim}{x} = 0$.) Although it is difficult to see why a non-symmetric solution would give a lower value for (3.19) than would a symmetric solution, we have not been able to disprove this possibility. If it should occur, that the function f is infinitely degenerate, it is necessary to modify our basic assumption that all wave-functions have the form $f(\underset{\sim}{x} - \underset{\sim}{x}_0)$ by including parameters α, β, and γ which describe the orientation of the function f.

The best variational estimate to the energy of an eigenstate would then be the value of $E(\underset{\sim}{x}_o; \alpha, \beta, \gamma)$ taken at a local minimum in <u>all</u> the parameters.

We may also mention, at this point, the modifications which occur when the exciton coordinate is not treated as a continuous variable, but is restricted to discrete lattice sites. The statement that $V_s(\underset{\sim}{y})$ is a local minimum at $\underset{\sim}{y} = \underset{\sim}{x}_o$ is to be interpreted to mean that $V_s(\underset{\sim}{y})$ is smaller at $\underset{\sim}{x}_o$ than at any immediate neighbors. As $T \to 0$, the number of points with $V_s(\underset{\sim}{y}) \leq E - \boldsymbol{\theta}$ becomes very small. For any such point, the probability that it is a local minimum is then very close to 1. In this case, $\rho_f(E)$, the approximation to the density of states, is simply the number of points per unit volume and per unit energy, with $V_s(y) \approx E - \boldsymbol{\theta}$. Thus we have

$$\rho_f(E) = \frac{N}{\Omega} \left\langle \delta[E - \boldsymbol{\theta} - V_s(\underset{\sim}{y})] \right\rangle , \qquad (3.22)$$

where $\frac{N}{\Omega}$ is the number of lattice points per unit volume, and $\underset{\sim}{y}$ is an arbitrary point on the lattice. For a linear system, the function ρ_f is then given simply by

$$\rho_f(E) = \frac{N}{\Omega (2\pi)^{\frac{1}{2}} T^{\frac{1}{2}} \sigma_o} \exp\left[- \frac{(E - \boldsymbol{\theta})^2}{2\sigma_o^2 T} \right]. \qquad (3.23)$$

If the function f varies slowly over adjacent lattice sites, however, so that the correlation between $V_s(y)$ at neighboring lattice sites is large, then this condition, that almost every point with $V_s(\underset{\sim}{y}) = E - \boldsymbol{\theta}$ be a local minimum, is not reached until T becomes very small (or until E is very far in the low energy tail). Thus there may be regions of interest where we are sufficiently far in the low energy tail for our general philosophy to be valid [i.e., for $\rho_1(E)$ to be a reasonable approximation to $\rho(E)$], but where $\rho_f(E)$ is not given accurately by (3.22) or (3.23). It is then necessary to include the conditional probability that $V_s(\underset{\sim}{y})$ is a minimum at $\underset{\sim}{y} = \underset{\sim}{x}_o$. In most cases where this is necessary, it is probably adequate to treat the positions as continuous variables and use the methods we have already described. The most important factor in the density of states, the exponential factor of (3.18) or (3.23) is the same in any case.

The trivial model of a flat exciton band is easily handled in the present formalism. In this case, the kinetic energy operator $\mathcal{T}$ is just a constant E_o, and $\boldsymbol{\theta}$ is therefore equal to E_o for any choice of f. Maximization of the exponential factor in the density of states gives a wave-function which is localized at a single lattice site, independent of E_o. The density of states $\rho_1(E)$, is given by Eq. (3.23) with σ_o independent of E. The function $\rho_1(E)$ is a simple Gaussian distribution, and happens to be exactly equal to the true density of states $\rho(E)$ for this model.

Section 4. Application to One-Dimensional Model

In order to check our approximation method, we have applied it to the model of a one-dimensional effective mass exciton in a white-Gaussian-noise potential. In Chapter II we showed that the spectral density and total density of states can be calculated exactly for this model. It also turns out that our approximate method is especially simple in this case: all quantities of interest can be obtained analytically, without the need of a computer.

The white-Gaussian-noise potential is characterized by Gaussian statistics, with

$$\left\langle V(x)\, V(x') \right\rangle = \frac{1}{2} D\, \delta(x - x'), \tag{4.1}$$

where D is a constant proportional to the temperature T. The kinetic energy operator $\mathcal{T}$ is given by

$$\mathcal{T} = -\frac{1}{2}\, d^2/dx^2 \; . \tag{4.2}$$

The formulas of the preceding sections were given for a three-dimensional model and need to be modified slightly for the one-dimensional case, in addition to the trivial substitution of one-dimensional for three-dimensional variables. Equation (3.5) becomes, in the one-dimensional case,

$$\rho_f(E) = \left\langle \delta[E - \theta - V_s(y)]\, \delta\left[\frac{dV_s(y)}{dy}\right] \frac{d^2V_s(y)}{dy^2} \right\rangle . \tag{4.3}$$

If the random potential obeys Gaussian statistics, (4.3) becomes

$$\rho_f(E) = \frac{\sigma_1}{2\pi\, T\, \sigma_o^3} \exp\left[-\frac{(\theta - E)^2}{2\, T\, \sigma_o^2}\right] , \tag{4.4}$$

where σ_o and θ are defined as before, but σ_1 is simply given by

$$T\, \sigma_1^2 \equiv \left\langle [V_s'(y)]^2 \right\rangle = -\, T\, G''(0) \; . \tag{4.5}$$

Note that the temperature dependence is slightly different in the one-dimensional case than the three dimensional case. The function f, which maximizes $\rho_f(E)$ in the low energy tail is that which maximizes the exponential factor in (4.4); applying variational calculus leads to an equation identical to Eq. (3.21). For the white-noise model, this equation takes the simple form

$$-\frac{1}{2} f''(x) - \mu\, f(x)^3 = E\, f(x) \; . \tag{4.6}$$

With the conditions that f(x) be normalized to 1 and have its maximum at x = 0, Eq. (4.6) has the solution

$$f(x) = \sqrt{\frac{\kappa}{2}} \operatorname{sech} \kappa x , \tag{4.7}$$

$$\mu = 2\kappa , \tag{4.8}$$

where κ is defined by

$$E = -\frac{1}{2} \kappa^2 . \tag{4.9}$$

In Appendix A we show that this solution is, in fact, unique, and we discuss the procedure for evaluating the constants in (4.4) for this choice of f. We find that

$$\rho_1(E) = \frac{4\kappa^2}{\pi D} \exp\left(-\frac{4}{3}\frac{\kappa^3}{D}\right) \cdot \frac{1}{\sqrt{5}} . \tag{4.10}$$

In Chapter II, we showed that the exact asymptotic form of $\rho(E)$, as $E \to -\infty$, or as $D \to 0$, is given by

$$\rho(E) \sim \frac{4\kappa^2}{\pi D} \exp\left(-\frac{4}{3}\frac{\kappa^3}{D}\right) . \tag{4.11}$$

The agreement between ρ_1 and the exact asymptotic form of ρ is remarkably good. The power of κ in the exponent is correct, the factor 4/3 is exactly correct, and the power of κ out in front of the exponential is correct. The overall constant in ρ_1 is too small by a factor of $\sqrt{5}$; in the low energy tail, where the density of states may change by many orders of magnitude, this error is not very significant. Even this error may be greatly reduced, however. If one includes the "average-higher-order-energy correction", described in the following section, the factor $1/\sqrt{5}$ in equation (4.10) is removed and replaced by the factor (0.921). Thus we can reproduce the exact asymptotic form with an error of less than 8 per cent.

We may also compare the form for $A(k, E)$ predicted by the approximate theory with the exact asymptotic form for the spectral density found in Chapter II. It was shown that in the limit $E \to -\infty$, with k/κ remaining finite, or equivalently with k and E held fixed and $D \to 0$,

$$\frac{A(k,\ E)}{\rho(E)} \sim \frac{\pi^2}{2\kappa} \ \operatorname{sech}^2\left(\frac{k\pi}{2\kappa}\right) \quad . \tag{4.12}$$

Our approximate theory says that the ratio (4.12) should be $|f(k)|^2$. If we take the Fourier transform of $(\kappa/2)^{\frac{1}{2}}$ sech κ x, we indeed find

$$|f(k)|^2 = \frac{\pi^2}{2\kappa} \ \operatorname{sech}^2\left(\frac{k\pi}{2\kappa}\right) \quad . \tag{4.13}$$

The good agreement between the results of our approximate theory and the exact asymptotic forms of $\rho(E)$ and $A(k, E)$, for the white-Gaussian-noise model, provides striking confirmation of the validity of the approximate theory in the low energy tail. One may still ask, however, where the low energy tail begins; i.e., we must be sure that the exact functions $\rho(E)$ and $A(k, E)$ achieve their asymptotic forms at energies high enough to make the asymptotic forms useful.

In Figure 1, at the end of this chapter, we have compared the exact value of $\rho(E)$ with its asymptotic form, Eq. (4.11). The error in the asymptotic form is found to be 27 per cent when $E/D^{2/3} = -1$, 6 per cent when $E/D^{2/3} = -2$, and ≈ 3 per cent when $E/D^{2/3} = -3$. The values of $\rho(E)/\rho(0)$ at these three points are .15, 3×10^{-4}, and 7×10^{-8}, respectively. Thus, over most of the range of interest, the error in the asymptotic form is of the same order of magnitude as the discrepancy between the asymptotic form and the approximate theory, when the average-higher-order-energy correlation is included in the latter.

We have also made comparisons, at several points, between the exact value of the ratio $A(k, E)/\rho(E)$ and its asymptotic form, (4.12). The results of these comparisons are shown in Figure 2.

Section 5. Average-Higher-Order-Energy Corrections

We now turn to a method for correcting some of the error introduced by the use of a trial function, $f(\underset{\sim}{x} - \underset{\sim}{x}_0)$, which has fixed shape at a given energy. The approximation $\rho_1(E)$ replaces the energy of each eigenstate $\psi_i(\underset{\sim}{x})$, in the low energy tail, by the corresponding local minimum in $E(\underset{\sim}{x}_0)$. If the shape of the wave-function $\psi_i(\underset{\sim}{x})$ were exactly the shape of f, then the energy E_i would be exactly the same as the value of $E(\underset{\sim}{x}_0)$ at the minimum. Because no one shape is <u>exact</u> for all the wave-functions, E_i will generally lie below $E(\underset{\sim}{x}_0)$. The effect of this can be partly included in our calculations by correcting the energy $E(\underset{\sim}{x}_0)$ by the <u>average</u> of the overestimate $[E(\underset{\sim}{x}_0) - E_i]$. To put this another way, let $S(E)$ be the conditional expectation value of $[E_i - E(x_0)]$, when it is known that $E(x_0) = E$ at its local minimum. Then our improved approximation to the density of states, "$\rho_2(E)$", is related to the old approximation $\rho_1(E)$ by

$$\rho_2[E + S(E)] = \rho_1(E) \frac{dE}{d[E + S(E)]} . \tag{5.1}$$

We shall find that $dS(E)/dE$ is small compared to 1 in the low energy tail, and we shall accordingly replace the derivative in the right-hand side of (5.1) by unity.

It should be noted that the approximation $\rho_2(E)$, though an improvement over $\rho_1(E)$, should still be lower than the true density of states $\rho(E)$, in the asymptotic limit. To see this, let $p(E'' - E'|E')$ be the conditional probability that an eigenstate ψ_i, assigned by ρ_2' to an energy E', (i.e., an eigenstate such that $E(x_0) + S[E(x_0)] = E'$ at the local minimum), really has energy $E_i = E''$. By definition of p and S, we have

$$\int p(E'' - E'|E')\, dE'' = 1 , \tag{5.2}$$

$$\int (E'' - E')\, p(E'' - E'|E')\, dE'' = 0 . \tag{5.3}$$

The true density of states is related to ρ_2 by

$$\rho(E'') = \int p(E'' - E'|E')\, \rho_2(E')\, dE' . \tag{5.4}$$

The integrand is presumably negligible except in a relatively small region about $E'' - E'$. In this region, the function $p(E'' - E'|E')$ will be a function primarily of the difference $E'' - E'$, with only slight additional dependence on E'. If we assume p is a function only of $E'' - E'$, we can make a Taylor expansion of $\rho_2(E')$ in Eq. (5.4) and use (5.2) and (5.3) to obtain

$$\rho(E'') = \rho_2(E'') + \int p(E'' - E')\, [\rho_2(E') - (E' - E'')\, \rho_2{}'(E'') - \rho_2(E'')]\, dE' . \tag{5.5}$$

If $\rho_2(E')$ is concave upwards in the region of integration, as it will be if the low energy tail is smooth, then the integrand of (5.5) is non-negative, and hence

$$\rho(E'') \geq \rho_2(E'') . \tag{5.6}$$

In order to find the approximation ρ_2, we must compute the average energy correction $S(E)$. We do this by means of perturbation theory. We restrict ourselves to the case that $V(\underset{\sim}{x})$ obeys Gaussian statistics.

We take as our unperturbed Hamiltonian,

$$H_o = \mathcal{T} + V_o(\underset{\sim}{x} - \underset{\sim}{y}) . \tag{5.7}$$

In (5.7), $\underset{\sim}{y}$ is the position of the local minimum in $E(\underset{\sim}{x}_0)$, and V_0 is given by

$$V_0(\underset{\sim}{x} - \underset{\sim}{y}) \equiv \frac{(E - \theta)}{G(0)} F(\underset{\sim}{x} - \underset{\sim}{y}) , \qquad (5.8)$$

where

$$F(\underset{\sim}{x} - \underset{\sim}{y}) \equiv \int f(\underset{\sim}{x} - \underset{\sim}{x}')^2 W(\underset{\sim}{x}' - \underset{\sim}{y}) d\underset{\sim}{x}' . \qquad (5.9)$$

We are going to expand the energy E_i of the eigenstate ψ_i as a perturbation series in $(V - V_0)$. The reason for our choice of V_0 is that, as will be shown below, the value of $V_0(\underset{\sim}{x} - \underset{\sim}{y})$ is the conditional expectation value of the potential $V(\underset{\sim}{x})$, when it is known that $V_s(\underset{\sim}{x}_0)$ has a local minimum at $\underset{\sim}{x}_0 = \underset{\sim}{y}$, with $V_s(\underset{\sim}{y}) = E - \theta$. When $T \to 0$, the fluctuations of $V(\underset{\sim}{x})$ about its expectation vlaue will be small, and hence we expect perturbation theory to be valid.

It is convenient to assume in the following that the local minimum $\underset{\sim}{y}$ is at the origin of the coordinate system. From Eqs. (3.21) and (3.11), we see that $f(\underset{\sim}{x})$ is an eigenfunction of the Hamiltonian H_0 with energy E:

$$H_0 f(\underset{\sim}{x}) = E f(\underset{\sim}{x}) . \qquad (5.10)$$

It can also be shown that f is the <u>ground</u> state of H_0. Let the remaining eigenfunctions of H_0 be denoted by $\varphi_j(x)$, $j = 1, 2, \ldots$, and let the corresponding energies be denoted by ϵ_j. The energies ϵ_j will form a continuum for energies greater than E_0 and may include one or more discrete boundstates. The minimum energy ϵ_j will always be greater than the ground-state energy E by a finite amount, which is auspicious for the use of perturbation theory.

The perturbation theory expansion for E_i may be written

$$E_i = E + \int f(\underset{\sim}{x})\,[V(\underset{\sim}{x}) - V_o(\underset{\sim}{x})]\,f(\underset{\sim}{x})\,d\underset{\sim}{x}$$
$$+ \int f(\underset{\sim}{x})\,[V(\underset{\sim}{x}) - V_o(\underset{\sim}{x})]\,\hat{G}(\underset{\sim}{x}, \underset{\sim}{x}')\,[V(\underset{\sim}{x}') - V_o(\underset{\sim}{x}')]\,f(\underset{\sim}{x}')\,d\underset{\sim}{x}d\underset{\sim}{x}'$$
$$+ \ldots \quad , \tag{5.11}$$

where

$$\hat{G}(\underset{\sim}{x}, \underset{\sim}{x}') \equiv \sum_j' \frac{\varphi_j(\underset{\sim}{x})\,\varphi_j(\underset{\sim}{x}')}{E - \epsilon_j} \quad . \tag{5.12}$$

The function $\hat{G}(\underset{\sim}{x}, \underset{\sim}{x}')$ is related to the Green's function G_o, of the Hamiltonian H_o, by

$$\hat{G}(\underset{\sim}{x}, \underset{\sim}{x}') = \lim_{E' \to E} \left[\hat{G}_o(\underset{\sim}{x}, \underset{\sim}{x}'; E') - \frac{f(\underset{\sim}{x})\,f(\underset{\sim}{x}')}{E' - E} \right] . \tag{5.13}$$

The function $\hat{G}(\underset{\sim}{x}, \underset{\sim}{x}')$ may also be defined by the equation

$$(E - H_o)\,\hat{G}(\underset{\sim}{x}, \underset{\sim}{x}') = \delta(\underset{\sim}{x} - \underset{\sim}{x}') - f(\underset{\sim}{x})\,f(\underset{\sim}{x}') \quad . \tag{5.14}$$

It is easily seen from the definition of $V_o(\underset{\sim}{x})$, that the first order correction to E_i in equation (5.11) vanishes identically if $V_s(0) = E - \theta$. Thus the lowest order contribution to $S(E)$ comes from the second order energy correction, i.e., the third term on the right-hand side of (5.11).

It is convenient to introduce the symbol $\ll \ldots \gg$ to indicate the conditional expectation value of a quantity, when it is known that $V_s(\underset{\sim}{x}_o)$ has a local minimum at the origin, with $V_s(0) = E - \theta$. Thus, for any variable ξ, we have

$$\ll \xi \gg \; \equiv \frac{\left\langle \xi\,\delta[E - \theta - V_s(0)]\,\delta[\underset{\sim}{\nabla} V_s(0)]\,\det \underset{\sim}{\nabla}\underset{\sim}{\nabla} V_s(0) \right\rangle}{\left\langle \delta[E - \theta - V_s(0)]\,\delta[\underset{\sim}{\nabla} V_s(0)]\,\det \underset{\sim}{\nabla}\underset{\sim}{\nabla} V_s(0) \right\rangle} . \tag{5.15}$$

Note that this differs from the conditional expectation value of ξ, given that $V_s(0) = 0$ and $\nabla V_s(0) = 0$, because the average in (5.15) is weighted by the factor $\det \nabla \nabla V_s(0)$. However, when $T \to 0$, the fluctuations of the determinant about its expected value become small, and hence to lowest order in T, we may drop this weighting factor. We then have

$$\langle\langle \xi \rangle\rangle = \frac{\langle \xi \, \delta[E - \boldsymbol{\theta} - V_s(0)] \, \delta[\nabla V_s(0)] \rangle}{\langle \delta[E - \boldsymbol{\theta} - V_s(0)] \, \delta[\nabla V_s(0)] \rangle} . \tag{5.16}$$

The quantity we wish to calculate, $S(E)$, can be written

$$S(E) \equiv \langle\langle E_i - E \rangle\rangle . \tag{5.17}$$

The contribution of the second order energy correction to this quantity may be written

$$S_2(E) = \int f(\mathbf{x}) \, \hat{G}(\mathbf{x}, \mathbf{x}') \, f(\mathbf{x}') \left\langle\!\!\left\langle [V(\mathbf{x}) - V_0(\mathbf{x})][V(\mathbf{x}') - V_0(\mathbf{x}')] \right\rangle\!\!\right\rangle d\mathbf{x} \, d\mathbf{x}' . \tag{5.18}$$

From (5.16) it follows by the usual manipulations of Gaussian statistics, that

$$\langle\langle V(\mathbf{x}) \rangle\rangle = \frac{\langle V(\mathbf{x}) \, V_s(0) \rangle}{\langle [V_s(0)]^2 \rangle} (E - \boldsymbol{\theta}) = V_0(\mathbf{x}) , \tag{5.19}$$

which is a result mentioned earlier. The expression $[V(\mathbf{x}) - V_0(\mathbf{x})] \times [V(\mathbf{x}') - V_0(\mathbf{x}')]$ is thus the product of two Gaussian variables with mean zero, and the expectation value of the product is given by

$$\left\langle\!\!\left\langle [V(x) - V_0(x)][V(x') - V_0(x')] \right\rangle\!\!\right\rangle = \langle V(x) \, V(x') \rangle - \frac{\langle V(\mathbf{x}) \, V_s(0) \rangle \langle V(\mathbf{x}') \, V_s(0) \rangle}{\langle V_s(0)^2 \rangle} - \sum_{\alpha=1}^{3} \frac{\langle V(\mathbf{x}) \nabla_\alpha V_s(0) \rangle \langle V(\mathbf{x}') \nabla_\alpha V_s(0) \rangle}{\langle [\nabla_\alpha V_s(0)]^2 \rangle} . \tag{5.20}$$

The summation on α is taken over the three coordinate directions, and we assume, as in section 3, that the axes have been chosen so as to eliminate the correlations between the first derivatives of V_s. It follows that

$$S_2(E) = T \int f(\underset{\sim}{x})\, G(\underset{\sim}{x}, \underset{\sim}{x}')\, f(\underset{\sim}{x}')\, w(\underset{\sim}{x}, \underset{\sim}{x}')\, d\underset{\sim}{x} d\underset{\sim}{x}' \, , \tag{5.21}$$

where

$$w(\underset{\sim}{x}, \underset{\sim}{x}') \equiv W(\underset{\sim}{x} - \underset{\sim}{x}') - \frac{F(\underset{\sim}{x})\, F(\underset{\sim}{x}')}{\sigma_o^2} - \sum_{\alpha=1}^{3} \frac{[\nabla_\alpha F(\underset{\sim}{x})][\nabla_\alpha F(\underset{\sim}{x}')]}{\sigma_\alpha^2} \, . \tag{5.22}$$

Note that we may write $S_2(E) = T\, C(E)$, where $C(E)$ is independent of the temperature. It may easily be seen that the contributions to $S(E)$ from third and higher order perturbation theory are of order T^2 and above, so that equations (5.21) and (5.22) give $S(E)$ exactly to order T.

If we assume $S(E)$ is small, then we may neglect the difference between E and $E + S(E)$, except in the exponential factor of the density of states. In this case we may write

$$\begin{aligned} \rho_2(E) &\approx \frac{\sigma_1\, \sigma_2\, \sigma_3\, (\boldsymbol{\theta} - E)^3}{(2\pi)^2\, \sigma_o^7\, T^2} \exp\left\{ - \frac{[\boldsymbol{\theta} - E + S(E)]^2}{2\, T\, \sigma_o^2} \right\} \\ &\approx \rho_1(E) \exp\left[\frac{(E - \boldsymbol{\theta})\, C(E)}{\sigma_o^2} \right] . \end{aligned} \tag{5.23}$$

In (5.23), we may evaluate $\boldsymbol{\theta}$, σ_o, etc., using the choice of f which maximizes $\rho_f(E)$, rather than $\rho_f[E - S(E)]$. This is permissible even in the exponent because the exponent is stationary with respect to small variations in f. Note that if we had kept terms of order T^2 or higher in $S(E)$, they would make no fractional change in $\rho_2(E)$, in the limit $T \to 0$.

We emphasize, however, that the fluctuations of $[E(\underset{\sim}{x}_o) - E_i]$ about its average value $S(E)$ can cause a percentage change in the density of states which does not vanish as $T \to 0$. Thus we do not expect $\rho_2(E)/\rho(E)$ to be exactly 1, even in the asymptotic limit.

There are some models to which we would like to apply the theory we have developed, for which the assumption that $S(E)$ is small is not valid for any reasonable T. For example, the three-dimensional model which is the equivalent of the white-Gaussian-noise model in one-dimension gives a divergent second order energy shift due to short wavelength phonons, unless the fluctuations are cut off below a certain wavelength. The second order shift due to large wave-vector fluctuations is independent of the energy E, however, and we can therefore write

$$S(E) = T[C_o + c(E)] \, , \tag{5.24}$$

where $|T\ c(E)|$ may be assumed small compared to $(\theta - E)$ for the region of interest. In this case, it is most convenient to write ρ_2 in the form

$$\rho_2(E + T\ C_o) \approx \rho_1(E) \exp\left[\frac{(E - \theta)\ c(E)}{\sigma_o^{\ 2}}\right] \, , \tag{5.25}$$

The term $T\ C_o$ has the effect of shifting the bottom of the exciton band as a whole.

In order to find the energy correction $S(E)$ it is necessary to find the modified Green's function $\hat{G}(\underset{\sim}{x}, \underset{\sim}{x}')$, and then evaluate the integrals in (5.21). In the general case this may be a formidable task. If the model is spherically symmetric, however, the functions $\hat{G}$ and w can be analyzed in terms of spherical harmonics, and the evaluation becomes quite feasible with a digital computer. In the case of the one-dimensional white-Gaussian-noise model, the function $\hat{G}$ and all of the integrals may be evaluated analytically, and one finds

$$S(E) = -\frac{13}{72} D \kappa^{-1} \quad . \tag{5.26}$$

The result for $\rho_2(E)$ is

$$\begin{aligned} \rho_2(E) &= \rho_1(E) \exp(13/18) \\ &= (0.921) \cdot \frac{4\kappa^2}{\pi D} \exp\left(-\frac{4}{3}\frac{\kappa^3}{D}\right). \end{aligned} \tag{5.27}$$

Details of the one-dimensional calculation are outlined in Appendix A.

Section 6. Higher order Corrections to the Spectral Density

The effect of having an improved estimate of the density of states is immediately reflected in our estimate of the spectral density, when we use formula (2.1):

$$A(\underset{\sim}{k}, E) = |f(\underset{\sim}{k})|^2 \rho(E) .$$

However, there are other effects which modify formula (2.1) itself. One obvious correction occurs when the self-energy correction is large, as in (5.24). In that case, to find the spectral density at energy E, one must use in Eq. (2.1) not the function f chosen to maximize $\rho_f(E)$ but rather the function f chosen to maximize $\rho_f(E - T C_o)$. This correction is consistent with the point of view that the principal effect of the large second order energy is to shift the band as a whole. In other words, the shape f, which we assigned to wave-functions at energy E in the original theory, really is appropriate for wave-functions with energy $E + T C_o$.

There is another correction that may be applied to $A(\underset{\sim}{k}, E)$, which is of importance, primarily, when $\underset{\sim}{k}$ is large. This may be illustrated with the case of the one-dimensional white-noise model. The function $f(k)$ decreases exponentially fast for $k \to \infty$, so that on the basis of Eq. (2.1), we would predict an exponential decay for $A(k, E)$ for large k. It is known, however, that coupling to very short wavelength fluctuations may be removed to lowest order in the coupling by a canonical transformation which, in effect, mixes in a certain amount of the high-wavenumber exciton states, with each of the low-wavenumber states. The effect of this is to guarantee that at any fixed E and D, for sufficiently large k,

$$A(k, E) \approx 2\,D\,k^{-4}\,\rho(E) \quad . \tag{6.1}$$

(Eq. (6.1) was also verified by the exact methods of Chapter II.) Thus, even when E is in the low energy tail, and $\rho(E)$ is accurately given by its asymptotic form, Eq. (2.1) may be inadequate if k is very large.

A formal method of including the short wavelength modifications of the spectral density is to approximate the wave-function $\psi_i(\underset{\sim}{x})$ by a wave-function which includes the first-order correction in the perturbation $[V(\underset{\sim}{x}) - V_o(\underset{\sim}{x})]$. We use

$$\psi_i(x) \approx f_1(\underset{\sim}{x}) \equiv f(\underset{\sim}{x}) + \int \hat{G}(\underset{\sim}{x}, \underset{\sim}{x}')\, f(\underset{\sim}{x}')\, [V(\underset{\sim}{x}') - V_o(\underset{\sim}{x}')]\, d\underset{\sim}{x}' \quad . \tag{6.2}$$

The expectation value of the absolute square of the $\underset{\sim}{k}^{th}$ Fourier component of the wave-function at energy E is then approximated by the conditional expectation value $\ll |f_1(\underset{\sim}{k})|^2 \gg$. If we use definition (5.16) for the expectation value $\ll \ldots \gg$, we are led to the result

$$\frac{A(\underset{\sim}{k}, E)}{\rho(E)} \approx |f(\underset{\sim}{k})|^2 + T \int e^{i\underset{\sim}{k}\cdot(\underset{\sim}{x}-\underset{\sim}{x}')} \hat{G}(\underset{\sim}{x}, \underset{\sim}{x}'') \hat{G}(\underset{\sim}{x}', \underset{\sim}{x}''')$$

$$\times f(\underset{\sim}{x}'') f(\underset{\sim}{x}''') w(\underset{\sim}{x}'', \underset{\sim}{x}''') d\underset{\sim}{x} \, d\underset{\sim}{x}' \, d\underset{\sim}{x}'' \, d\underset{\sim}{x}''' \quad . \qquad (6.3)$$

It can be shown that in the one-dimensional white-Gaussian-noise model, Eq. (6.3) leads to Eq. (6.1) when k is sufficiently large. No calculations have been made, however, using formula (6.3) for intermediate values of k. It should be mentioned that there are other corrections to the ratio $A(\underset{\sim}{k}, E)/\rho(E)$ which are first order in T and have not been included in equation (6.3). Although these corrections are negligible compared to the terms kept in (6.3) when $\underset{\sim}{k}$ is either very large or very small, they may be of importance in intermediate regions.

Section 7. Three-Dimensional White-Noise Model

Let us now consider the three-dimensional analog of the white-Gaussian-noise potential model. We assume a kinetic energy of the form

$$\mathcal{T} = -\frac{\nabla^2}{2m^*} , \qquad (7.1)$$

and a potential $V(\underset{\sim}{x})$ which obeys Gaussian statistics, with

$$< V(\underset{\sim}{x}) V(\underset{\sim}{x}') > = \frac{1}{2} D \, \delta(\underset{\sim}{x} - \underset{\sim}{x}') \quad , \qquad (7.2)$$

where D is a constant proportional to the temperature. The white-noise model is appropriate for a non-degenerate exciton band when the wave-functions of interest vary slowly compared to the lattice spacing, and when the random potential, arising from either a local deformation potential or from optical phonon modes, has a correlation distance of the order of one lattice constant. This model has been studied by Toyozawa,[4] by means of the perturbation techniques mentioned in Chapter I. As we mentioned in section 5 of the present chapter, it is necessary to introduce a cutoff, either in the exciton states or in the potential fluctuations at short wavelengths, in order to prevent a divergence of the second-order self energy. The only quantity which depends on the choice of cutoff is the uniform second order shift, $T\,C_o$. The first order density of states $\rho_1(E)$ does not diverge as the cutoff wave-vector becomes infinite, and hence will be independent of the cutoff, if the cutoff is sufficiently high. Thus (in general units), $\rho_1(E)$ can be a function only of the four parameters E, m^*, $\hbar$, and D. The only dimensionless ratio which can be formed from these parameters is $E/(m^{*3}\,D^2\,\hbar^{-6})$. [Note that D has dimensions $(\text{energy})^2\ (\text{length})^3$ in the three-dimensional model.] The density of states has dimensions $(\text{energy x volume})^{-1}$. If the approximation ρ_1 is to have the temperature dependence required by Eq. (3.20), it must have the form

$$\rho_1(E) \;=\; \frac{A\,\hbar^3}{m^{*3/2}}\;\frac{|E|^{3/2}}{D^2}\;\exp\left(-\,\frac{B\,\hbar^3}{m^{*3/2}}\;\frac{|E|^{1/2}}{D}\right)\;, \qquad (7.3)$$

where A and B are constants. Alternatively, one can obtain form (7.3) by noting that the function f, being independent of D, must have a shape which is independent of E except for an overall scaling length $\hbar(m^*\,E)^{-1/2}$. If the higher order corrections are introduced according to Eq. (5.25), we have

$$\rho_2(E) \;=\; \frac{A'\,\hbar^3}{m^{*3/2}}\;\frac{|E - T\,C_o|^{3/2}}{D^2}\;\exp\left(-\,\frac{B\,\hbar^3}{m^{*3/2}}\;\frac{|E - T\,C_o|^{1/2}}{D}\right), \qquad (7.4)$$

where A' is a constant different from A. The spectral density, in the low energy tail, should be given by

$$A(\underset{\sim}{k}, E) \approx \rho(E)\, \kappa^{-3} \times \left[\text{function of } (k/\kappa)\right] , \qquad (7.5)$$

where

$$\kappa = \hbar^{-1} \, [2m^*(E - T\, C_o)]^{-1/2} \quad . \qquad (7.6)$$

Section 8. Non-Linear Systems

For a model which does not have a harmonic lattice and linear exciton-phonon coupling, and where $V(\underset{\sim}{x})$ therefore does not obey Gaussian statistics, the calculation of the approximation $\rho_1(E)$ or the improved approximation $\rho_2(E)$ becomes more difficult. Nonetheless, calculations are possible with the use of a high-speed computer. There is also a great deal one can say about the low energy tail, on the basis of our theory, without making any difficult calculations. We shall discuss primarily the case of a discrete lattice.

The function $\rho_f(E)$ is given, as in the Gaussian case, by the number of local minima in $E(\underset{\sim}{x}_o)$ per unit volume and unit energy, such that at the minima, $E(\underset{\sim}{x}_o) = E$. As in the Gaussian case, $\rho_f(E)$ is equal to the probability that $V_s(\underset{\sim}{y}) = E - \boldsymbol{\theta}$, at any given lattice point $\underset{\sim}{y}$, multiplied by the conditional probability that V_s is a local minimum at such a point, and multiplied by the number of lattice points per unit volume. Again, as in the Gaussian case, the behavior of the density of states in the low energy tail is dominated by the behavior of the first factor, the probability that $V_s(\underset{\sim}{y}) = E - \boldsymbol{\theta}$. The second factor, the conditional probability that V_s is a local minimum, will generally be a relatively slowly varying function of E, T, and the wave-function f. In fact, we saw that in a discrete lattice this second factor will often be very close to 1. The probability distribution of $V_s(\underset{\sim}{y})$ is given by

$$p_f(\lambda) \equiv \frac{\int \exp[-U(Q)/k_BT]\,\delta[\lambda - V_s(y)]\,dQ}{Z}, \tag{8.1}$$

where, as in Eq. (1.4),

$$Z = \int \exp[-U(Q)/k_BT]\,dQ \quad , \tag{8.2}$$

and the symbol Q represents the configuration of the entire lattice. We are interested in p_f when $\lambda = E - \boldsymbol{\theta}$.

For any fixed f, there will usually be one lattice configuration, $Q_o(f, E)$, which has the minimum lattice energy U of all the configurations satisfying $V_s(\underset{\sim}{y}) = E - \boldsymbol{\theta}$. We call the corresponding minimum lattice energy $U_o(f, E)$. If T is sufficiently small, all the contribution to the integral in the numerator of (8.1) will come from Q close to $Q_o(f, E)$, with U(Q) close to $U_o(f, E)$. The contributions to the denominator will come from Q close to the equilibrium position, with U(Q) close to zero. It is clear that the dominant factor in $p_f(\lambda)$ will be the ratio of the value of $\exp[-U(Q)/k_BT]$ for the important configurations in the numerator to the corresponding value in the denominator; i.e., the dominant factor will be $\exp[-U_o(f, E)/k_BT]$. Thus we claim that

$$p_f(E - \boldsymbol{\theta}) = C(E, f, T)\exp[-U_o(f, E)/k_BT] \quad , \tag{8.3}$$

where the factor C(E, f, T) is relatively slowly varying in the range of interest. In Appendix B, we discuss this point more carefully, and show that in the limit $T \rightarrow 0$, C(E, f, T) has the form $C(E, f)T^{-\frac{1}{2}}$.

In order to get the best approximation to the density of states, we must pick f so as to maximize $p_f(E - \theta)$. Since the most important factor in p_f is the exponential factor, it is a good approximation to choose f to minimize the quantity $U_o(f, E)$. We call the minimum value of the lattice potential so obtained $U_o(E)$. The choice of f, and the value of $U_o(E)$ are independent of the temperature T. Thus we find that the density of states ρ_1 has the form

$$\rho_1(E) = B(E, T) \exp[- U_o(E)/k_B T] \quad . \tag{8.4}$$

where U_o is a function only of E, and B(E, T) is a slowly varying function of E and T. This result is quite general. It applies to an exciton band of arbitrary band structure and degeneracy, with an arbitrary lattice Hamiltonian and arbitrary exciton-phonon interactions. (We have assumed, of course, that the nuclei are infinitely massive, and that E is sufficiently far in the low energy tail.) We may note that the function $U_o(E)$ will be a monotonically increasing function of $|E - E_o|$.

It is convenient to exhibit explicitly the dependence of $V(\underset{\sim}{x})$ and $V_s(\underset{\sim}{y})$ on the lattice configuration Q, by writing $V_Q(\underset{\sim}{x})$ and $V_s(\underset{\sim}{y}, Q)$. In order to find $U_o(E)$, we have to find the trial function f, and lattice configuration Q_o such that $U(Q_o)$ is a minimum while $V_s(\underset{\sim}{y},Q) = E - \theta$. Alternatively, one could find f and Q_o by requiring the variational energy $[\theta + V_s(\underset{\sim}{y}, Q)]$ to be a minimum, while U(Q) is held fixed, because $U_o(E)$ is a monotonic function of E, for $E < E_o$. It follows that f must be the ground state wave-function of the Hamiltonian $[\mathcal{T} + V_{Q_o}(\underset{\sim}{x})]$, and that

$$[\mathcal{T} + V_{Q_o}(\underset{\sim}{x})] f(\underset{\sim}{x} - \underset{\sim}{y}) = E f(\underset{\sim}{x} - \underset{\sim}{y}) \quad . \tag{8.5}$$

The average-higher-order-energy correction to the density of states can be calculated in much the same fashion in the non-linear system as for a Gaussian random potential. One uses, as an "unperturbed Hamiltonian", the operator $H_o = \mathcal{T} + V_{Q_o}(\underset{\sim}{x})$, and expands the energy E_i in the perturbation $[V(\underset{\sim}{x}) - V_{Q_o}(\underset{\sim}{x})]$. The lowest order contribution to the average energy shift, S(E), again comes from second order perturbation theory. It is again given by equation (5.18). The conditional expectation value $\ll [V(\underset{\sim}{x}) - V_{Q_o}(\underset{\sim}{x})][V(\underset{\sim}{x}') - V_{Q_o}(\underset{\sim}{x}')] \gg$ is in general more difficult to calculate than in the Gaussian case. When T is small, however, all the contribution to the expectation value comes from Q close to Q_o. If one expands U(Q) and $V_Q(\underset{\sim}{x})$ in powers of $(Q - Q_o)$, and throws away all terms higher than the quadratic, one can then apply the methods of Gaussian statistics ot the problem. Thus the lowest order energy correction can be computed as before. The form of the correction, as in the Gaussian case, is

$$S(E) \approx T\,C(E) , \qquad (8.6)$$

where C(E) is independent of temperature. If T is sufficiently small, this will result in a correction factor to the density of states which is independent of T and slowly varying in E. As was remarked in section 5 and section 7, there are interesting cases in the low energy tail where T C(E) is not small compared to $|E - \theta|$, but where one can write

$$C(E) = C_o + c(E) , \qquad (8.7)$$

with $|T\,c(E)| \ll \theta - E$. In this case, the term T C_o results in a temperature-dependent shift of the band edge as a whole, and we should write

$$\rho_2(E) = B'(E, T) \exp [- U_o(E - T\,C_o)/k_B T] , \quad (8.8)$$

where B'(E, T) is a relatively slowly varying function of E and T.

Some of the effects of non-Gaussian statistics should be treated on the same footing as the average-second-order-energy correction. As seen in Appendix B, the non-Gaussian statistics makes a contribution to B'(E, T) which is a constant factor independent of T, when T is sufficiently small. In some cases of physical interest, where T is not sufficiently small, it may be better to include some of the effects of the non-Gaussian statistics in the uniform second order energy shift $T\,C_o$. The energy shift due to thermal lattice expansion of an anharmonic crystal is one term which may contribute significantly to $T\,C_o$. In a crystal with nuclei of infinite mass, the lattice expansion is linear in temperature for small temperatures. If one assumes a simple linear deformation potential, a linear lattice expansion will produce a shift of the band edge which is also linear in temperature. Similarly, a crystal with harmonic phonons but a deformation potential which is non-linear in the phonon amplitudes will have a corresponding overall energy shift which is linear in temperature for small T.

In order to compute the optical absorption for particular crystal, we must compute the functions and constants found in Eq. (8.8). At the present time, the exciton band structure and lattice elastic constants are not known very precisely for any real crystal. The linear phonon-exciton coupling constants are known, if at all, only in the long-wavelength limit, and the anharmonic elastic constants and non-linear phonon-exciton coupling constants are completely unknown. A possible procedure for calculating these parameters, for a real crystal, was outlined in Chapter I; although the difficulties of such a calculation are formidable, it is reasonable to hope for substantial progress on these problems, and the necessary parameters may become available at some time in the not too distant future. I believe that if the parameters become available, it will be quite feasible to carry out the calculation of spectral density, using Eq. (8.8) and (2.1), even for rather complicated band structure and random potentials. Upper bounds to the function $U_o(E)$ can be readily obtained by picking various trial functions f and lattice configurations Q, and calculating the values of $U(Q)$ and $[\theta + V_s(\underset{\sim}{y}, Q)]$. With an intelligent search procedure, a digital computer can probably come very close to the function $U_o(E)$ and to the optimizing wave-functions and configurations, f and Q_o, in a reasonable amount of time. Once these are known, the function $B'(E, T)$ can be computed to a reasonable degree of accuracy, using the mathematical techniques of Appendix B and the average-second-order-energy correction procedure outlined above.

A few observations may be made here about a question we have largely avoided in the past, namely, "How far must we go in the low energy tail before the methods we have described are valid?" It is certainly not possible to give a general quantitative answer to this question at the present time. The crucial condition for validity of the various assumptions we have made appears to be that the behavior of the density of states be dominated by the rapid variation of the exponential factor in Eq. (8.8). We expect this to occur when the argument of the exponential is large compared to 1,

$$U_o(E - T\,C_o)/k_B T \gg 1. \tag{8.9}$$

For a linear system this may be written

$$(E - \theta - T\,C_o)^2/2T\,\sigma_o^2 \gg 1. \tag{8.10}$$

If there is no large second-order-energy shift of the band edge as a whole, then the term $T C_o$ will be absent from (8.9) and (8.10). In our one-dimensional calculation, we find that the theory makes sense when the left-hand side of (8.10) or (8.9) is roughly equal to, or greater than, 4. It is tempting to use this as a criterion in a general system -- i.e., we would hope that our theory is generally valid when the left-hand side of (8.9) or (8.10) is $\gtrsim 4$.

APPENDIX A

Evaluation of Formulas in the One-Dimensional Model

Equation (4.6) for f(x) may be written

$$- \frac{f''(x)}{2} - \mu f(x)^3 = - \frac{\kappa^2}{2} f(x) . \qquad (A1)$$

Multiplying by $f'(x)$ and integrating, we have

$$[f'(x)]^2 = \kappa^2 f(x)^2 - \mu f(x)^4 + \text{const.} \qquad (A2)$$

Since $f'(x) = f(x) = 0$ when $x = \infty$, the constant in (A2) must equal zero. We have chosen our origin so that f(0) is a maximum and hence, $f'(0) = 0$. Equation (A2) thus implies

$$\frac{\mu f(0)^2}{\kappa^2} = 1 . \qquad (A3)$$

If we define

$$u(x) \equiv f(\kappa^{-1} x)/f(0) , \qquad (A4)$$

then we have $u(0) = 1$, and

$$u'(x) = - [u(x)^2 - u(x)^4]^{\frac{1}{2}} \text{ for } x \geq 0 . \qquad (A5)$$

The sign of (A5) is fixed by noting that u(x) is a maximum at $x = 0$. From (A5) it follows that for $x \geq 0$,

$$x = \int_u^1 \frac{dv}{v(1 - v^2)^{\frac{1}{2}}} = \tanh^{-1}[(1 - u^2)^{\frac{1}{2}}] = \operatorname{sech}^{-1} u. \qquad (A6)$$

Similar procedures may be used for $x < 0$, and we find that for all x,

$$u(x) = \operatorname{sech} x . \qquad (A7)$$

The normalization of f(x) requires that

$$f(x) = \sqrt{\frac{\kappa}{2}} \operatorname{sech} \kappa x , \qquad (A8)$$

$$f(0) = \sqrt{\frac{\kappa}{2}} \,, \tag{A9}$$

$$\mu = 2\kappa \,. \tag{A10}$$

The normalization integral, and most other integrals involving f(x), can be performed by changing the variable of integration from x to $e^{-2\kappa x}$. We also use the fact that d sech x/dx = - sech x tanh x. We find:

$$\begin{aligned} < V_s(y)^2 > &= \frac{D}{2}\int_{-\infty}^{\infty} f^4(x)\, dx \\ &= \frac{D}{6}\kappa \,, \end{aligned} \tag{A11}$$

$$\begin{aligned} < V_s'(y)^2 > &= \frac{D}{2}\int_{-\infty}^{\infty} \{d[f(x)]^2/dx\}^2\, dx \\ &= \frac{2}{15}\kappa^3 \,, \end{aligned} \tag{A12}$$

$$\theta = \frac{1}{2}\int_{-\infty}^{\infty} f'(x)^2\, dx = \frac{1}{6}\kappa^2 \tag{A13}$$

The Fourier transform of f(x) is included by a different method. In the integral

$$f(k) = \int_{-\infty}^{\infty} e^{-ikx} f(x)\, dx \,, \tag{A14}$$

we can close the contour of integration in the upper or lower half-plane according to the sign of k. Poles of f(x) occur when $x = i\pi\kappa^{-1}(n + \frac{1}{2})$, where n is any integer. The residues of the integrand at these poles form a geometric series which may be easily summed, giving

$$f(k) = \pi(2\kappa)^{-\frac{1}{2}} \operatorname{sech}\, (k\pi/2\kappa) \;. \tag{A15}$$

Equations (5.21) and (5.22) for the average-second-order-energy correction, $S_2(E)$, may be written

$$S_2(E) = \frac{D}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f(x)\,\hat{G}(x, x')\,f(x)\,w(x, x')\,dx\,dx' , \qquad \text{(A16)}$$

where

$$w(x, x') = \delta(x - x') - \frac{3\kappa \operatorname{sech}^2 \kappa x \operatorname{sech}^2 \kappa x'}{4}$$
$$- \frac{15\kappa}{4} \operatorname{sech}^2 \kappa x \tanh \kappa x \operatorname{sech}^2 \kappa x' \tanh \kappa x' . \qquad \text{(A17)}$$

The function $\hat{G}$ is defined by equation (5.14), which may be written

$$\left(-\frac{\kappa^2}{2} + \frac{1}{2}\frac{d^2}{dx^2} + \kappa^2 \operatorname{sech}^2 \kappa x\right)\hat{G}(x, x') = \delta(x - x')$$
$$- \frac{\kappa}{2} \operatorname{sech} \kappa x \operatorname{sech} \kappa x' . \qquad \text{(A18)}$$

It may be easily verified that solution to Eq. (A18) is given by

$$\hat{G}(x, x') = \frac{\kappa^{-1}}{2} \operatorname{sech} \kappa x \operatorname{sech} \kappa x' \left[\kappa x' - \kappa x - \frac{1}{2} e^{2\kappa x} - \frac{1}{2} e^{-2\kappa x'}\right] \quad \text{for } x' \geq x$$
$$= \frac{\kappa^{-1}}{2} \operatorname{sech} \kappa x \operatorname{sech} \kappa x' \left[\kappa x - \kappa x' - \frac{1}{2} e^{2\kappa x'} - \frac{1}{2} e^{-2\kappa x}\right] \quad \text{for } x \geq x' . \qquad \text{(A19)}$$

All the integrals in Equation (A16) may be evaluated using the methods mentioned above. After many pages of straightforward computation, we obtain the simple result quoted in Eq. (5.26):

$$S(E) = -\frac{13}{72} D\,\kappa^{-1} . \qquad \text{(A20)}$$

Equation (5.27) for $\rho_2(E)$ is then obtained by using Eq. (5.23).

APPENDIX B

Calculations for a Non-Linear System

We wish to find the function $p_f(\lambda)$, given by Eqs. (8.1) and (8.2). The value of $V_s(\underset{\sim}{y})$ will depend only very slightly on the position of nuclei very far from the point $\underset{\sim}{y}$, and the integration over the corresponding lattice coordinates will essentially make the same proportional contribution to the numerator and denominator of Eq. (8.1). It is thus a good approximation to assume the integrations in (8.1) and (8.2) to be integrations over a finite number of nuclear coordinates.

The major contribution to the partition function Z comes from Q in the vicinity of the equilibrium configuration. Let us designate the configuration Q by the n coordinates q_i, $(i = 1, \ldots, n)$ with $q_i = 0$ at equilibrium. We may expand the lattice potential energy U(Q) as

$$U(Q) = \sum_{ij} U_{ij}\, q_i\, q_j + \sum_{ijk} U_{ijk}\, q_i\, q_j\, q_k + \cdots \quad . \tag{B1}$$

The matrices U_{ij}, U_{ijk}, etc., are defined to be symmetric in their indices. If the temperature T is sufficiently small, we may keep only the quadratic terms in (B1), and the integrand of (8.2) is simply a Gaussian. The stability of the lattice implies that the matrix U_{ij} is positive definite. Equation (8.2) becomes

$$Z = (\pi k_B T)^{\frac{1}{2}n} (\det U_{ij})^{-\frac{1}{2}} \quad . \tag{B2}$$

The major contribution to the integral in the numerator of (8.1) comes from configurations in the vicinity of $Q_o(f, E)$. If we expand U(Q) and $V_s(\underset{\sim}{y}, Q)$

for $Q \approx Q_o$, we have

$$U(Q) = U(Q_o) + \sum_i W_i \, \delta q_i + \sum_{ij} W_{ij} \, \delta q_i \, \delta q_j \ , \qquad (B3)$$

$$V_s(y, Q) = V_s(y, Q_o) + \sum_i V_i \, \delta q_i + \sum_{ij} V_{ij} \, \delta q_i \, \delta q_j \ , \qquad (B4)$$

where δq_i is the deviation of q_i from its value at Q_o. In (B3) and (B4) we have thrown away all terms higher than quadratic in $Q - Q_o$; this is a permissible approximation when T is sufficiently small. Note that in an anharmonic lattice the coefficients W_{ij} will not be the same as the coefficients U_{ij} of Eq. (B2).

By the definition of Q_o, we must have $V_s(\underset{\sim}{y}, Q_o) = E - \theta$. The potential energy $U(Q)$ is a minimum at $Q = Q_o$, if Q is restricted to the surface where $V_s = E - \theta$. According to the method of Lagrange multipliers, this implies that the vector W_i is simply proportional to V_i. We can therefore choose the coordinate system in such a manner that $W_i = V_i = 0$, for all $i \geq 2$, while W_1 and V_1 are nonzero. We shall assume, for convenience that this choice of coordinate system has been made.

The integrand in the numerator of (8.1) vanishes except on the surface where $V_s = E - \theta$. On this surface, we find, according to (B4):

$$\delta q_1 \approx - V_1^{-1} \sum_{i,j=2}^{n} V_{ij} \, \delta q_i \, \delta q_j \ . \qquad (B5)$$

If we substitute (B5) into (B3), we find

$$U(Q) = \sum_{i,j=2}^{n} M_{ij} \, \delta q_i \, \delta q_j + U(Q_o) \ . \qquad (B6)$$

where M_{ij} is an $(n - 1)$ dimensional matrix defined by

$$M_{ij} = W_{ij} - (W_1/V_1)\, V_{ij}, \qquad (\text{for } i,\ j = 2,\ \ldots,\ n) \qquad \text{(B7)}$$

In (B5) and (B6) we have dropped terms higher than quadratic in δq. Because $U(Q)$ is a minimum at Q_o, M_{ij} is positive definite.

The numerator of (8.1) may be written as

$$\int \exp[-\ U(Q)/k_B T]\ \delta[E - \boldsymbol{\theta} - V_s(\underset{\sim}{y},\ Q)]\ \left|\frac{\partial q_1}{\partial V_s}\right|\ dV_s\ dq_2 \cdots dq_n \ . \qquad \text{(B8)}$$

If we approximate $|\partial q_1/\partial V_s|$ by $|1/V_1|$, its value at Q_o, then we may use Eq. (B6) to put (B8) in the form

$$\left|\frac{1}{V_1}\right|\ (\pi\ k_B T)^{(n-1)/2}\ (\det M_{ij})^{-\frac{1}{2}} \exp[\ -\ U(Q_o)/k_B T]\ . \qquad \text{(B9)}$$

Thus we find

$$p_f(E - \boldsymbol{\theta}) = C(E,\ f)\ T^{-\frac{1}{2}} \exp[-\ U(Q_o)/k_B T]\ , \qquad \text{(B10)}$$

where $C(E,\ f)$ is independent of T and is given by

$$C(E,\ f) = \left|\frac{1}{V_1}\right|\ (\pi\ k_B)^{-\frac{1}{2}}\ [\det U_{ij}/\det M_{ij}]^{\frac{1}{2}}\ , \qquad \text{(B11)}$$

According to our earlier discussion, we expect that the calculated value of $C(E,\ f)$ will be independent of the number n of coordinates used in the calculation, provided n is sufficiently large. A rigorous study of the convergence of (B10), as $n \to \infty$, has not been attempted.

If we compare Eq. (B10) with the known result for $p_f(\lambda)$ in the case of Gaussian statistics, we see that for a linear system, $U(Q_o) = \frac{1}{2}\, k_B\ (E - \boldsymbol{\theta})^2/G(0)$ and $C(E,\ f) = (2\pi)^{-\frac{1}{2}}\ G(0)^{-\frac{1}{2}}$.

If the function f is sufficiently peaked at a single lattice site, then the density of states $\rho_f(E)$ is equal to N/Ω times $p_f(E - \theta)$. Since the function f is chosen independent of the temperature, according to the remarks following Eq. (8.3), we see that the density of states $\rho_1(E)$ has the form

$$\rho_1(E) = B(E)\, T^{-\frac{1}{2}} \exp[-U_o(E)/k_B T] , \qquad \text{(B12)}$$

This is exactly the same form as was found in the Gaussian case, for a discrete lattice at low enough temperatures. [Cf. Eq. (3.23).] Thus the only effect of the non-Gaussian statistics is to change the functions U_o and B.

When the temperature is sufficiently high the expansions (B1), (B3) and (B4) cannot be cut off after the quadratic terms. The coefficients C(E, f) and B(E) in (B10) and (B12), respectively, are no longer independent of T, and are considerably harder to compute. As long as E is far enough in the low energy tail, however, these factors will be much more slowly varying than the exponential factors in (B10) and (B12).

The effect of a small average-higher-order-energy correction is to change the value of E in the argument of the exponential factor in (B12) by the amount - S(E). If the energy correction S(E) is equal to T C(E), where C(E) is independent of the temperature, then we find

$$\rho_2(E) = \rho_1(E) \exp[C(E)\, U_o'(E)/k_B] , \qquad \text{(B13)}$$

where U_o' is the derivative of U_o. As in the Gaussian case, ρ_2 and ρ_1 differ by a factor independent of the temperature.

REFERENCES FOR CHAPTER III

1. B. I. Halperin and M. Lax, (to be published); Bul. Am. Phys. Soc. 10, 302 (1965).

2. S. O. Rice, Bell System Tech. J. 23, 282 (1944).

3. D. R. Hartree, The Calculation of Atomic Structures, (John Wiley and Sons, Inc., New York, 1957) pp. 63-100.

4. Y. Toyozawa, Progr. Theor. Phys. 27, 89 (1962).

FIGURE CAPTIONS

Figure 1. Density of states for one-dimensional white-noise model: Comparison of $\rho(E)$ and its asymptotic form $(4\kappa^2/\pi D) \times \exp(-4\kappa^3/3D)$, where $\kappa = |2E|^{\frac{1}{2}}$. Energy is measured in units of $\epsilon_0 = D^{2/3}$, the density of states in units of $(\epsilon_0 \ell_0)^{-1} = D^{-1/3}$.

Figure 2. Momentum dependence of spectral density for one-dimensional white-noise model, at energy $E = -D^{2/3}$: Comparison of $A(k, E)$ and its asymptotic form $|f(k)|^2 \rho(E)$, where $|f(k)|^2 = (\pi^2/2\kappa) \times \operatorname{sech}^2(\pi k/2\kappa)$. Momentum k is measured in units of $\ell_0^{-1} = D^{1/3}$, spectral density in units of $\epsilon_0^{-1} = D^{-2/3}$.

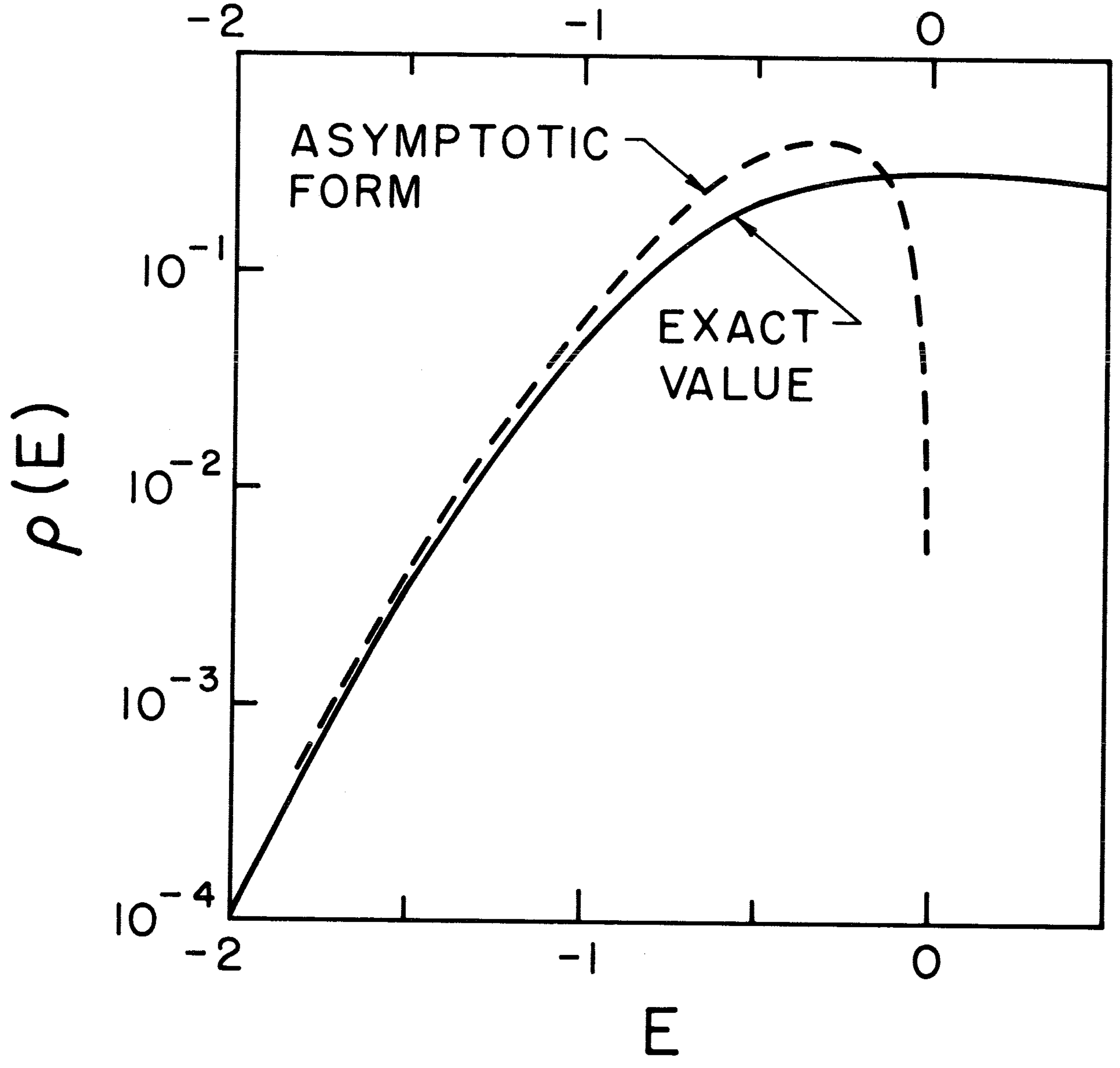

FIGURE 1.

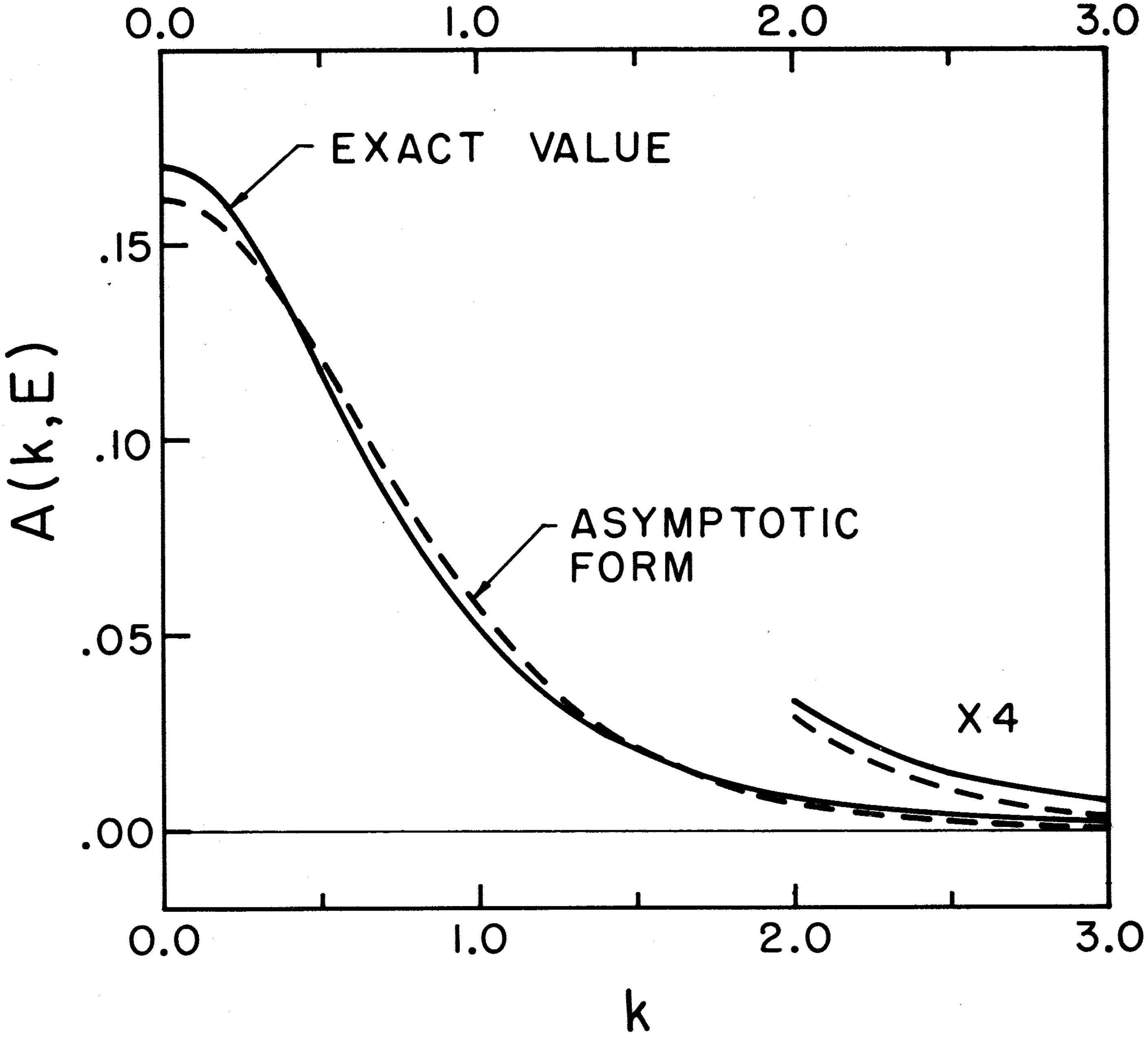

FIGURE 2.

CHAPTER IV

LOW ENERGY TAIL -- COMPARISON OF THEORY AND EXPERIMENT

Section 1. Urbach's Rule

Experimental studies of the low energy tail of the fundamental absorption edge in a wide variety of non-metallic crystals have led to the formulation of a very simple empirical law. This law, the so-called Urbach's rule,[1,2] states that the optical absorption, at frequency ω, in the low energy tail, is given by

$$\alpha(\omega) = A_o \exp[- \sigma(\omega_o - \omega)/k_B T] , \qquad (1.1)$$

where A_o, σ, and ω_o are constants of the material, independent of temperature. In the range of energies and temperatures over which Urbach's rule has been observed, $\omega_o - \omega$ is much smaller than ω_o, while $\alpha(\omega)$ varies over several orders of magnitude. The variation in the real part of the index of refraction is sufficiently small over the region of interest so that the behavior of $\alpha(\omega)$ is almost entirely due to the variation in the imaginary part of the dielectric constant, or equivalently, of the response function Λ.

The energy ω_o corresponds roughly to the position of the lowest optical absorption peak at zero temperature, in direct band gap solids, and appears to correspond to the indirect absorption edge in indirect solids. Thus ω_o corresponds roughly to the energy E_o of the lowest lying exciton state in the perfect lattice. In most crystals, the optical absorption edge (i.e., the point where the optical absorption begins to decrease rapidly with further decrease in energy) shifts linearly with temperature towards lower energies. Note that (1.1) may be written

$$\alpha(\omega) = A_o' \exp[\sigma(\omega - \omega_o + \nu T)/k_B T] , \qquad (1.2)$$

where $-\nu T$ is the shift of the band edge and $A_o' \equiv A_o \exp(-\sigma\nu/k_B)$. The low energy tail begins, roughly, when the exponent of (1.2) becomes much smaller than -1; the constant A_o' is of the order of magnitude of the absorption in the region above the band edge. The form (1.2) has the disadvantage that the choice of ν and A_o' is not completely unambiguous. On the other hand, it is somewhat more transparent than (1.1) in that it exhibits explicitly the observed shift of the absorption edge as well as the change in shape of the edge. In some cases ν is sufficiently small so that it is better to omit it.

According to Urbach's rule, the optical absorption in the low energy tail, when plotted on a semilogarithmic scale, forms a straight line whose slope is $\sigma/k_B T$. The straight lines for various temperatures, if extrapolated, intersect at energy ω_o. In many of the materials, it has been found that as the temperature approaches absolute zero, the line does not become infinitely steep, but becomes independent of the temperature below a certain temperature T_o. The quantity T, in Urbach's rule, should be replaced by an effective temperature, T_{eff}, which is equal to T, for $T \gg T_o$, and is equal to T_o, for $T \ll T_o$. This deviation from the simple temperature dependence of (1.1) and (1.2) is almost certainly due to nonzero phonon energies, and we shall ignore it for the moment.

The form of Eq. (1.1) or (1.2) is in agreement with the temperature dependence predicted by the theory of the previous chapter. According to Eq. (8.8) of Chapter III, the optical absorption should have the form

$$\alpha(\omega) = \alpha_o \exp[-U_o(\omega - C_o T)/k_B T] \quad , \qquad (1.3)$$

where α_o is a relatively slowly varying function of ω and T. However, there was nothing in the theory to suggest that the form of $U_o(\omega)$ should be a straight line. Indeed, the two simplest models applicable to a three-dimensional crystal, the model of zero exciton band-width, and the white-noise model, with infinite exciton band width, have $U_o(\omega)$ proportional to $(\omega_o - \omega)^2$ and $(\omega_o - \omega)^{\frac{1}{2}}$ respectively. Yet the remarkable experimental fact is that for a wide variety of crystals, ranging from semiconductors to insulators, the logarithm of α, in the low energy tail, is linear in ω to a very high degree of accuracy. A list of the experimental confirmations of Urbach's rule, according to Toyozawa,[2] is given in Table 1. Some of the ranges of observation given in Toyozawa's table appear to be based on extrapolations, rather than purely on experimental data, but to quibble about these ranges would not do justice to the essential experimental fact: in most of the regions where Urbach's rule has been observed, a semilogarithmic plot of $\alpha(\omega)$ appears to be ruler-straight.

According to the theory of the previous chapter, the function $U_o(\omega)$ depends sensitively on the structure of the exciton bands, phonon elastic constants, and exciton-lattice interactions. The large number of different materials in which Urbach's rule has been observed inevitably suggests, however, that there should be some simple explanation. Toyozawa has attempted to give such an explanation.[2,3] He assumes that the exciton band has zero width, so that the exciton may be treated as localized at a single lattice site. He also assumes that the exciton-lattice interaction is proportional to the square of a local deformation at each lattice site.

Since the deformation at each site has a Gaussian distribution, the potential seen by a localized exciton will have a distribution appropriate to the square of a Gaussian variable. Except for a slowly varying factor, this will be an exponential with "steepness" inversely proportional to the temperature. [This model is a special case of the theory of Chapter III, so the temperature dependence of the exponential factor is automatically given by Eq. (1.3).] The exponential tail of the distribution will lie on the low energy side, provided that the coefficient of the deformation potential is negative.

Toyozawa's theory has two major weaknesses. The first is the neglect of the exciton band width. The exciton eigenstates will be localized at a single lattice site only if the kinetic energy which arises from localization at a single site is small compared to the potential energy fluctuation needed to give a state with energy ω. This occurs when $|\omega - \omega_0|$ is large compared to the band width. Since exciton band widths are generally of the order of 1 eV or more, this situation does not seem to apply in most of the cases where Urbach's rule has been observed. Toyozawa has attempted to extend his theory to the case of a non-negligible band width,[2] but his arguments on this point seem quite unconvincing. A possible justification for neglect of band width can be made, however. In most of the materials considered, the exciton bands are degenerate at $\underset{\sim}{k} = 0$, and one or more of these bands may be extremely flat. If the flat band is the lowest band in most of the Brillouin zone, and if the flat band couples sufficiently strongly to the phonons, we would expect eigenstates in the low energy tail to consist primarily of excitons from the flat band, and neglect of the other bands may be justified. Some support to the assumption of a localized exciton is lent by the fact that Urbach tails have been observed in localized absorption due to Br and I impurities in KCl.[4,5]

The second objection to Toyozawa's work is the use of a quadratic exciton-phonon interaction. Toyozawa considers the various possible modes of lattice distortion about a localized exciton, and shows, by symmetry considerations, that there will generally be <u>some</u> modes of distortion which can only interact with the exciton by an even function of the phonon amplitude, and hence, in lowest approximation, by a quadratic interaction. However, there will always be some modes which have a linear interaction with the exciton, and in general, we would not expect the linear coupling constants to be small. If one mode has a quadratic interaction while the remaining modes have a linear interaction, the quadratic mode will determine the behavior for low enough energies, (large phonon displacements). The exponential portion of the tail will not begin, however, until the quadratic term becomes more important than the linear term. (At low temperatures the exponential portion will begin when the lattice energy U(Q) necessary to produce a deformation potential $(\omega - \omega_o)$ through the linear mode becomes more than half as great as the lattice energy necessary to produce the same energy shift by the quadratic mode.) In the absence of strong reasons to the contrary, it is natural to assume that whenever quadratic terms are more important than linear terms, quartic and higher order terms will also not be negligible. If quartic terms must be added to the quadratic mode, Urbach's rule will no longer be obeyed. Toyozawa's explanation requires that quadratic terms be larger than linear terms, and much larger than quartic terms, over a large region of energy, and in a wide variety of materials. Unless some general reason for such an effect can be found, this would seem almost as much of a remarkable coincidence as the linearity of $U_o(E)$ which it seeks to explain.

If a convincing simple explanation for the linearity of $U_o(E)$ is not found, a full computation of $U_o(E)$ for each crystal may be necessary. Such a calculation would require knowledge of the exciton band structure, elastic constants and exciton-phonon coupling, which is not yet available. Before declaring the solution of the low energy tail to have been reduced to a matter of computation, however, it is certainly necessary to make a thorough investigation of the weaknesses of the theory of Chapter III, to be sure that the theory is applicable at all.

Section 2. Effects of Finite Phonon Energies

The most obvious weakness in the theory of Chapter III, in its application to real crystals, is its assumption of infinitely massive nuclei. The simplest effect of finite nuclear mass is that, because of the zero-point lattice motion, the lattice fluctuations do not go to zero as $T \to 0$. The probability distribution of the instantaneous displacement of a phonon mode of frequency ω_p is a Gaussian distribution with variance proportional to an effective temperature defined by

$$k_B T_{eff} = \frac{1}{2} \omega_p \coth \frac{\omega_p}{2k_B T} . \qquad (2.1)$$

The effective temperature is equal to T, when $T \gg \frac{1}{2} \omega_p$, and is equal to $\frac{1}{2} \omega_p$ when $T \ll \frac{1}{2} \omega_p$.

A semiclassical approximation consists in treating the phonons as static fluctuations, with the same probability distribution as the distribution of the instantaneous values of the fluctuations in the quantum mechanical crystal. If all the contribution to the low energy tail comes from phonons of approximately the same frequency, then the semiclassical approximation simply substitutes T_{eff} for T throughout Chapter III. The optical absorption then has the form

$$\alpha(\omega) = \alpha_o \exp[U_o(\omega)/k_B T_{eff}] \quad . \qquad (2.2)$$

In addition there may be a temperature dependent average-second-order-energy shift of the band edge, which may or may not be due to phonons of this same frequency, and which therefore may or may not be proportional to the same effective temperature T_{eff}. The semiclassical theory provides a natural explanation for the observed deviations from the simple temperature dependence of Urbach's rule at low temperatures, in some materials.

If different parts of the low energy tail are caused by phonons of different frequency, the relatively simple temperature dependence of Eq. (2.2) will not hold at low temperatures, since there will be different T_{eff} for different parts of the spectrum. At temperatures larger than the highest contributing phonon energies, T_{eff} becomes equal to T for all modes, and the semiclassical theory becomes identical to the classical theory of Chapter III.

In addition to the static effects of zero-point fluctuations included in the semiclassical theory, there are dynamic effects of non-zero phonon energies which are much more difficult to include, and which may even have an effect on the absorption tail at temperatures larger than the phonon frequencies. One effect is that the absorption of a phonon is accompanied by a decrease in energy of the phonon system. Thus, speaking in the language of perturbation theory, if an exciton created by a photon is scattered several times by the phonon system, absorbing a phonon in each case, the final state may have a total energy relative to the initial state which is considerably lower than the energy of the exciton alone. This effect, of course, will tend to increase the absorption of photons below the energy E_0.

The opposite effect will tend to decrease absorption in the low energy tail to a value below that predicted by the semiclassical approximation. When the exciton emits a phonon, the energy of the phonon system is increased; if the exciton is scattered a number of times, emitting a phonon each time, the final state will have an energy greater than that of the exciton alone. If the probabilities were equal of emitting or absorbing a phonon, the net effect of sometimes gaining and sometimes losing energy would be certain to increase the absorption in the low energy tail. However, at low temperatures, the probability of emitting a phonon greatly exceeds that of absorbing a phonon, and the net effect may be to produce less absorption in the low energy tail than is calculated in the semiclassical theory.

Localized exciton with linear phonon coupling. In order to understand the nature of the dynamic effects of phonon energies, we shall first study a simple model. We consider an exciton in a band of zero width, interacting with phonons of non-zero frequency, with an exciton-phonon interaction linear in the phonon coordinates and independent of the exciton momentum:

$$H = \sum_{\underset{\sim}{k}} \omega_{\underset{\sim}{k}} b^{+}_{\underset{\sim}{k}} b_{\underset{\sim}{k}} + \sum_{\underset{\sim}{k}} E_o a^{+}_{\underset{\sim}{k}} a_{\underset{\sim}{k}}$$

$$+ \sum_{\underset{\sim\sim}{kk'}} (C_{\underset{\sim}{k}} a^{+}_{\underset{\sim}{k}'} a_{\underset{\sim}{k}+\underset{\sim}{k}'} b^{+}_{\underset{\sim}{k}} + \text{Hermitian conjugate})$$

$$= \sum_{\underset{\sim}{k}} \omega_{\underset{\sim}{k}} b^{+}_{\underset{\sim}{k}} b_{\underset{\sim}{k}} + \sum_{\underset{\sim}{x}} a^{+}_{\underset{\sim}{x}} a_{\underset{\sim}{x}} \left[E_o + \sum_{\underset{\sim}{k}} \left(C_{\underset{\sim}{k}} e^{-i\underset{\sim}{k}\cdot\underset{\sim}{x}} b^{+}_{\underset{\sim}{k}} + C_{\underset{\sim}{k}} e^{i\underset{\sim}{k}\cdot\underset{\sim}{x}} b_{\underset{\sim}{k}} \right) \right] . \qquad (2.3)$$

In (2.3), $a^{+}_{\underset{\sim}{x}}$ is the creation operator for an exciton at the lattice site $\underset{\sim}{x}$. The exciton position is a constant of the motion, in this model; the Green's function $G(\underset{\sim}{x}, \underset{\sim}{x}'; E)$ for the exciton is diagonal in position, and the spectral density $A(\underset{\sim}{k}, E)$ is independent of $\underset{\sim}{k}$ and is equal to the imaginary part of $G(\underset{\sim}{x}, \underset{\sim}{x}'; E)$.

The model described above is exactly solvable, as shown by Lax.[6] The spectral density $A(E)$ is given by the equation

$$A(E) = \frac{1}{2\pi} \int e^{i(E-E_o)t} A(t)\, dt , \qquad (2.4)$$

where

$$A(t) = \exp[F(t)] , \qquad (2.5)$$

and $F(t)$ in turn is defined by

$$F(t) = \sum_{\underset{\sim}{k}} \frac{|C_{\underset{\sim}{k}}|^2}{\omega_{\underset{\sim}{k}}^2} \left\{ [n(\omega_{\underset{\sim}{k}}) + 1] e^{-i\omega_{\underset{\sim}{k}} t} + n(\omega_{\underset{\sim}{k}}) e^{i\omega_{\underset{\sim}{k}} t} + i\omega_{\underset{\sim}{k}} t - [2n(\omega_{\underset{\sim}{k}}) + 1] \right\} . \qquad (2.6)$$

Here, as in the previous chapters, $n(\omega)$ is the thermal occupation of a phonon of frequency ω. In the future we shall often denote $n(\omega_{\underset{\sim}{k}})$ simply by $n_{\underset{\sim}{k}}$. An alternative solution for A(E), which in many cases is more suited to computer calculations, has been derived by Hopfield.[7] He introduces an overall coupling constant, $\lambda^{\frac{1}{2}}$, in front of all the $C_{\underset{\sim}{k}}$, and examines the behavior of A(E) as a function of λ. He finds that A(E) obeys a "transport equation"

$$\frac{\partial A(E)}{\partial \lambda} = \int F(E - E')\, A(E')\, dE' \quad , \qquad (2.7)$$

where the kernel F(E - E') is the fourier transform of F(t). As an "initial condition" to this transport equation, we note that $A(E) = \delta(E-E_o)$, when $\lambda = 0$. In cases where an analytic expression can be found for A(t), numerical calculations can be more easily performed by using (2.4) and (2.6) than by using (2.7). Duke and Mahan[8] have performed calculations using (2.4) - (2.6) of the density of one-electron states for models appropriate to several kinds of localized electronic states, coupled to the phonons via longitudinal optical, piezoelectric, and deformation potential interactions.

If all the phonons have the same frequency ω_p, the spectral density has a relatively simple form. It is a series of δ-functions separated in energy by integral multiples of ω_p. The weights of the δ-functions may be expressed in terms of modified Bessel's functions of integral order.[6]

In order to study small deviations from semiclassical behavior caused by non-zero phonon frequencies, we shall work with Equations (2.4) - (2.6). If we expand F(t) in powers of $\omega_{\underset{\sim}{k}} t$, we find

$$F(t) = \sum_{\underset{\sim}{k}} |C_{\underset{\sim}{k}}|^2 \left[(2n_{\underset{\sim}{k}}+1)\frac{(it)^2}{2} - \omega_{\underset{\sim}{k}} \frac{(it)^3}{6} + \frac{(2n_{\underset{\sim}{k}} + 1)\omega_{\underset{\sim}{k}}^{\,2}\,(it)^4}{24} + \dots \right] . \qquad (2.8)$$

If we keep only the lowest term in this expansion, we find

$$A(t) = \exp(-\eta t^2/2) \quad , \tag{2.9}$$

where

$$\eta = \sum_{\underset{\sim}{k}} |C_{\underset{\sim}{k}}|^2 (2n_{\underset{\sim}{k}} + 1) \quad . \tag{2.10}$$

Taking the Fourier transform of (2.9) we obtain the semiclassical result

$$A(E) = (2\pi\eta)^{-\frac{1}{2}} \exp[-(E - E_o)^2/2\eta] \quad . \tag{2.11}$$

The temperature dependence of η is contained in the factor $(2n_{\underset{\sim}{k}} + 1)$. For high temperatures this is proportional to the temperature T; for general temperatures it is proportional to the effective temperature defind by Eq. (2.1).

When higher terms in the expansion (2.8) are taken into account, (2.11) will no longer be exact. In general, we may write

$$A(E) \equiv (2\pi\eta)^{-\frac{1}{2}} \exp[-(E - E_o)^2/2\eta + \triangle(E, T)] \quad . \tag{2.12}$$

We shall say that the semiclassical approximation is good at energy E, if $|\triangle(E, T)|$ is small compared to $[(E - E_o)^2/2\eta]$. The magnitude of $\triangle(E, T)$ can best be estimated by examining the Laplace transform of A(E). The Laplace transform can be found by analytically continuing the Fourier transform, A(t), to imaginary values of t. Thus we have

$$A(-i\tau) = \int e^{-\epsilon\tau} A(E_o + \epsilon)\, d\epsilon \quad . \tag{2.12a}$$

To estimate the magnitude of $\triangle(E, T)$, we examine $A(-i\tau)$ when $\tau = (E_o - E)/\eta$. If we assume that $\triangle(E, T)$ is small compared to $(E - E_o)^2/2\eta$ and not too rapidly varying, then it follows from (2.12) and (2.12a) that when $\tau = (E_o - E)/\eta$,

$$A(-i\tau) \approx e^{\frac{1}{2}\eta\tau^2} e^{\Delta(E,T)} = \exp\left[\frac{(E - E_o)^2}{2\eta} + \Delta(E, T)\right] . \quad (2.13)$$

Thus, if $\Delta(E, T)$ is small compared to $(E - E_o)^2/2\eta$, the logarithm of the Laplace transform will be dominated by the semiclassical term, $\frac{1}{2}\eta\tau^2$, when $\tau = \frac{(E_o - E)}{\eta}$. With Eq. (2.5), this implies

$$|F(-i\tau) - \frac{1}{2}\eta\tau^2| \ll \frac{1}{2}\eta\tau^2 \quad , \quad \text{when } \tau = (E_o - E)/\eta. \quad (2.14)$$

We should also like to prove the converse of the above, i.e., that (2.14) implies $|\Delta(E, T)| \ll \frac{1}{2}(E - E_o)^2/\eta$. Unfortunately, if $|\Delta(E, T)| > \frac{1}{2}(E - E_o)^2/\eta$, then the approximation (2.13) does not necessarily hold, and (2.14) is not necessarily violated. However, if $\Delta(E, T)$ is reasonably slowly varying, it can be shown that $|\Delta(E, T)| > \frac{1}{2}(E_o - E)^2/\eta$ does imply violation of (2.14) for some τ less than $(E_o - E)^2/\eta$ and greater than zero. Thus, a necessary and sufficient criterion for the semiclassical approximation to be valid for energies greater than E and less than E_o, is that (2.14) hold for $0 < \tau < (E_o - E)/\eta$. Using the expansion (2.8) for $F(-i\tau)$, we find that the condition for validity of the semiclassical approximation is

$$\left| \frac{-\epsilon \sum_{\underset{\sim}{k}} |C_{\underset{\sim}{k}}|^2 \omega_{\underset{\sim}{k}}}{3\eta^2} + \frac{\epsilon^2 \sum_{\underset{\sim}{k}} |C_{\underset{\sim}{k}}|^2 \omega_{\underset{\sim}{k}}^2 (2n_{\underset{\sim}{k}} + 1)}{12\eta^3} \right| \ll 1 \quad ,$$

$$\text{for } 0 < \epsilon < (E_o - E) . \quad (2.15)$$

In (2.15) we have kept terms arising from both the t^3 and t^4 terms in $F(t)$, because the even terms involve $(2n_{\underset{\sim}{k}} + 1)$ and can be more important than the odd terms at high temperatures. If E and $\omega_{\underset{\sim}{k}}$ are held fixed, (2.15) will be satisfied if either the temperature or the coupling constants are large. If the coupling constants are sufficiently large, the semiclassical approximation will be valid even at T = 0; if the coupling constants are very small, the semiclassical approximation will be valid only at very high temperatures. It should also be noted, that for fixed temperature, phonon frequencies, and coupling constants, the semiclassical approximation will become invalid if $|E - E_o|$ is made sufficiently large.

<u>General exciton band with linear phonon coupling.</u> We now wish to consider the effects of finite phonon frequencies when the exciton band is not flat. We still assume harmonic phonons with linear exciton phonon coupling. The Hamiltonian for the model is given by

$$H = \sum_{\underset{\sim}{k}} \epsilon_{\underset{\sim}{k}} a^{+}_{\underset{\sim}{k}} a_{\underset{\sim}{k}} + \sum_{\underset{\sim}{k}} \omega_{\underset{\sim}{k}} b^{+}_{\underset{\sim}{k}} b_{\underset{\sim}{k}}$$

$$+ \sum_{\underset{\sim}{k}\underset{\sim}{k}'} (c_{\underset{\sim}{k}\underset{\sim}{k}'} a^{+}_{\underset{\sim}{k}'} a_{\underset{\sim}{k}+\underset{\sim}{k}'} b^{+}_{\underset{\sim}{k}} + \text{Hermitian conjugate}) .$$

For this model, of course, an exact theory has not been discovered, and we shall be forced to use a somewhat crude approximation. We shall first assume that when the exciton is present in the system, it always has the wave-function $f(\underset{\sim}{x} - \underset{\sim}{x}_o)$, where f is a fixed function and $\underset{\sim}{x}_o$ is a <u>fixed</u> lattice site. Thus, when the exciton is present, we project the Hamiltonian of (2.16) onto the subspace where the exciton has wave-function f. If $a^{+}_{[f]\underset{\sim}{x}_o}$ is the creation operator for an exciton with wave-function $f(\underset{\sim}{x} - \underset{\sim}{x}_o)$, we obtain the reduced Hamiltonian

$$H_{\text{red}} = \sum_{\underset{\sim}{k}} \omega_{\underset{\sim}{k}} b^{+}_{\underset{\sim}{k}} b_{\underset{\sim}{k}} + a^{+}_{[f]\underset{\sim}{x}_0} a_{[f]\underset{\sim}{x}_0} \left[\theta + \sum_{\underset{\sim}{k}} (C_{\underset{\sim}{k}} b^{+}_{\underset{\sim}{k}} + C_{\underset{\sim}{k}}^{*} b_{\underset{\sim}{k}}) \right], \tag{2.17}$$

where

$$\theta \equiv \sum_{\underset{\sim}{k}} \epsilon_{\underset{\sim}{k}} |f(\underset{\sim}{k})|^2 , \tag{2.18}$$

$$C_{\underset{\sim}{k}} \equiv \sum_{\underset{\sim}{k}'} c_{\underset{\sim}{k}\underset{\sim}{k}'} f(\underset{\sim}{k}')^{*} f(\underset{\sim}{k} + \underset{\sim}{k}') e^{-i\underset{\sim}{k}\cdot\underset{\sim}{x}_0} . \tag{2.19}$$

The reduced Hamiltonian is essentially identical in form to the Hamiltonian of an exciton localized at a single lattice site in a flat band, and the exciton density of states for the reduced Hamiltonian can be found in the same manner as for Hamiltonian (2.3).

In the semiclassical approximation, the density of states of the reduced Hamiltonian (2.17) is identical to $p_f(E - \theta)$, the probability distribution of the variational energy $E(\underset{\sim}{x}_0)$ at the given point $\underset{\sim}{x}_0$. In Chapter III, we found that when the width of the trial function f was of the order of a few lattice constants, it was a good approximation to say that the total density of states of the system is just N/Ω times $p_f(E - \theta)$, where N/Ω is the number of lattice sites per unit volume. The probability of counting an eigenstate twice by this procedure was found to be negligible in the low energy tail. We shall make a similar approximation in our present study: we approximate the density of states of the true Hamiltonian by N/Ω times the density of states of the reduced Hamiltonian at a single point $\underset{\sim}{x}_0$.

Our approximation for the density of states is thus

$$\rho_f(E) = (N/\Omega)\, B(E) , \tag{2.20}$$

where

$$B(E) = \frac{1}{2\pi} \int e^{i(E-\theta)t} A(t)\, dt \quad . \tag{2.21}$$

The function A(t) is given by Eq. (2.5) and (2.6). The spectral density $A(\underset{\sim}{k}, E)$ is approximated by

$$A(\underset{\sim}{k}, E) = (N/\Omega)\ |f(\underset{\sim}{k})|^2\, B(E) \quad . \tag{2.22}$$

If $f(\underset{\sim}{x})$ is spread over a small number of lattice sites, $|f(\underset{\sim}{k})|^2$ will be of the order of Ω/N, and the factor $(N/\Omega)|f(k)|^2$ in (2.22) will be of order unity.

The approximations $\rho_f(E)$ and $A(\underset{\sim}{k}, E)$, of course, depend on the choice of trial function f. In the case of zero-frequency phonons, we chose f by a variational principle requiring that we maximize $\rho_f(E)$. It is not clear how we should choose f when the phonon frequencies are finite. In the region where the phonon frequencies are not too great, it seems a reasonable choice for f to use just that function which maximizes $\rho_f(E)$ in the semiclassical approximation. Since the semiclassical $\rho_f(E)$ is stationary with respect to small changes of f from its optimum value, the quantum mechanical ρ_f will not be too sensitive to small deviations of f from its correct value, at least if the phonon energies are not too great. It should be emphasized that, as in Chapter III, a different function f will be chosen for each energy E at which we wish to calculate the density of states of the true Hamiltonian.

The approximation we have just described is certainly a crude one, and a completely satisfactory justification for it cannot be given at the present time. It should be noted, however, that the approximation gives exactly the correct density of states and spectral density for a flat exciton band, for any magnitude of phonon energies, and for a general exciton band the approximation agrees with the classical calculations of Chapter III, if the nuclei are infinitely massive. We do not expect great accuracy for the approximation when both the phonon frequencies and the exciton band widths are large, but we do expect the approximation to be good enough for our main purpose: to answer the question of whether or not the semiclassical approximation is valid.

Because the function B(E) is calculated in the same manner as the function A(E) one calculates in the case of a flat exciton band, we can use the techniques developed in the flat band case to decide whether or not a semiclassical calculation of B(E) is a good approximation to a quantum-mechanical calculation. The semiclassical approximation will be valid if the inequality (2.15) is satisfied, with the coupling constants $C_{\underset{\sim}{k}}$ given by (2.19) and with θ substituted for E_o in (2.15). It should be remembered, that the values of θ and $C_{\underset{\sim}{k}}$ depend on the function f, and consequently on the value of E.

Because we do not know the band structure and coupling constants of the real materials we wish to investigate, we must somehow estimate the value of $C_{\underset{\sim}{k}}$ from experiment. We shall do this from Urbach's rule itself. We shall assume that Urbach's rule holds in the form

$$\alpha(E) = A_o{}' \exp[\,\sigma(E - E_o + \nu T_{eff})/k_B T_{eff}] \ , \qquad (2.23)$$

where $-\nu T_{eff}$ is the second order energy shift of the band edge as a whole, and $A_o{}'$ is of the order of magnitude of the optical absorption above the band edge. We have not yet included the second order energy shift in our quantum mechanical procedure for calculating the density of states and spectral density, and we assume that we can do so by simply adding the energy shift to the kinetic energy θ. We shall also assume that the important phonons all have approximately the same frequency, ω_p, and that T_{eff} is given by Eq. (2.1).

The semiclassical theory tells us that the optical absorption $\alpha(E)$, which is proportional to $A(\underset{\sim}{Q}, E)$, is given in the low energy tail by

$$\alpha(E) = \beta_o(E, T) \exp[- (E - \theta + \nu T_{eff})^2/2\eta] \quad , \tag{2.24}$$

where $\beta_o(E, T)$ is a slowly varying function of E and T, which has the order of magnitude of the optical absorption above the band edge. The function η is given by Eq. (2.10) and is proportional to T_{eff}. If we equate the exponents of (2.23) and (2.24), we find

$$\sum |C_{\underset{\sim}{k}}|^2 = -(E - \theta + \nu T_{eff})\omega_p/4\sigma' \tag{2.25}$$

where

$$\sigma' = \sigma(E - E_o + \nu T_{eff})/(E - \theta + \nu T_{eff}) \tag{2.26}$$

Since $\theta - E_o$ is greater than zero and is of the order of magnitude of $|(E - E_o + \nu T_{eff})|$, it follows that σ' is of the order of, but somewhat smaller than, the steepness constant σ. The constant σ' may have some energy dependence.

The condition (2.15) for the validity of the semiclassical approximation may be written:

$$\left| - \frac{\epsilon}{3} \frac{\omega_p^{\,3}}{(2\, k_B\, T_{eff})^2\, \Sigma |C_{\underset{\sim}{k}}|^2} + \frac{\epsilon^2}{12} \frac{\omega_p^{\,4}}{(2\, k_B\, T_{eff})^2 (\Sigma |C_{\underset{\sim}{k}}|^2)^2} \right| \ll 1, \tag{2.27}$$
$$\text{for all } 0 < \epsilon < (\theta - \nu T_{eff} - E).$$

If we substitute (2.25) into (2.27), we find the criterion

$$\frac{4}{3}\left|\gamma^2 - \gamma\right|\left(\frac{\omega_p}{2k_B T_{eff}}\right)^2 \ll 1\ , \quad \text{for all } \gamma \text{ such that } 0 < \gamma < \sigma' \ . \tag{2.28}$$

The fact that (2.28) is independent of E, except for possible energy dependence of σ', is a coincidence. The factor $(\omega_p/2k_B T_{eff})^2$ is equal to 1 at absolute zero temperature, and is equal to $(\omega_p/2k_B T)^2$ at temperatures larger than ω_p/k_B.

For many of the materials in Table 1, σ is in the vicinity of 1. The maximum value of $|\gamma^2 - \gamma|$, in the domain $0 < \gamma < 1.2$, occurs at $\gamma = \frac{1}{2}$, and has the value $|\gamma^2 - \gamma| = \frac{1}{4}$. Thus for these materials at absolute zero, the left-hand side of the inequality (2.28) has the maximum value 1/3. The inequality is thus only weakly satisfied, and it is not clear whether or not the semiclassical approximation is valid at $T = 0$. At high temperatures, however, the inequality (2.28) is very well satisfied. The exact value of (2.28) depends on what one puts in for the relevant phonon frequency. The most conservative choice is to use the highest possible phonon frequency, generally the frequency of the longitudinal optical mode. The optical mode frequencies for some of the materials exhibiting Urbach's rule are given in Table 2.

The highest temperature at which Urbach's rule has been observed is 1000°K. This measurement was made in potassium bromide, which has a longitudinal optical phonon frequency $\omega_L = 230^\circ$K. The left-hand side of (2.28) in this case is less than 0.005.

For the materials in Table 1 which have steepness constant $\sigma \geq 2$, it is probable that a semiclassical theory would not be valid at 0°K.

Whether or not a semiclassical theory would be valid at the actual temperatures at which data have been taken depends critically on the frequencies of the relevant phonons. If the important phonons in these materials are long wavelength acoustic phonons, then the classical theory may well be valid. The fact that in these materials the slope of log $\alpha(\omega)$ is inversely proportional to temperature down to the lowest temperatures studied, is consistent with this possibility.

An interesting example of a material in which a semiclassical theory would not be valid at low temperatures is CdTe.[9] Marple and Segall have observed the low energy absorption tail of CdTe over the temperature range 2.1° - 177°K. At temperatures from 39° to 90°K a clearly defined shoulder appears in the optical absorption at an energy one longitudinal-optical-phonon frequency below the band edge. At temperatures 90° to 150°K a second bump is apparent two longitudinal-optical-phonon frequencies below the band edge. At 177°K the optical absorption looks almost straight on a semilogarithmic scale, corresponding to an Urbach's rule tail with $\sigma \approx 4$.

The implication of these observations is that at low temperatures the low energy tail is simply due to the absorption by the exciton of one or two optical phonons. This is borne out by the fact that the height of the first shoulder, at low temperatures, is roughly proportional to $\exp(-\omega_L/k_BT)$, the population of the optical phonon mode. When the absorption of only one or two phonons is involved, we expect to obtain good results from the first few orders of perturbation theory, or from a self-consistent Green's function calculation. Segall and Marple have made a perturbation theoretic calculation for CdTe, and have found that they could fit the experimental data quite well over the entire range of observations.

There are other examples where effects of finite phonon frequencies appear. In the case of anthracene, mentioned in Table 1, the Urbach's rule tail, which falls from the absorption edge, levels off into a shoulder which occurs at one optical-phonon frequency below the absorption edge.[10] The Urbach's tail is probably due to acoustic phonons, while the shoulder is clearly due to the absorption of one optical phonon. A similar situation may occur in CdS at low temperatures.[11]

Nonlinear systems. Thus far, we have considered the dynamic effects of finite phonon frequencies under the assumption that the excitons are coupled linearly to harmonic phonons. If nonlinear terms are important in the exciton-phonon coupling, or if anharmonic terms are important in the phonon Hamiltonian, it becomes much more difficult to say anything about the effect of phonon energies. In a linear system, the interaction Hamiltonian only couples states which differ by one phonon occupation number; as a consequence, one cannot obtain a lot of energy from the phonon system except in very high orders of perturbation theory. In a system with nonlinear phonon-exciton coupling or anharmonic phonons, the interaction Hamiltonian can connect states differing by two or more phonon numbers, and it may be easier to get energy from the phonons. Thus the possibility exists that phonon energies may be important in real materials, when estimates based on the assumptions of a linear-system indicate that they would not be important. This possibility may even exist when the semiclassical approach indicates that the nonlinear phonon coupling is small compared to the linear coupling. Although this problem has been studied at some length, we are not in a position to shed much light on the matter at the present time. A few results of our study should be mentioned, however.

We have examined the model proposed by Toyozawa[2,3] to explain Urbach's rule which we mentioned in section 1: a localized exciton interacting with harmonic phonons via an interaction proportional to the square of a local deformation. Toyozawa has studied this model semiclassically, and he has found a spectral density proportional to $(E_o - E)^{-\frac{1}{2}} \exp[\sigma(E - E_o) /k_B T_{eff}]$ for $E < E_o$ and zero spectral density for $E > E_o$. Toyozawa's model can be solved exactly, quantum mechanically, if all the phonons have the same frequency, provided that the coupling is not too strong (σ, computed semiclassically, must be ≥ 1).[12] Although given in analytic form, the results are not too easy to interpret at finite temperatures. At 0^oK, however, they show an important qualitative deviation from the semiclassical results. The spectral density has an exponential tail on the positive energy side, and vanishes completely for energies more than one-half phonon frequency below E_o. If the coupling is strong ($\sigma < 1$), then the oscillator is unstable when the exciton is present, and a quantum-mechanical calculation is more difficult to make. A low energy tail will exist in this case, even at 0^oK, but it will almost certainly fall off much more rapidly than the semiclassical estimate if σ is not too different from 1. Thus Toyozawa's model is apparently incorrect at low temperatures in those materials of Table 1 where the steepness of the Urbach's tail has been observed to become independent of temperature as $T \rightarrow 0^o$K.

We have also attempted to get information about Toyozawa's model at finite temperatures by studying the Laplace transform of the spectral density. We have set upper and lower bounds to the asymptotic form of the spectral density as $E - E_0 \rightarrow - \infty$, which assure us that the semiclassical analysis is essentially correct when $k_B T_{eff}/\sigma$ is sufficiently large compared to the phonon energy. These bounds are only of marginal usefulness, however, for the parameters appropriate to the experimental results which have been so far obtained.

We have also considered phonon systems which are extremely anharmonic, i.e., systems in which the lattice potential energy becomes infinite when an atom is displaced from equilibrium, in some direction, by an amount comparable to the zero-point fluctuation. One finds, at least in some cases, that a linear exciton phonon interaction can appreciably couple very high excited phonon states directly to the ground state of the oscillator. It is then possible for the exciton to obtain all the phonon energy at a single lattice site by scattering in first order perturbation theory. One finds a low energy tail of optical absorption which essentially varies as $\exp[(E - E_0)/k_B T]$. If this extreme anharmonic picture wer valid, we would have an explanation of Urbach's rule (with $\sigma = 1$) which was independent of the exciton band structure and other details of the particular material. Unfortunately, all estimates of real materials indicate that the anharmonicity is much too small to produce such a simple explanation of Urbach's rule.

Section 3. Terms Left out of the Model

Before abandoning our search for a simple explanation of Urbach's rule, it is necessary to examine some of the terms present in the general theory of optical absorption outlined in Chapter I, which have been dropped from the models we have thus far considered. These terms have generally been dismissed because they are considered "small" or "negligible" compared to the terms which have been kept in our models. However, in the low energy tail, where the absorption is in any case very small, one must be sure that the "small" terms do not dominate.

One approximation which may be reexamined is the neglect of the dependence of the electronic current operator on the displacements of the nuclei, arising from the dependence of the definition of "unperturbed" exciton creation operators $a^{+}_{\underset{\sim}{k}\mu}$ themselves on the lattice configuration. [Cf. Eq. (2.10), Chapter I.] Thus, the virtual exciton created by an incident photon in a deformed lattice is not necessarily placed in the zero-momentum state, but it may be put in a state which has somewhat larger or smaller amplitudes in regions of large deformations. In a lattice of infinitely massive nuclei, this may lead to an enhancement of the optical absorption in the low energy tail, because the virtual state so created may have a larger overlap with a low energy eigenstate, localized in a region of large deformation, than does the zero momentum exciton state. However, a dependence of the current operator on the lattice configuration cannot lead to any change in the most important factor affecting the optical absorption in the low energy tail, namely, the total exciton density of states, $\rho(E)$. Thus, although a deformation dependence of the current operator could conceivably produce a factor of two in the optical absorption at low energies, it could not lead to a significant change in the exponential drop off of the absorption. It can also be shown that the deformation dependence of the current operator will not be important in the low energy tail when the nuclei have finite mass, as long as the current operator is a smooth function of the deformation. It should be mentioned, however, that there is no apparent reason why the deformation dependence of the current operator will not play an important role in the magnitude of optical absoption due to indirect transitions, above the fundamental edge.

Another possible source for optical attentuation in the low energy tail is Brillouin or Raman scattering of light. (See Eq. (1.17), Chapter I, and the following discussion.) This possibility has in fact been considered by Agronovich and Konobeev.[13] Ordinarily, the scattering of light by phonons is extremely weak, leading to attenuation lengths of the order of 10^4 cm. In the vicinity of the fundamental absorption edge, however, where the dielectric constant is a rapidly varying function of energy, a lattice distortion which produces a small change in the band gap can result in a large change in dielectric constant. Thus the Brillouin and Raman scattering of light may be several orders of magnitude greater near the band edge than would otherwise be expected. There are a number of reasons, however, why this cannot be the explanation of Urbach's rule. In the first place, the temperature dependence is wrong -- at a given distance below the absorption edge the Brillouin and Raman scattering should be roughly proportional to the temperature, for temperatures larger than the phonon frequencies. In the second place, although the coupling between phonons and photons does depend on the distance of the photon energy from the absorption threshhold, it does not lead to anything as rapid as an exponential decrease in the scattering with decreasing energy. Agranovich and Konobeev find in their model, that $\alpha(E)$ is proportional to $|E - E_o|^{-9/2}$, when E is well below E_o. They also find that $\alpha(E)$ increases very rapidly as E gets close to E_o, but this result is due to their manner of treating the dielectric constant. They essentially assume that the dielectric constant has a pole corresponding to an exciton of infinite transport lifetime, whose energy may be shifted by a deformation. If the broadening of the exciton pole due to phonon scattering were included properly, they would not find such a large Brillouin scattering right near the threshhold. A rough estimate of the magnitude of the Brillouin and Raman scattering, using experimentally observed exciton line widths, indicates that the attenuation due to scattering would be smaller than the observed low energy tails in most, if not all, of the region of observation.

Section 4. Conclusions

The theory of the low energy tail developed in Chapter III is consistent with, but does not explain, the empirically observed Urbach's rule. Because of the great success of our theory in its application to an exactly solvable one-dimensional model, we strongly believe that, if it is indeed correct to treat the phonons as static thermal fluctuations, then the theory of Chapter III should be applicable to real crystals, with semiclassical modification to include zero-point fluctuations at low temperatures. Our investigation of possible dynamic effects of phonons indicates that the assumption of static phonons is permissible in at least some, and possibly all, of the materials and temperatures where Urbach's rule has been observed, provided that one may assume harmonic phonons and a linear exciton-phonon interaction. The possibility of enhanced dynamic effects, due to nonlinear exciton-phonon interactions or anharmonic terms in the phonon Hamiltonian, has not been definitely ruled out. The search for a simple alternative explanation of Urbach's rule has not met with any success.

REFERENCES FOR CHAPTER IV

1. R. S. Knox, Theory of Excitons, Solid State Physics, Supplement 5 (Academic Press, New York, 1963) p. 152.
2. Y. Toyozawa, Technical Report, Ser. A., No. 119, Institute for Solid State Physics, University of Tokyo (1964). Extensive references to the experimental literature are contained in this reference and in Reference 1.
3. Y. Toyozawa, Progr. Theor. Phys. 22, 455 (1959).
4. H. Mahr, Phys. Rev. 125, 1510 (1962); Phys. Rev. 132, 1880 (1963).
5. K. Kobayashi and T. Tomiki, J. Phys. Soc. Japan 15, 1982 (1960); J. Phys. Chem. Solids 22, 73 (1961).
6. M. Lax, J. Chem. Phys. 20, 1752 (1952).
7. J. J. Hopfield in International Conference on the Physics of Semiconductors, Exeter, 1962 (The Institute of Physics and the Physical Society, London, 1962) p. 75.
8. C. B. Duke and G. D. Mahan (to be published).
9. B. Segall (private communication); B. Segall and D. T. F. Marple, Bull. Am. Phys. Soc. 9, 223 (1964).
10. I. Nakada, J. Phys. Soc. Japan 20, 346 (1965).
11. J. J. Hopfield, J. Phys. Chem. Solids 22, 63 (1961).
12. T. H. Keil, Ph.D. thesis, University of Rochester (1965).
13. V. M. Agranovich and Yu. V. Konobeev, Soviet Phys. -- Solid State 3, 260 (1961).

TABLES FOR CHAPTER IV

Table 1. Experimental Confirmations of Urbach's Rule
Taken from Toyozawa, Reference 2, p. 61. References to the experimental literature are given in the original table.

The constants σ and ω_o are defined in Eq. (2.1), Chapter IV, of the present text. The constant T_o, where observed, is the limiting value of the effective temperature in Urbach's rule, as the true temperature T approaches 0^oK. The quantity ϵ_o is the energy of the absorption peak at the lowest temperature or that extrapolated to 0^oK.

The case of TlCl requires special explanation. This crystal appears to be a direct material at low temperatures. At high temperatures, another position of the Brillouin zone appears to be shifted down to energies lower than the local minimum at $\underset{\sim}{k} = 0$. The coupling between the indirect edge and the $\underset{\sim}{k} = 0$ states is sufficiently weak so that the indirect absorption is several orders of magnitude weaker than the direct absorption. At high temperatures, two absorption edges appear, each with its own Urbach's tail, one made up of states near the indirect edge, and one made up of states near the direct edge. The absorption drops rapidly in an Urbach tail from the direct edge and levels off at the "background level" of indirect absorption. At the indirect absorption edge, this "background" itself drops off in an Urbach tail.

TABLE 1

Substance	Nature of transition	ϵ_o (eV) peak at 0^oK	ω_o (eV)	σ	Validity Range		T_o (^oK)
					$\alpha(cm^{-1})$	T (^oK)	
KBr	direct	6.76	$\approx \epsilon_o$	0.79	$10^{-2} \sim 3 \times 10^3$	$20 \sim 1000$	69
KCl	direct	7.76	$\approx \epsilon_o$	0.80	$1 \sim 200$	$299 \sim 469$	
KI	direct	5.89	$\approx \epsilon_o$	0.82	$10^{-2} \sim 7 \times 10^3$	$20 \sim 90$	80
AgBr	indirect	-	2.81	1.0	$10^{-2} \sim 30$ < 0.5	$100 \sim 650$ > 65	
TlCl	direct indirect	3.44 -	3.46 3.5	1.1 1.16	$30 \sim 10^4$ $10^{-2} \sim 1$	$20 \sim 600$ $300 \sim 600$	≈ 200
PbI_2	direct	2.525		1.3	$1 \sim 10^3$	$77 \sim 300$	
CdS	direct $\|\|c$ $\perp c$	2.586 2.570	2.608 2.584	2.17	$10^2 \sim 10^4$	$90 \sim 340$	$\lesssim 100$
InAs				5.6 3.8	$3 \sim 10^3$	78 300	
InSb				$\gtrsim 5.34$ $\gtrsim 5.0$	$10^2 \sim 5 \times 10^2$ $2 \sim 4 \times 10^2$	295 300, 78	
$ZnIn_2S_4$	$\perp c$			(σ/T_o) $=(970^oK)^{-1}$	$10^2 \sim 10^4$	$91 \sim 368$	$\gtrsim 400$
Anthracene	$\|\|a$ $\|\|b$	3.16 3.13	3.14 3.12	1.70 .96	$10 \sim 7 \times 10^3$ $40 \sim 2 \times 10^3$	$93 \sim 355$	$\lesssim 100$
KCl: Br	localized		7.35	0.51	$1 \sim 100$ (1.3×10^{-4} mol)	$299 \sim 469$	
KCl: I	localized	6.6		0.77	$0.4 \sim 6 \times 10^3$ (10^{-3} mol)	$80 \sim 700$	360
AgCl	indirect		3.33	0.82	$10^{-2} \sim 30$ < 0.5	$100 \sim 650$ > 65	

TABLE 2

TRANSVERSE AND LONGITUDINAL OPTICAL PHONON FREQUENCIES

Natural	ω_T	ω_L	Ref.
KBr	160°K	230°K	a
KI	140	210	a
KCl	200	300	a
AgCl	150	250	a
AgBr	110	180	a
TlCl	120	310	a
InAs	300	330	b
InSb	250	260	b

a) M. Born and K. Huang, Dynamical Theory of Crystal Lattices, (Oxford University Press, Oxford, 1954) p. 85.

b) H. P. R. Frederikse in American Institute of Physics Handbook, (McGraw-Hill Book Company, Inc., New York, 1963), 2nd ed., p. 9-62.

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