# Solids with thermal or static disorder. II. Optical properties

B. Chakraborty and P. B. Allen

*Department of Physics, State University of New York, Stony Brook, New York 11794*

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The effect of temperature and impurities on optical properties of solids is discussed with particular emphasis on features absent for free electrons but present for Bloch electrons. Using an equation-of-motion method, a generalized Boltzmann equation valid for both intraband and interband conduction is obtained. This is formally solved to give an expression for the conductivity $\sigma(\omega)$ nearly identical to the usual Kramers-Heisenberg dispersion formula except for a complex, frequency-dependent function $M_{knn'}(\omega)$ which serves to shift and broaden the energy denominators. When the external frequency $\omega$ is on resonance with an interband transition $\epsilon_{\vec{k}n} - \epsilon_{\vec{k}n'}$, the function $M$ becomes to good approximation $\Sigma(kn,\epsilon_{\vec{k}n}) - \Sigma^*(kn',\epsilon_{\vec{k}n'})$, i.e., the one-electron self-energy shift. When $\omega$ is on resonance with an indirect transition $\epsilon_{\vec{k}n} - \epsilon_{\vec{k}'n'}$, the standard theory of phonon- or impurity-induced indirect absorption is obtained. New results are given for the shift of the dc dielectric constant. The connection with Holstein's and other quantum Boltzmann-like equations (for intraband conductivity) is described in an appendix.

## I. INTRODUCTION

In the preceding paper[1] (referred to as I), the effect of thermal and static disorder on one-electron properties has been discussed. An optical excitation involves both an electron and a hole. The effect of disorder is twofold: (a) it alters the properties of the electron and hole separately, as described by one-electron theory; (b) the electron and hole interact with each other via the disorder. The processes of type (b) make the theory for optical response functions much more complicated than one-electron theory. As in I, we emphasize the new features that emerge when the electron states are Bloch waves and not plane waves.

Our motivation for starting this work arose from a particular problem: the shift with temperature of interband edges in the optical spectra of both semiconductors and metals. Typically the shift is of the order of $4 \times 10^{-4}$ eV/°K. The primary cause for this is electron-phonon interaction. Various one-electron theories of the phenomenon exist. Fan[2] suggested a self-energy theory keeping only intraband terms. Antoncik[3] pointed out the importance of Debye-Waller terms. Recently it has been realized[4] that both types of terms are needed in a complete theory. Allen and Heine[5] have systematically discussed the one-electron problem, and show how both corrections enter on equal footing in the theory, including interband self-energy terms omitted by Fan. There exists an alternative formulation[6] of the problem due to Brooks. This theory is a simple consequence of thermodynamics, and expresses the temperature variation of the gap as the effect of electron-hole pairs on phonon frequencies. The method has been applied by Heine and Van Vechten to explain the temperature dependence of band gaps in Si. In making comparison with experimental data, it is implicitly assumed that shift of interband edges is given by the change in one-electron energies. The neglect of interference effects between the electron and the hole worried us, so we proceeded to get a theory for the effect of disorder on optical response functions. In the process we obtained a generalized Boltzmann equation for a particle-hole amplitude function. This equation can be used for various purposes, and is much more general than the specific problem it was intended for.

The combined effect of disorder and interband transitions has not received much attention in the literature. A simple method for getting the conductivity is to use the Fermi golden rule for the real part, and Kramers-Kronig analysis for the imaginary part. This is the approach[7] taken by both Stevenson and Nettel. They have considered the effect of electron-phonon interaction using low-order perturbation theory. Nettel's calculation is restricted to one-phonon processes. Stevenson's work includes multiphonon, Debye-Waller, and anharmonic effects. His calculation, using a local pseudopotential approximation for sodium shows excellent agreement with experiment at low frequencies, even beyond the Drude absorption region. He has also calculated the temperature dependence of the spectrum due to lattice expansion and Debye-Waller factors. The effect of a single impurity on interband absorption has been studied by Parlebas and Mills.[8] They have used a more sophisticated perturbative method. The expression for $\epsilon_2(\omega)$ (imaginary part of the dielectric constant) in terms of Green's functions [Eq. (2.12), Ref. 8] is exact and can be used for a dilute alloy after ensemble

averaging over impurity configurations. Parlebas and Mills deal with a single impurity and as a further simplification they consider a two-band model. This greatly simplifies the task of evaluating $\epsilon_2(\omega)$. The expression they get at this stage though much simpler, is still difficult to analyze for information about the structure of $\epsilon_2(\omega)$. For this purpose the authors assume a one-dimenional form for each of the two bands and calculate $\epsilon_2(\omega)$ for this model. Their calculation shows that new features arise in the spectrum due to impurity-induced absorption. Our expression for the conductivity includes these effects in a more complete way, since it takes into account the effect of more than one impurity (the dilute approximation is made however), and a completely general band structure.

The analogous problem of dc transport in a solid has been considered by Kohn and Luttinger.[9] They use an equation-of-motion method to get a dc transport equation for an electron-impurity system. Interband effects are not included properly in their work. As the frequency is increased to infrared values, quantum effects become important. Ron[10] and Yamada[11] have generalized Kohn and Luttinger's method to finite frequencies, but treated the electrons as free and not Bloch electrons. A more systematic way of attacking the problem is by Green's functions and Feynman-diagram techniques. The Green's-function theory of Kadanoff and Baym[12] has been used by Prange and Kadanoff[13] for the electron-phonon system. Holstein[14] has derived a transport equation using diagrammatic methods. To the best of our knowledge no attempt has been made to generalize these treatments to include interband transitions. We have generalized Kohn and Luttinger's method to obtain a theory which properly takes into account interband effects. We have not used diagrammatic or Green's-function techniques since the equation-of-motion method itself gets complicated enough and gives the level of accuracy we need. Some of the above-mentioned equations are dealt with more completely in Appendix B, and a comparison between these and the present work made.

The definition of a generalized distribution function and the Boltzmann-type equation that it satisfies are presented in Sec. II. In this section we also examine the equation in various limits and see how familiar results can be recovered. In Sec. III a transformation of the equation is presented which enables us to write down a general solution for the optical conductivity. This section also deals with applications of the general results to specific cases of interest, primarily in semiconductors. A brief derivation of the equation is presented in Appendix A, and Appendix B discusses relevant previous work, and their relation

to our work.

Some of the results of this paper have already been presented in a brief Note.[15] Since then we have found a more systematic method of getting a solution for the conductivity, and have rederived the previous results using the new method. Terms in the dc dielectric constant have been found which were missing before because of a mistake in the earlier treatment. It is clear from the expression for $\sigma(\omega)$ in Sec. III, that it predicts corrections to the Boltzmann result for the dc resistivity. These corrections seem to us the proper way of incorporating temperature dependence of energy bands into transport theory. This is not discussed here, but we plan to do a detailed investigation soon.

## II. GENERALIZED BOLTZMANN EQUATION

The semiclassical Boltzmann equation deals with a distribution function defined by the diagonal elements of the density matrix $\rho$. This is obviously not satisfactory for a quantum treatment, since the off-diagonal elements of $\rho$ are essential for calculating any physical quantity and have to be treated at par with the diagonal elements. Getting a generalized distribution function therefore seems to be the first step towards obtaining a generalized Boltzmann equation.

The optical conductivity $\sigma$ is related to the macroscopic current by the relation $J = \sigma E$, where the $E$ field is in the $x$ direction and we are only concerned with the component of $J$ in the same direction,

$$J = \mathrm{Tr}\{\rho j\}, \tag{1}$$

where $j$ is the current operator. For a system of Bloch electrons characterized by wave vector $\vec{k}$, band index $n$, and energy $\epsilon_{\vec{k}n}$ the operator $j$ can be written

$$j = -e \sum_{\vec{k}nn'} v_{\vec{k}n'n} c_{\vec{k}n'}^{\dagger} c_{\vec{k}n}, \tag{2}$$

$$v_{\vec{k}n'n} = \langle \vec{k}n'|(p_x/m)|\vec{k}n\rangle.$$

Here $c_{\vec{k}n}^{\dagger}$ is the creation operator for the state $(\vec{k}, n)$, $v_{\vec{k}n'n}$ is the velocity matrix element, and for $n = n'$ is the one-electron velocity $v_{\vec{k}n} = \partial \epsilon_{\vec{k}n}/\partial \vec{k}$ (units of $\hbar = 1$). Equation (1) can now be rewritten

$$J = -e \sum_{\vec{k}nn'} v_{\vec{k}n'n} F_{\vec{k}nn'}, \tag{3a}$$

$$F_{\vec{k}nn'} \equiv F_{\vec{k}n,\vec{k}n'}, \tag{3b}$$

$$F_{\vec{k}n,\vec{k}'n'} = \mathrm{Tr}(\rho c_{\vec{k}'n'}^{\dagger} c_{\vec{k}n}). \tag{3c}$$

Throughout this paper, subscripts are truncated when possible. Thus when $\vec{k}' = \vec{k}$, $F_{\vec{k}n,\vec{k}'n'}$ is written $F_{\vec{k}nn'}$, and when $n' = n$, it is further truncated

to $F_{\bar{k}n}$. The semiclassical expression for the macroscopic current $J$ is

$$J = -e \sum_{\bar{k}n} v_{\bar{k}n} F_{\bar{k}n} , \tag{4a}$$

$$F_{\bar{k}n} = F_{\bar{k}nn} = \mathrm{Tr}(\rho c^{\dagger}_{\bar{k}n} c_{\bar{k}n}) . \tag{4b}$$

Here $F_{\bar{k}n}$ is the semiclassical distribution function for electrons in state $\bar{k}n$ and $v_{\bar{k}n}$ is the one-electron velocity. Comparing Eqs. (4) with Eqs. (3) shows that $F_{\bar{k}n,\bar{k}'n'}$ is a natural generalization of $F_{\bar{k}n}$. The physical interpretation of $F_{\bar{k}n}$ is that it gives the probability of finding an electron in state $\bar{k}n$. The generalized function $F_{\bar{k}n,\bar{k}'n'}$ has a simple physical meaning too. It is an average amplitude for finding the electron-hole pair, with electron in state $\bar{k}'n'$ and hole in $\bar{k}n$, mixed into the state of the system. Because the wave vector of the external electric field is assumed to be zero, the macroscopic current involves only those pairs which have zero total momentum. This can be seen from Eq. (3a). The semiclassical distribution function satisfies a Boltzmann equation, and this can be used to determine the dc and infrared optical conductivity. For the generalized theory of the optical conductivity, what is needed therefore is a Boltzmann-type equation satisfied by $F_{\bar{k}nn'}$. The off-diagonal elements $(n' \neq n)$ will give the nonclassical interband conductivity.

In linear-response theory $F_{\bar{k}nn'}$ can be expanded to first order in the electric field

$$F_{\bar{k}nn'} = F^{0}_{\bar{k}nn'} + \Phi_{\bar{k}nn'} , \tag{5a}$$

$$F^{0}_{\bar{k}nn'} = \mathrm{Tr}(\rho_0 c^{\dagger}_{\bar{k}n'} c_{\bar{k}n}) , \tag{5b}$$

$$\Phi_{\bar{k}nn'} = \mathrm{Tr}(\rho_E c^{\dagger}_{\bar{k}n'} c_{\bar{k}n}) . \tag{5c}$$

Here $\rho_0$ is the equilibrium density matrix, $\rho_0 = e^{-\beta \mathcal{H}}/Z$, and $\rho_E$ is the deviation to first order in the electric field. Equation (5b) defines the generalized equilibrium distribution function $F^{0}_{\bar{k}nn'}$. This is almost the same as a Fermi function,

$$f(\epsilon_{\bar{k}n}) = (e^{\beta \epsilon_{\bar{k}n}} + 1)^{-1} \delta_{n,n'} .$$

But even in equilibrium, electron-phonon and electron-impurity interactions mix in electron-hole pairs somewhat, and give corrections to the Fermi function. The deviation from equilibrium of the distribution function is given by $\Phi_{\bar{k}nn'}$. Since the current vanishes in equilibrium, $J$ involves $\Phi_{\bar{k}nn'}$ only. By decoupling in second order, we get a closed-form transport equation for $\Phi_{\bar{k}nn'}$, starting from the equation of motion of the density matrix. The theory is not band diagonal except in the semiclassical case. The derivation of the equation is presented in Appendix A. We now present the equation for the case where both electron-phonon and electron-impurity interactions are present:

$$-i(z - \hat{\Omega})\Phi = eEX + \hat{K}\Phi . \tag{6}$$

Here $z$ is a complex external frequency and will be set equal to $\omega + i\delta$, where $\omega$ is real and $\delta$ is a positive infinitesimal. The notation $\hat{Q}$ means that $\hat{Q}$ is a tetradic; i.e., $\hat{Q}$ operates on a matrix $A$, according to the definition $(\hat{Q}A)_{12} = \sum_{34} Q_{12;34} A_{34}$. The tetradic elements of $\hat{\Omega}$ are given by

$$\Omega_{12;34} \equiv (\epsilon_1 - \epsilon_2) \delta_{1,3} \delta_{2,4} . \tag{7}$$

Equation (6) has a simple interpretation as a generalized Boltzmann equation. The first term on the right-hand side, $eEX_{\bar{k}nn'}$, gives the rate at which electron-hole pairs are created by light. The second term describes how the electron-hole pair is scattered by the disorder (phonons and impurities) in the system. The factor on the left-hand side is an inertial term, being 90° out of phase with the electric field. This factor inhibits the production of electron-hole pairs, unless $\omega$ is near resonance, i.e., almost equal to $\epsilon_{\bar{k}n} - \epsilon_{\bar{k}n'}$. The explicit form of the driving term is

$$X_{\bar{k}nn'} = X^{(0)}_{\bar{k}nn'} + X^{(2)}_{\bar{k}nn'} + \cdots , \tag{8a}$$

$$X^{(0)}_{\bar{k}nn'} = v_{\bar{k}nn'} \frac{f_{\bar{k}n'} - f_{\bar{k}n}}{\epsilon_{\bar{k}n'} - \epsilon_{\bar{k}n}} . \tag{8b}$$

The terms $X^{(2)}$ and beyond involve second and higher powers of the scattering matrix element. The expression for $X^{(2)}$ is presented in Appendix A; its explicit form is used in this paper only for calculating the dc dielectric constant of a semiconductor. The factor $v_{\bar{k}nn'}/(\epsilon_{\bar{k}n} - \epsilon_{\bar{k}n'})$ in Eq. (8b) is the dipole matrix element, $-i\langle \bar{k}n|x|\bar{k}n'\rangle$. The tetradic $\hat{K}$ in (6) is the scattering operator. In general it is complex and $z$ dependent, but in the appropriate limit (to be specified soon) it becomes the real Boltzmann scattering operator.

### A. Collisionless limit

The collisionless optical properties can be easily derived from Eq. (6). In the absence of any collision processes, the solution for $\Phi_{\bar{k}nn'}$ is given by

$$\Phi_{\bar{k}nn'} = eEv_{\bar{k}nn'} \frac{f_{\bar{k}n'} - f_{\bar{k}n}}{\epsilon_{\bar{k}n'} - \epsilon_{\bar{k}n}} \frac{1}{i(\epsilon_{\bar{k}n} - \epsilon_{\bar{k}n'} - \omega - i\delta)} . \tag{9}$$

The solution for $\sigma(\omega)$, using Eq. (9) is

$$\sigma_0(\omega) = -ie^2 \sum_{\bar{k}nn'} |v_{\bar{k}nn'}|^2 \frac{f_{\bar{k}n'} - f_{\bar{k}n}}{\epsilon_{\bar{k}n'} - \epsilon_{\bar{k}n}}$$
$$\times \frac{1}{(\epsilon_{\bar{k}n} - \epsilon_{\bar{k}n'} - \omega - i\delta)} . \tag{10}$$

This is the standard formula for optical properties of solids.[16] The intraband $(n = n')$ part gives the collisionless Drude term.

### B. Collision term

The effect of collisions is contained in $X^{(2)}_{\vec{k}nn'}$ and higher-order terms of $X_{\vec{k}nn'}$ and the scattering operator $\hat{K}$. The discussion of the $X_{\vec{k}nn'}$ terms will be left for Appendix A. The scattering operator will now be discussed. Although our equation has not been derived by the technique of Feynman diagrams, we can nevertheless understand (in a quali-

tative fashion) the scattering operator $\hat{K}$ as the collection of irreducible scattering graphs shown in Fig. 1. The formal expression for $\hat{K}$ can be written as follows:

$$i\hat{K}(z) = \hat{\Xi}(z) - \hat{\Xi}^\dagger(-z), \tag{11a}$$

$$\hat{\Xi}(z) = \hat{\Xi}^{\text{out}}(z) + \hat{\Xi}^{\text{in}}(z), \tag{11b}$$

$$\Xi^{\text{out}}_{\vec{k}nn', \vec{p}mm'}(z) = \Sigma(\vec{k}nm, \epsilon_{\vec{k}n'} + z)\delta_{k,p}\delta_{n',m'}, \tag{11c}$$

$$\Xi^{\text{in}}_{\vec{k}nn', \vec{p}mm'}(z) = -V^{(1)}_{\vec{k}n, \vec{p}m} V^{(1)}_{\vec{p}m', \vec{k}n'}\left(\frac{1 + N(\omega_{\vec{p}-\vec{k}}) - f(\epsilon_{\vec{k}n})}{z + \epsilon_{\vec{p}m'} - \epsilon_{\vec{k}n} - \omega_{\vec{p}-\vec{k}}} + \frac{N(\omega_{\vec{p}-\vec{k}}) + f(\epsilon_{\vec{k}n})}{z + \epsilon_{\vec{p}m'} - \epsilon_{\vec{k}n} + \omega_{\vec{p}-\vec{k}}}\right)$$

$$+ N_{\text{imp}}\frac{\langle \vec{k}n| V_{\text{imp}}|\vec{p}m\rangle\langle pm'| V_{\text{imp}}|\vec{k}n'\rangle}{z + \epsilon_{\vec{p}m'} - \epsilon_{\vec{k}n}}. \tag{11d}$$

In Eq. (11a) $\hat{\Xi}^\dagger$ is the Hermitian conjugate of $\hat{\Xi}$, i.e., $\hat{\Xi}^\dagger_{\vec{k}nn'; \vec{p}mm'}(-z) = \Xi^*_{\vec{k}n'n; \vec{p}m'm}(-z)$. The $\Sigma$ in Eq. (11c) is the matrix self-energy discussed in I. It includes the self-energy due to both phonons and impurities, and is the sum of $\Sigma^{(1)}$ and $\Sigma^{(2)}$ as defined in I. The symbols used in Eqs. (11) are the same as in I. The terms $\hat{\Xi}^{\text{out}}$ and $\hat{\Xi}^{\text{in}}$ correspond to the scattering-out and scattering-in terms of semiclassical theory. Comparing the expression for $\hat{K}$ with the graphs in Fig. 1, we see that the first two graphs comprise the scattering-out terms, whereas the scattering-in terms arise from the last two graphs. The order of magnitude of the electron-phonon part of the collision term is either $kT$ or $\hbar\omega_D$, whichever is larger. This is of the same order as the shift in interband edges with temperature.

### C. Semiclassical limit

It is worthwhile to see how the semiclassical Boltzmann equation emerges from Eq. (6). If we keep only diagonal parts of $\Phi$, throw away all
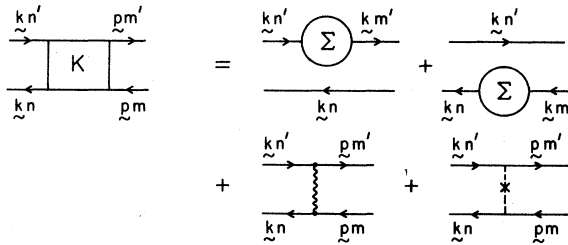


FIG. 1. Diagrammatic representation of processes contributing to the scattering operator $K$; $\Sigma$ represents self-energy graphs.

terms beyond $X^{(0)}_{\vec{k}nn'}$ in $X_{\vec{k}nn'}$, and take the small-frequency limit of $\hat{K}$, Eq. (6) reads

$$-i\omega\Phi_{\vec{k}n} = eEv_{\vec{k}n}\frac{\partial f(\epsilon_{\vec{k}n})}{\partial\epsilon_{\vec{k}n}} + \sum_{\vec{k}'n'}K_{\vec{k}n; \vec{k}'n'}\Phi_{\vec{k}'n'}, \tag{12}$$

where $\Phi_{\vec{k}n}$ is short for $\Phi_{\vec{k}nn}$ and a similar shorthand is used for $K$. This is the semiclassical equation. In general $\hat{K}$ is complex, but in the small-frequency limit, it has only real parts. In getting Eq. (12) we have used the fact that when $n = n'$, $(f_{\vec{k}n} - f_{\vec{k}n'})/(\epsilon_{\vec{k}n} - \epsilon_{\vec{k}n'})$ becomes $\partial f(\epsilon_{\vec{k}n})/\partial\epsilon_{\vec{k}n}$.

### III. SOLUTION FOR OPTICAL CONDUCTIVITY

This section is devoted to finding a general solution for $\sigma$, and applications of this solution to certain special cases. A formal solution to Eq. (6) is

$$\Phi = eE(\hat{G}(z)X), \quad \hat{G}(z) = [i(\hat{\Omega} - z) - \hat{K}(z)]^{-1}. \tag{13}$$

The function $\hat{G}$ is a two-particle analog of a one-particle Green's function. Although Eq. (13) is formally exact, inverting the operator involved in $\hat{G}$ is by no means easy. Therefore some alternative way has to be found for solving Eq. (6). The scattering operator $\hat{K}$ has the following useful properties:

$$K_{\vec{k}nn'; \vec{p}mm'}(z) = -K^*_{\vec{p}mm'; \vec{k}nn'}(z) = -K_{\vec{p}m'm; \vec{k}n'n}(-z). \tag{14}$$

The operator $i(\hat{\Omega} - z)$ clearly has the same symmetries. It then follows that the tetradic elements of $\hat{G}$, $G_{\vec{k}nn'; \vec{p}mm'}(z)$, have the above symmetry properties. These symmetries can be used profitably

if one looks at the expression for $\sigma$ instead of $\Phi$:

$$\sigma = -e^2 \sum_{knn'} v^{\dagger}_{\vec{k}n'n}(\hat{G}(z)X)^{\dagger}_{\vec{k}nn'} . \tag{15}$$

This equation can be transformed using the symmetry of $\hat{G}$, into a form where $G$ acts on the matrix $v^{\dagger}_{\vec{k}nn'}$ instead of $X^{\dagger}_{\vec{k}nn'}$:

$$\sigma(z) = -e^2 \sum_{knn'} X^{\dagger}_{\vec{k}n'n}(-\hat{G}(-z)\,v)^{\dagger}_{\vec{k}nn'} . \tag{16}$$

We now look for a solution for $\sigma$, of the form

$$\sigma(z) = -e^2 \sum X^{\dagger}_{\vec{k}n'n}\; \frac{v^{\dagger}_{\vec{k}nn'}}{-i\left[\omega^{\dagger}_{\vec{k}n,\vec{k}n'} + z + M^{\dagger}_{\vec{k}nn'}(z)\right]} , \tag{17a}$$

where $\omega^{\dagger}_{\vec{k}n,\vec{k}n'}$ is short for $\epsilon^{\dagger}_{\vec{k}n} - \epsilon^{\dagger}_{\vec{k}n'}$, and a memory function $M$ has been defined by

$$\left\{-\left[i\,(\hat{\Omega}+z)-\hat{K}(-z)\right]^{-1}v\right\}^{\dagger}_{\vec{k}nn'}$$

$$= \frac{v^{\dagger}_{\vec{k}nn'}}{-i\left[\omega^{\dagger}_{\vec{k}n,\vec{k}n'} + z + M^{\dagger}_{\vec{k}nn'}(z)\right]} . \tag{17b}$$

Operating through by $G^{-1}$, this becomes

$$v^{\dagger}_{\vec{k}nn'} = \sum_{pmm'} -\left[i\,(\hat{\Omega}+z)-\hat{K}(-z)\right]^{\dagger}_{\vec{k}nn',\vec{p}mm'}$$

$$\times \frac{v^{\dagger}_{\vec{p}mm'}}{-i\left[\omega^{\dagger}_{\vec{p}m,\vec{p}m'} + z + M^{\dagger}_{\vec{p}mm'}(z)\right]} . \tag{18}$$

An exact nonlinear integral equation for $M$ can be derived from Eq. (18). Multiplying through by $-i\left[\omega^{\dagger}_{\vec{k}n,\vec{k}n'} + z + M^{\dagger}_{\vec{k}nn'}(z)\right]/v^{\dagger}_{\vec{k}nn'}$ and using Eq. (7) for $\hat{\Omega}$, we get

$$M^{\dagger}_{\vec{k}nn'}(z) = i \sum_{pmm'} K^{\dagger}_{\vec{k}nn';\vec{p}mm'}(-z)\left[\frac{v^{\dagger}_{\vec{p}mm'}}{v^{\dagger}_{\vec{k}nn'}}\left(\frac{M^{\dagger}_{\vec{k}nn'}(z)+\omega^{\dagger}_{\vec{k}n,\vec{k}n'}+z}{M^{\dagger}_{\vec{p}mm'}(z)+\omega^{\dagger}_{\vec{p}m,\vec{p}m'}+z}\right)\right]. \tag{19}$$

Although an exact solution of Eq. (19) is difficult, good approximations are available. A low-order perturbative solution of Eq. (19) for $M$ gives a much better approximation to $\sigma$ than a straight-forward expansion of $\Phi$. From Eq. (19) it is evident that $M$ has the symmetry $M^{\dagger}_{\vec{k}nn'}(z) = -M^{*\dagger}_{\vec{k}n'n}(-z)$. The size of the leading contributions to $M$ is the same as that of $\hat{K}$. The magnitude of $M$ is therefore of order $kT$, or $\hbar\omega_D$.

In the following parts of this section we discuss some effects of interest in semiconductors, namely, (a) Van Hove edges, (b) indirect absorption, and (c) dc dielectric constant.

### A. Van Hove edges

In a collisionless optical spectrum, the interband or Van Hove edges occur at frequencies $\omega = \omega^{\dagger}_{\vec{k}n',\vec{k}n}$,

where $\epsilon^{\dagger}_{\vec{k}n'}$ and $\epsilon^{\dagger}_{\vec{k}n}$ satisfy the condition

$$\nabla_{\vec{k}}(\omega^{\dagger}_{\vec{k}n',\vec{k}n})\big|_{\omega^{\dagger}_{\vec{k}n',\vec{k}n}=\omega} = 0 . \tag{20}$$

In the presence of collisions $\sigma$ gets modified according to Eq. (17) and the condition determining interband edges, becomes

$$\nabla_{\vec{k}}(\omega^{\dagger}_{\vec{k}n',\vec{k}n}-M^{\dagger}_{\vec{k}nn'}(\omega))\big|_{\omega^{\dagger}_{\vec{k}n',\vec{k}n}-M^{\dagger}_{\vec{k}nn'}(\omega)=\omega} = 0 . \tag{21}$$

The change in Van Hove edges is therefore determined by $M^{\dagger}_{\vec{k}nn'}(\omega^{\dagger}_{\vec{k}n',\vec{k}n}-\Delta\omega)$, where $\Delta\omega$ is small, corresponding to $\omega$ slightly shifted from the unperturbed edge. The integral equation for $M$, Eq. (19) in this limit is,

$$M^{\dagger}_{\vec{k}nn'}(\omega^{\dagger}_{\vec{k}n',\vec{k}n}-\Delta\omega) = i \sum_{pmm'} K^{\dagger}_{\vec{k}nn';\vec{p}mm'}(\omega^{\dagger}_{\vec{k}n,\vec{k}n'}+\Delta\omega)$$

$$\times \left(\frac{v^{\dagger}_{\vec{p}mm'}}{v^{\dagger}_{\vec{k}nn'}}\; \frac{M^{\dagger}_{\vec{k}nn'}(\omega^{\dagger}_{\vec{k}n',\vec{k}n}-\Delta\omega)-\Delta\omega}{M^{\dagger}_{\vec{p}mm'}(\omega^{\dagger}_{\vec{k}n',\vec{k}n}-\Delta\omega)+\omega^{\dagger}_{\vec{p}m,\vec{p}m'}-\omega^{\dagger}_{\vec{k}n,\vec{k}n'}-\Delta\omega}\right). \tag{22}$$

The quantity $M_{\vec{k}nn'} - \Delta\omega$ in the numerator is very small for $\omega$ near the edge and vanishes at the exact edge as seen from Eq. (21). So the leading contribution to $M_{\vec{k}nn'}$ comes from those terms in the sum where the denominator is small too, which in general happens only when $\vec{p}m = \vec{k}n$ and $\vec{p}m' = \vec{k}n'$,

$$M_{\vec{k}nn'}^{(1)} = iK_{\vec{k}nn';\,\vec{k}nn'}(\omega_{\vec{k}n,\vec{k}n'} + \Delta\omega)$$

$$= \Sigma(\vec{k}n,\,\epsilon_{kn} + \Delta\omega) - \Sigma^*(\vec{k}n',\,\epsilon_{\vec{k}n'} - \Delta\omega).$$

(23)

The second relation follows by using Eq. (11). The scattering-in term is smaller by a factor $N^{-1}$ and thus does not contribute. The shift with temperature or disorder of the Van Hove edges is therefore determined by the real part of the diagonal elements of the self-energy matrix. In a semiconductor it is accurate to neglect the dependence of $\mathrm{Re}\,\Sigma$ on $\Delta\omega$ and the phonon frequencies, this is however, not a good approximation for metals at low temperature (see Appendix B). The resulting

expression for the shift of interband edges is identical to the one obtained by using one-electron perturbation theory.[5] The edges are also broadened by the imaginary part of $M$. For this part the neglect of $\Delta\omega$ and phonon frequencies in the energy denominators is not justified even for a semiconductor, except at high temperature. In this problem therefore, the non-self-energy parts of $K$ do not play an important role at least to lowest order. The next-higher-order corrections can be easily worked out. They are much smaller than the self-energy corrections, and do not contribute significantly.

### B. Indirect absorption edge

To get the essential features of this effect it suffices to consider a simplified model of a semiconductor. We consider a two-band model, with a small indirect gap $\epsilon_g^I$, and investigate the behavior of $\mathrm{Re}\,\sigma(\omega)$ for $\omega$ near $\epsilon_g^I$. We also assume that $\omega$ is smaller than any direct gap. For the model considered, Eq. (17) can be written

$$\sigma(\omega + i\delta) = -ie^2 \sum_{\vec{k}} |v_{\vec{k}v,\vec{k}c}|^2 \frac{f_{\vec{k}v} - f_{\vec{k}c}}{\epsilon_{\vec{k}v} - \epsilon_{\vec{k}c}} \left( \frac{1}{\epsilon_{\vec{k}v} - \epsilon_{\vec{k}c} + \omega + M_{\vec{k}vc}(\omega + i\delta)} - \frac{1}{\epsilon_{\vec{k}v} - \epsilon_{\vec{k}c} - \omega - M_{\vec{k}cv}(\omega + i\delta)} \right).$$

(24)

Here subscripts $c, v$ denote conduction and valence bands, respectively. Since we are interested in the lowest-order effects $X$ has been replaced by $X^{(0)}$. Contributions from $X^{(2)}$ are higher order in the interaction. The function of interest is $\mathrm{Re}\,\sigma(\omega + i\delta)$ for $\omega$ almost equal to $\epsilon_g^I$. We can separate $M$ into its real and imaginary parts, and $\mathrm{Re}\,\sigma$ can be written

$$\mathrm{Re}\,\sigma(\omega + i\delta) = -e^2 \sum_{\vec{k}} |v_{kv,kc}|^2 \frac{f_{\vec{k}c} - f_{\vec{k}v}}{\epsilon_{\vec{k}c} - \epsilon_{\vec{k}v}}$$

$$\times \left( \frac{M_{\vec{k}vc}''(\omega)}{(\epsilon_{\vec{k}v} - \epsilon_{\vec{k}c} + \omega)^2} + (v \leftrightarrow c) \right),$$

(25a)

$$M_{\vec{k}vc}(\omega + i\delta) = M_{\vec{k}vc}'(\omega) + iM_{\vec{k}vc}''(\omega).$$

(25b)

In getting Eq. (25a) from Eq. (24) we have neglected

$M'$ and $M''$ in the denominators since for $\omega \simeq \epsilon_g^I$, $|\omega - (\epsilon_{\vec{k}c} - \epsilon_{\vec{k}v})| \gg M_{\vec{k}vc}(\omega)$. To lowest order, $\sigma$ can be obtained by taking the first iteration of Eq. (19) for $M$. This is justified in the case of a semiconductor because the intraband parts give vanishingly small contributions. The expression we obtain for $M''$ can be written

$$M_{\vec{k}vc}''(\omega) = M_{\vec{k}vc}''^{out}(\omega) + M_{\vec{k}vc}''^{in}(\omega),$$

$$M_{\vec{k}vc}''^{out}(\omega) = \mathrm{Im}\left[\Sigma(\vec{k}v,\,\epsilon_{\vec{k}c} - \omega) - \Sigma^*(\vec{k}c,\,\epsilon_{\vec{k}v} + \omega)\right],$$

$$M_{\vec{k}vc}''^{in}(\omega) = \sum_{k'} \mathrm{Im}[\Xi_{\vec{k}vc,\vec{k}'vc}^{in}(\omega) - \Xi_{\vec{k}cv,\vec{k}'cv}^{*\,in}(-\omega)]$$

$$\times \left( \frac{v_{\vec{k}'vc}}{v_{\vec{k}vc}} \frac{\omega + \epsilon_{\vec{k}v} - \epsilon_{\vec{k}c}}{\omega + \epsilon_{\vec{k}'v} - \epsilon_{\vec{k}'c}} \right). \quad (26)$$

The notation used is the same as in Eqs. (11). The expression for $\mathrm{Im}\,\Sigma(\vec{k}v,\,\epsilon_{\vec{k}c} - \omega)$ can be written

$$\mathrm{Im}\,\Sigma(\vec{k}v,\,\epsilon_{\vec{k}c} - \omega) = \pi \sum_{k'} (|V_{\vec{k}v,\vec{k}'v}^{(1)}|^2 \{[f_{\vec{k}'v} + N(\omega_{\vec{k}'-\vec{k}})]\,\delta(\epsilon_{\vec{k}c} - \epsilon_{\vec{k}'v} + \omega_{\vec{k}'-\vec{k}} - \omega)$$

$$+ [1 - f_{\vec{k}'v} + N(\omega_{\vec{k}'-\vec{k}})]\,\delta(\epsilon_{\vec{k}c} - \epsilon_{\vec{k}'v} - \omega_{\vec{k}'-\vec{k}} - \omega)\}$$

$$+ N_{\mathrm{imp}} \langle \vec{k}v | V_{\mathrm{imp}} | \vec{k}'v \rangle|^2 \delta(\epsilon_{\vec{k}c} - \epsilon_{\vec{k}'v} - \omega)).$$

(27)

Equation (27) can be derived from Eqs. (14) and (24) of I, and we have thrown away $\delta$ functions of the type $\delta(\epsilon_{\vec{k}c} - \epsilon_{\vec{k}'c} - \omega)$, since it can be shown that these contributions cancel with similar ones from $\text{Im}\Sigma^*(kc, \epsilon_{kv} + \omega)$ when substituted into the expression for $\text{Re}\sigma(\omega)$. The contribution of $M''^{\text{out}}(\omega)$ to $\text{Re}\sigma(\omega)$ can be obtained by substituting in Eq. (25a), Eq. (27) for $\text{Im}\Sigma(\vec{k}v, \epsilon_{\vec{k}c} - \omega)$ and the similar expression for $\text{Im}\Sigma^*(\vec{k}c, \epsilon_{\vec{k}v} + \omega)$. In the sum over $\vec{k}, \vec{k}'$, only the terms with $\vec{k}$ near the conduction-band minimum and $\vec{k}'$ near the valence-band maximum or vice versa, contribute. The result is the same as obtained from standard theory,[17] showing an edge of the type $(\omega - \epsilon_g^I)^2$. The contribution of $M''^{\text{in}}(\omega)$ remains to be investigated. A typical term in $\text{Re}\sigma(\omega)$ arising from $M''^{\text{in}}(\omega)$ is

$\text{Re}\sigma^{\text{in}}(\omega)$

$$= -e^2 \sum_{kk'} \frac{v_{\vec{k}cv}}{\epsilon_{\vec{k}c} - \epsilon_{\vec{k}v} - \omega} \frac{f_{\vec{k}c} - f_{\vec{k}v}}{\epsilon_{\vec{k}c} - \epsilon_{\vec{k}v}}$$

$$\times \left[ \text{Im}\Xi_{\vec{k}vc, \vec{k}'vc}^{\text{in}} \left( \frac{v_{\vec{k}'vc}}{\epsilon_{\vec{k}'c} - \epsilon_{\vec{k}'v} - \omega} \right) \right].$$

$$(28)$$

These terms involving $v_{\vec{k}'vc}$ are frequently left out of standard theories.[18] The evaluation of Eq. (28) and similar terms proceeds exactly in the same way as for $M''^{\text{out}}(\omega)$. The expressions for $\text{Im}\Xi_{\vec{k}vc, \vec{k}'vc}^{\text{in}}$, etc., can be obtained from Eqs. (11). The result shows the same type of edge and has the same magnitude as the contribution from $M''^{\text{out}}(\omega)$. Our theory therefore predicts an indirect absorption edge in agreement with standard theory.

### C. dc dielectric constant of a semiconductor

In this section we calculate the real part of the dc dielectric constant $\epsilon(\omega = 0)$. By the Kramers-Kronig relations, $\text{Re}\epsilon(0)$ can be written

$$\text{Re}\epsilon(0) = 1 + 4 \int_{-\infty}^{\infty} \frac{d\omega}{\omega^2} \text{Re}\sigma(\omega). \qquad (29)$$

For a semiconductor only the interband parts of $\sigma(\omega)$ are needed, the intraband contributions being exponentially small. Using Eq. (17a), the expression for $\text{Re}\sigma(\omega)$ is

$$\text{Re}\sigma(\omega) = -e^2 \sum_{\substack{\vec{k}nn' \\ n \neq n'}} \text{Re}\left[ v_{\vec{k}nn'} X_{\vec{k}n'n}(\omega) \right] \frac{\text{Im}M_{\vec{k}n'n}(-\omega)}{[\omega - \omega_{\vec{k}n', \vec{k}n} - \text{Re}M_{\vec{k}n'n}(-\omega)]^2 + [\text{Im}M_{\vec{k}n'n}(-\omega)]^2}$$

$$- \text{Im}\left[ v_{\vec{k}nn'} X_{\vec{k}n'n}^{(2)}(\omega) \right] \frac{\omega - \omega_{\vec{k}n', \vec{k}n} - \text{Re}M_{\vec{k}n'n}(-\omega)}{[\omega - \omega_{\vec{k}n', \vec{k}n} - \text{Re}M_{\vec{k}n'n}(-\omega)]^2 + [\text{Im}M_{\vec{k}n'n}(-\omega)]^2}. \qquad (30)$$

In the second term of Eq. (30), $M_{\vec{k}n'n}(-\omega)$ can be neglected since $X^{(2)}$ is already second order in the interaction. It can be shown that to lowest order, the Lorentzian part of the first term can be replaced by a $\delta$ function, $\pi\delta(\omega - \omega_{\vec{k}n'\vec{k}n} - \text{Re}M_{\vec{k}n'n}(-\omega))$. Within the $\delta$ function, it is accurate to expand $M_{\vec{k}n'n}(-\omega)$ about $\omega = \omega_{\vec{k}n', kn}$, to first order. The $\delta$ function can then be written

$$\delta(\omega - \omega_{\vec{k}n', \vec{k}n} - \text{Re}M_{\vec{k}n'n}(-\omega))$$

$$= \frac{\delta(\omega - \omega_{\vec{k}n'\vec{k}n} - \bar{M}_{\vec{k}n'n}(\omega_{\vec{k}n}, \vec{k}n'))}{|1 - (d/d\omega)\text{Re}M_{\vec{k}n'n}(-\omega)|_{\omega = \omega_{\vec{k}n', kn}}}, \qquad (31a)$$

$$\bar{M}_{\vec{k}n'n}(\omega_{\vec{k}n}, \vec{k}n')$$

$$= \text{Re}M_{\vec{k}n'n}(\omega_{\vec{k}n, kn'})$$

$$\times \left(1 - \frac{d}{d\omega}\text{Re}M_{\vec{k}n'n}(-\omega)\Big|_{\omega = \omega_{\vec{k}n', kn}}\right)^{-1}. \qquad (31b)$$

The factor $(1 - dM/d\omega)^{-1}$ is closely analogous to the renormalization factor $(1 - \partial\Sigma/\partial\omega)^{-1}$ in the theory of metals. Because of nonadiabatic effects near the Fermi surface of metal, the correction $dM/d\omega$ is of order 1 at low temperatures. However, in the adiabatic approximation (which is certainly accurate in a semiconductor) the factor $dM/d\omega$ is small, of the order of $kT/E_g$. The difference between $\bar{M}$ and $\text{Re}M$ is then of the order of $(kT)^2/E_g$, since $M$ is of order $kT$. Therefore $\bar{M}$ can be replaced by $\text{Re}M$ in Eq. (31a). The renormalization factor in the denominator in Eq. (31a) must be kept because it gives corrections of order $kT/E_g$ to the noninteracting dielectric constant.

The expression for $\text{Re}\epsilon(0)$ can be written as a sum of three parts:

$$\text{Re}\epsilon(0) = \epsilon^a(0) + \epsilon^b(0) + \epsilon^c(0), \qquad (32a)$$

$$\epsilon^a(0) = 1 - 4\pi e^2 \sum_{\substack{\vec{k}nn' \\ n \neq n'}} \frac{X^{(o)}_{\vec{k}n'n} v_{\vec{k}nn'}}{(E_{\vec{k}n'} - E_{\vec{k}n})^2} \left(1 - \frac{d}{d\omega}[\text{Re}M_{\vec{k}nn'}(\omega)]\Big|_{\omega = \omega_{\vec{k}n',\vec{k}n}}\right)^{-1},$$  (32b)

$$\epsilon^b(0) = -4\pi e^2 \sum_{\substack{\vec{k}nn' \\ n \neq n'}} \text{Re}\frac{X^{(2)}_{\vec{k}n'n}(\omega_{\vec{k}n',\vec{k}n}) v_{\vec{k}nn'}}{(E_{\vec{k}n'} - E_{\vec{k}n})^2},$$  (32c)

$$\epsilon^c(0) = 4e^2 \sum_{\substack{\vec{k}nn' \\ n \neq n'}} \int_{-\infty}^{\infty} \frac{d\omega}{\omega^2} \frac{\text{Im}[v_{\vec{k}nn'} X^{(2)}_{\vec{k}n'n}(\omega)]}{\omega + \omega_{\vec{k}n,\vec{k}n'}},$$  (32d)

$$E_{kn} = \epsilon_{kn} + \text{Re}\Sigma(\vec{k}n, \epsilon_{\vec{k}n}).$$  (32e)

In writing Eqs. (32), use has been made of the fact that $\text{Re}M_{\vec{k}n'n}(\omega_{\vec{k}n},\vec{k}n')$, to lowest order is the difference in self-energies of the states $\vec{k}n'$ and $\vec{k}n$ [see Eqs. (22) and (23)]. The most extensive calculations of the temperature dependence of $\text{Re}\epsilon(0)$ are those of Yu and Cardona.[19] Their formalism is equivalent to neglecting $\epsilon^b$ and $\epsilon^c$, and keeping only the part of $\epsilon^a$ not involving $dM/d\omega$. Moreover, they keep only the Debye-Waller corrections in $E_{\vec{k}n}$. The agreement that they get with experiments is reasonably good. From the formal results presented here, it is difficult to see why these corrections should dominate. A more detailed and maybe more specific calculation will be needed to see if there are any major cancellations. The Yu and Cardona terms involve only the corrections to band energies. The other terms occurring in Eqs. (32) arise from the fact that the dipole matrix elements and occupation probabilities also get altered by the interaction.

## APPENDIX A

In this appendix we present the derivation of the transport equation. The method used is that of Kohn and Luttinger,[9] generalized to include band-structure effects and phonons. The evolution in time of a many-electron density matrix is given by

$$i\frac{\partial\rho}{\partial t} = [\mathcal{H}_T, \rho].$$  (A1)

The complete Hamiltonian $\mathcal{H}_T$ is a sum of the complete unperturbed system Hamiltonian $\mathcal{H}$ and the external field Hamiltonian $\mathcal{H}_E$. We want to examine in linear approximation the deviation $\rho_E = \rho - \rho_0$ from the equilibrium value $\rho_0 = e^{-\beta\mathcal{H}}/z$. This deviation $\rho_E(t) = \rho_E e^{-i(\omega + i\delta)t}$, then satisfies the equation

$$(\omega + i\delta)\rho_E = [\mathcal{H}, \rho_E] + e[Ex, \rho_0],$$  (A2)

where we have kept only terms linear in $E$. The two parts of the distribution function $F^0$ and $\Phi$ correspond, respectively, to

$$F^0_{\vec{k}n,\vec{k}'n'} = \text{Tr}(\rho_0 c^\dagger_{\vec{k}'n'} c_{\vec{k}n}) \equiv \langle c^\dagger_{\vec{k}'n'} c_{\vec{k}n}\rangle_0,$$

$$\Phi_{\vec{k}n,\vec{k}'n'} = \text{Tr}(\rho_E c^\dagger_{\vec{k}'n'} c_{\vec{k}n}) \equiv \langle c^\dagger_{\vec{k}'n'} c_{\vec{k}n}\rangle_E.$$  (A3)

Using Eqs. (A2) and (A3) we get the following equation for $\Phi$:

$$(\omega + i\delta)\Phi_{\vec{k}nn'} = \langle[c^\dagger_{\vec{k}n'} c_{\vec{k}n}, \mathcal{H}]\rangle_E + eE\langle[c^\dagger_{\vec{k}n'} c_{\vec{k}n}, x]\rangle_0.$$  (A4)

We can see that this formalism will lead to a hierarchy of equations, $\Phi_{\vec{k}nn'}$ will be given in terms of a higher-order correlation function, and so on. To get a closed equation for $\Phi$, we need to truncate the scheme somewhere. We truncate it such that all correlation effects up to second order in the interaction are included. For the electron-phonon interaction we factorize correlation functions like $\langle c^\dagger_2 c_1 b_Q b^\dagger_{Q'}\rangle$, and for electron-impurity interaction we factorize at the stage $\langle c^\dagger_2 c_1 S(\vec{Q}) S(\vec{Q}')\rangle$, or at $\langle c^\dagger_2 c_1 S(0)\rangle$. From the second term of Eq. (A4) we see that the equation will involve equilibrium correlation functions, and these have to be perturbatively expanded too. This is done by getting the expansion of the equilibrium density matrix to second order in the interaction

$$\rho_I(t) = \rho_{00} + \frac{1}{i}\int_{-\infty}^{t} dt'[\mathcal{H}'_I(t'), \rho_I(t)],$$  (A5a)

$$\rho_{00} = e^{-\beta\mathcal{H}_0}/z,$$  (A5b)

$$\rho_I(t) = e^{i\mathcal{H}_0 t}\rho_0 e^{-i\mathcal{H}_0 t},$$  (A5c)

$$\mathcal{H}_I(t) = e^{i\mathcal{H}_0 t}\mathcal{H}' e^{-i\mathcal{H}_0 t}.$$  (A5d)

Here $\mathcal{H}'$ is the sum of electron-phonon and electron-impurity Hamiltonians, defined in I, Eqs. (10), (18), and (19). We get the first- and second-order terms by iterating the equation for $\rho_I(t)$. Writing $\mathcal{H}$ as $\mathcal{H}_0 + \mathcal{H}'$ and using (A3), Eq. (A4) becomes

$$(z + \omega_{\vec{k}n',\vec{k}n})\Phi_{knn'} = eE\sum_m (x_{\vec{k}nm} F^0_{\vec{k}mn'} - F^0_{\vec{k}nm} x_{\vec{k}mn'})$$
$$+ \langle[c^\dagger_{\vec{k}n'} c_{\vec{k}n}, \mathcal{H}']\rangle_E.$$  (A6)

The last term in Eq. (A6) is the one that depends explicitly on the interaction. It involves four parts, corresponding to matrix elements of $V^{(1)}$ and $V^{(2)}$ of the electron-phonon interaction, and first- and second-order matrix elements of $V_{\text{imp}}$.

$$(z + \omega_{\vec{k}n',\vec{k}n})\Phi_{\vec{k}nn'} = eE\sum_m (x_{\vec{k}nm}F^0_{\vec{k}mn'} - F^0_{\vec{k}nm}x_{\vec{k}mn'}) + \sum_{\vec{p}m}(V^{(1)}_{\vec{k}n,\vec{p}m}g^{(1)}_{\vec{p}m,\vec{k}n'} - g^{(1)}_{\vec{k}n,\vec{p}m}V^{(1)}_{\vec{p}m,\vec{k}n'})$$

$$+ \sum_{mQ}(V^{(2)}_{\vec{k}nm}\Phi_{\vec{k}mn'} - V^{(2)}_{\vec{k}mn'}\Phi_{\vec{k}nm})[2N(\omega_Q)+1] + N_{\text{imp}}\sum_m (\langle\vec{k}n|V_{\text{imp}}|\vec{k}m\rangle\Phi_{\vec{k}mn'}$$

$$- \langle\vec{k}m|V_{\text{imp}}|\vec{k}n'\rangle\Phi_{\vec{k}nm})$$

$$+ \sum_{\vec{p}m}(\langle\vec{k}n|V_{\text{imp}}|\vec{p}m\rangle g^{\text{imp}}_{\vec{p}m,\vec{k}n'} - g^{\text{imp}}_{\vec{k}n,\vec{p}m}\langle\vec{p}m|V_{\text{imp}}|\vec{k}n'\rangle). \qquad (A7)$$

The definitions of the $g$'s are

$$g^{(1)}_{1,2} = \langle c^\dagger_2 c_1(b_{2-1} + b^\dagger_{1-2})\rangle_E,$$

$$g^{\text{imp}}_{1,2} = \langle c^\dagger_2 c_1 S(2-1)\rangle_E. \qquad (A8)$$

We have treated the phonons as being in equilibrium; $N(\omega_Q)$ is the Bose factor.

The next step would be to write down an equation for the $g$'s starting from Eq. (A2). The process is the same as before, and we end up with an equation involving $\langle c^\dagger_2 c_1 b^\dagger_Q b_{Q'}\rangle$ or $\langle c^\dagger_2 c_1 S(Q) S(Q')\rangle$. This is the stage at which our approximation enters, we decouple the equations. The coefficients of the above correlation functions in the equation are already second order in the interaction. Now if there were no interaction, these functions would be decoupled into a product of electron and phonon or electron and impurity distribution functions. Any correlation effects would therefore contribute to the equation only in higher order. So in a second-order theory we factorize $\langle c^\dagger_2 c_1 b^\dagger_Q b_{Q'}\rangle$ into $\langle c^\dagger_2 c_1\rangle\langle b^\dagger_Q b_{Q'}\rangle$ and similarly for the impurity case. This then leads to a closed equation for $\Phi$, which is the transport equation presented in Sec. II of the paper

$$-i(z - \omega_{\vec{k}n,\vec{k}n'})\Phi_{\vec{k}nn'} = eEX_{knn'} + \sum_{\vec{p}mm'} K_{\vec{k}nn';\vec{p}mm'}(z)\Phi_{\vec{p}mm'}. \qquad (A9)$$

We present the expression for $X_{knn'}$ only for the adiabatic case where the phonon frequencies can be neglected in the energy denominators. The full nonadiabatic form is not needed for the purposes of this paper.

$$X_{\vec{k}nn'} = X^{(0)}_{\vec{k}nn'} + X^{(2)}_{\vec{k}nn'},$$

$$X^{(2)}_{\vec{k}nn'} = (R_{\vec{k}nn'} + R^*_{\vec{k}n'n}) + [S_{\vec{k}nn'}(z) + S^*_{\vec{k}n'n}(-z)],$$

$$R_{\vec{k}nn'} = \sum_{\vec{p}mm'}(2N_{\vec{p}-\vec{k}}+1)\frac{v_{\vec{k}nm}}{\omega_{\vec{k}m,\vec{k}n}}\left[V^{(2)}_{\vec{k}m,\vec{k}n'}G_{\vec{k}m,\vec{k}n'}\delta_{m,m'} + V^{(1)}_{\vec{k}m,\vec{p}m'}V^{(1)}_{\vec{p}m',\vec{k}n'}\left(\frac{G_{\vec{p}m',\vec{k}n'}}{\omega_{\vec{p}m',\vec{k}m}} + \frac{G_{\vec{k}m,\vec{p}m'}}{\omega_{\vec{k}n',\vec{p}m'}}\right)\right],$$

$$S_{\vec{k}nn'}(z) = \sum_{\vec{p}mm'}(2N_{\vec{p}-\vec{k}}+1)\left(\frac{v_{\vec{k}nm}}{\omega_{\vec{k}n,\vec{k}m}}V^{(1)}_{\vec{k}m,\vec{p}m'}V^{(1)}_{\vec{p}m',\vec{k}n'}G_{\vec{k}m,\vec{p}m'} - \frac{v_{\vec{p}mm'}}{\omega_{\vec{p}m,\vec{p}m'}}\right.$$

$$\left. \times V^{(1)}_{\vec{k}n,\vec{p}m}V^{(1)}_{\vec{p}m',\vec{k}n'}G_{\vec{k}n,\vec{p}m}\right)\Big/(\omega_{\vec{p}m',\vec{k}n}+z), \qquad (A10)$$

where $G$ is defined by

$$G_{\vec{k}n,\vec{p}m} = (f_{\vec{k}n} - f_{\vec{p}m})/(\epsilon_{\vec{k}n} - \epsilon_{\vec{p}m}). \qquad (A11)$$

Equation (A10) is written for the case where electron-impurity interaction is absent. It can be easily generalized to include both interactions. Terms looking similar to $X^{(2)}_{\vec{k}nn}$ have been obtained before by Kohn and Luttinger and other authors. These terms do not arise if a Green's-function formalism is used. For the free-electron case, the discrepancy has been resolved by Moore.[20] He shows that the extra field-dependent terms in Kohn and Luttinger's equation can be absorbed into the collision terms by defining a quasiparticle distribution function, and converting the equation for the one-electron distribution function to an equation satisfied by the quasiparticle distribution function. The method of Kohn and Luttinger which we have followed is less powerful than the various Green's-function methods,[12-14] but it has sufficient accuracy for most purposes. The virtue of the present method is that it yields a final result, (A9), which is a direct generalization of the Boltzmann equation and thus physically fairly transparent.

## APPENDIX B

As mentioned in the Introduction, there is quite a great deal of literature existing on the subject of quantum transport equations. The purpose of this appendix is to compare this work with the previous calculations. Yamada[11] has an equation valid for spatially inhomogeneous electric fields, but treats the electrons as plane waves. The spatially homogeneous version of his equations [Eqs. (24) and (48), Ref. 11], has been compared with Eq. (6), after throwing away all interband terms, but keeping $X_{kn}^{(2)}$ and the complex frequency-dependent parts of $\hat{K}$. Except for the terms which arise from the change in the Fermi factor due to disorder, they agree, and Yamada states that he omits these terms because they are purely real. The equations of Ron[10] are the same as Yamada's, when they are linearized and phonon drag neglected. Kohn and Luttinger's[9] work deals with static electric field and electron-impurity interaction only. Moreover, they assume that the electrons obey classical statistics. To second order in the inter-

action, their equation looks very similar to the dc intraband version of Eq. (6), there are, however, certain differences arising from the fact that they assumed a Maxwell-Boltzmann distribution for the unperturbed electrons. They have also considered the nondiagonal part of $\Phi$ but treat it perturbatively, and their perturbation expansion can be readily obtained from Eq. (6).

All the equations described above were derived by using equation-of-motion methods. Diagrammatic techniques provide a more systematic method of including perturbative corrections, and lead to more accurate, but more complicated, equations. The most careful derivation of a Boltzmann-type equation by diagrammatic techniques is Holstein's[14] equation for the electron-phonon system. We devote the rest of this section to a comparison of Eq. (6) to the Holstein-Boltzmann equation. Assuming the phonons to be in equilibrium, Holstein's equations can be written[21]

$$\sigma = 2e^2 \sum_k v_k \Phi_k \left( \frac{f(\epsilon_k) - f(\epsilon_k + \omega)}{\omega} \right), \qquad \text{(B1a)}$$

$$i(q \cdot v_k - \omega)\Phi_k = v_k + i \sum_{k'} |V_{kk'}^{(1)}|^2 (\Phi_k - \Phi_{k'}) \left( \frac{f(\epsilon_{k'}) + N(\omega_{k'-k})}{\epsilon_k - \epsilon_{k'} + \omega_{k'-k} - i\delta} + \frac{1 - f(\epsilon_{k'}) + N(\omega_{k'-k})}{\epsilon_k - \epsilon_{k'} - \omega_{k-k'} - i\delta} \right.$$
$$\left. - \frac{f(\epsilon_{k'} + \omega) + N(\omega_{k'-k})}{\epsilon_k - \epsilon_{k'} + \omega_{k'-k} + i\delta} - \frac{1 - f(\epsilon_{k'} + \omega) + N(\omega_{k'-k})}{\epsilon_k - \epsilon_{k'} - \omega_{k'-k} + i\delta} \right). \qquad \text{(B1b)}$$

In these equations $k$ stands for both the wave vector and the band index. To compare this with Eq. (6), we have to take the $q \to 0$ limit of (B1) and neglect off-diagonal terms in Eq. (6). Even in this limit Eq. (6) looks different because of the presence of the $X_k^{(2)}$ terms. These give higher-order corrections to $\sigma$, and we neglect them for the present. In order to make a detailed comparison between Eqs. (B1) and (6) it is helpful to simplify things further by neglecting the scattering-in terms. Experience with Eq. (B1) has shown[21] that the omitted terms cause only minor quantitative modifications in the results. The solution of Eq. (6) for $\sigma(\omega)$ can then be written

$$\sigma = 2e^2 \sum_k v_k^2 \left( -\frac{\partial f}{\partial \epsilon_k} \right) \frac{1}{-i[\omega + M_k(\omega)]}, \qquad \text{(B2a)}$$

$$M_k(\omega) = \Sigma_k(\epsilon_k - \omega - i\delta) - \Sigma_k(\epsilon_k + \omega + i\delta). \qquad \text{(B2b)}$$

The solution from Holstein's equation is[21]

$$\sigma = 2e^2 \sum_k v_k^2 \frac{f(\epsilon_k) - f(\epsilon_k + \omega)}{\omega} \frac{1}{-i[\omega + W_k(\omega)]}, \qquad \text{(B3a)}$$

$$W_k(\omega) = \Sigma_k(\epsilon_k - i\delta) - \Sigma_k(\epsilon_k + \omega + i\delta). \qquad \text{(B3b)}$$

We can write $M$ and $W$ as

$$M = \omega \lambda^*(\epsilon, \omega) + i/\tau^*(\epsilon, \omega), \qquad \text{(B4a)}$$

$$W = \omega \lambda(\epsilon, \omega) + i/\tau(\epsilon, \omega), \qquad \text{(B4b)}$$

$$\lambda^* = [\text{Re}\Sigma(\epsilon - \omega) - \text{Re}\Sigma(\epsilon + \omega)]/\omega, \qquad \text{(B4c)}$$

$$1/\tau^* = \text{Im}\Sigma(\epsilon - \omega) + \text{Im}\Sigma(\epsilon + \omega). \qquad \text{(B4d)}$$

The expressions for $\lambda$ and $1/\tau$ are given in Ref. 21. Explicit expressions for these can be written down at $T = 0$, so we look at the two solutions in this limit. In this limit the factor $-\partial f/\partial \epsilon_k$ becomes a $\delta$ function at the Fermi energy and the solution to $\sigma(\omega)$ from Eq. (6) reads,

$$\sigma(\omega) = ie^2 N(0) \left\langle \frac{v_k^2}{\omega[1 + \lambda^*(\omega)] + i/\tau^*(\omega)} \right\rangle. \quad (B5)$$

Here the angular brackets denote averaging over the Fermi surface; $N(0)$ is the density of states at the Fermi energy; and $\lambda^*(\omega) \equiv \lambda^*(0, \omega)$, $1/\tau^*(\omega) = 1/\tau^*(0, \omega)$. The solution from Holstein's equation in the weak-coupling limit[21] is

$$\sigma(\omega) = ie^2 N(0) \left\langle \frac{v_k^2}{\omega[1 + \bar\lambda(\omega)] + i/\bar\tau(\omega)} \right\rangle, \quad (B6a)$$

$$\bar\lambda(\omega) = \int_{-\omega}^0 \frac{d\epsilon}{\omega} \lambda(\omega), \quad (B6b)$$

$$\frac{1}{\bar\tau(\omega)} = \int_{-\omega}^0 \frac{d\epsilon}{\omega} \frac{1}{\tau(\omega)}. \quad (B6c)$$

To see the difference between the two solutions, we have to compare $\lambda^*(\omega)$, $1/\tau^*(\omega)$ with $\bar\lambda(\omega)$ and $1/\bar\tau(\omega)$ at $T = 0$. Using the formulas of Ref. 21,

$$\bar\lambda(\omega) = -\frac{2}{\omega} \int_0^{\omega_D} d\omega' \, \alpha_0^2 F(\omega')$$
$$\times \left( \ln \left| \frac{\omega - \omega'}{\omega + \omega'} \right| - \frac{\omega'}{\omega} \ln \left| \frac{\omega^2 - \omega'^2}{\omega'^2} \right| \right), \quad (B7)$$

and

$$\lambda^*(\omega) = -\frac{2}{\omega} \int_0^{\omega_D} d\omega' \, \alpha_0^2 F(\omega') \ln \left| \frac{\omega - \omega'}{\omega + \omega'} \right|. \quad (B8)$$

At the dc limit, Holstein's equation and Eq. (6) are identical after throwing away $X^{(2)}$. But from Eqs. (B7) and (B8) we see that at frequencies $\omega$ small compared with $\omega_D$, $\lambda^*(\omega)$ differs from $\bar\lambda(\omega)$ [in fact $\lambda^*(\omega) \cong 2\bar\lambda(\omega)$]. The expressions for $1/\tau^*(\omega)$ and $1/\bar\tau(\omega)$ are

$$\frac{1}{\tau^*(\omega)} = 2\pi \int_0^\omega d\omega' \, \alpha_0^2 F(\omega'), \quad (B9a)$$

$$\frac{1}{\bar\tau(\omega)} = 2\pi \int_0^\omega d\omega' \left(1 - \frac{\omega'}{\omega}\right) \alpha_0^2 F(\omega'). \quad (B9b)$$

From these equations it seems that our equation neglects terms of the order of $\omega'/\omega$, so our theory should be valid for external frequencies large compared to phonon frequencies. But at low temperatures and low frequencies it does not give a correct account of the nonadiabatic electron-phonon corrections (assuming, as we do, the accuracy of Holstein's theory). As mentioned before, the dc limit of both theories concur if $X^{(2)}$ is neglected.

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