Quantum Theory of Kinetic Equations for Electrons in Phonon Fields

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A method is presented which yields a kinetic equation for the time development of the one-electron density matrix for dynamically independent electrons in phonon and other arbitrary static fields of force under the influence of a weak but otherwise general external dynamical disturbance. The exclusion principle, the finiteness of the phonon energies, and the quantum-mechanical nature of the processes involved are taken into account rigorously. The effects of the electron-phonon interaction are described only in the Born approximation. A kinetic equation for the steady state is also derived in an arbitrary one-electron representation. An iterative solution of the kinetic equation is discussed and the power absorption due to direct and indirect transitions is derived from the general kinetic equation. The case of a uniform but oscillating electric field is considered in detail for free, Landau, and Bloch electrons, for which special kinetic equations are derived. A "local density matrix"—useful in the calculation of space-varying densities of various physical observables—is introduced and a kinetic equation for it is obtained from the general theory. Applications of it are made to the case of free and Landau electrons for disturbances of arbitrary space-time variation. The applicability of the method to more general situations is indicated.

1. INTRODUCTION

KINETIC (transport or master) equations have been very useful in fundamental and practical studies of the irreversible phenomena of approach either to thermal equilibrium or to a driven steady state.

In the study of solids the steady-state response to a weak external disturbance has been the object of a great deal of experimental and theoretical work. In the usual models of a solid such a steady state depends crucially on the impurities in the solid. The commonest examples of these are static impurities, that scatter the electrons elastically, and the dynamical lattice vibrations, that can change not only the momentum but also the energy of the electrons.

The basic theory of transport for the case of scattering by static impurities has been given rather recently in the well-known work of Kohn and Luttinger[1,2] and others.[3] In these works the usual Boltzmann transport equation (and generalizations) for the occupation probability in the case of a weak, uniform, and static electric field was established on the basis of quantum statistical mechanics without unnecessary statistical assumptions. It was proved[1] quite generally that in the case of static impurities the exclusion principle for the electrons has no effect at all on the scattering term of the transport equation. It has also been recognized[4] that other subsets of the density matrix, more useful than its diagonal elements when a magnetic field is present, satisfy analogous transport equations.

In the case of scattering by phonons, where the electrons scatter inelastically, the exclusion principle plays a very important role and the transport problem is more involved. This has been studied by various methods for special cases. Gurzhi[5] has derived a transport equation for the distribution function for free electrons on the basis of a method due to Bogoliubov.[6] Lang[7] and the author[8] have developed the transport equation for a static and uniform electric field along the lines of the work[1] for the static impurity scattering. Konstantinov and Perel'[9] have used a diagrammatic technique to extract a transport equation for free electrons from the general expression for the linear response due to Kubo[10] and Lax.[11] Gurevich and Nedlin[12] and Horing and the author[13] have also developed transport equations for electrons in a uniform magnetic field of arbitrary strength (Landau electrons) and a weak, uniform and static electric field. Recently, after the work reported here was finished, Yamada[14] has presented a transport theory for free electrons for weak but space- and time-varying electric fields starting from Kubo's[10] formalism.

In this paper[15] we present a direct and general method for the derivation of a kinetic equation for the one-electron density matrix for electrons in phonon and other arbitrary fields of force. The unsatisfactory repeated random phase assumption is avoided in this treatment. The kinetic equation is valid for all times

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[1] W. Kohn and J. M. Luttinger, Phys. Rev. **108**, 590 (1957).
[2] J. M. Luttinger and W. Kohn, Phys. Rev. **109**, 1892 (1958).
[3] D. A. Greenwood, Proc. Phys. Soc. (London) **71**, 585 (1958).
[4] P. N. Argyres, Phys. Rev. **117**, 315 (1960).
[5] R. N. Gurzhi, Zh. Eksperim. i Teor. Fiz. **33**, 451 (1957) [translation: Soviet Phys.—JETP **6**, 352 (1958)].
[6] N. N. Bogoliubov and K. P. Gurov, Zh. Eksperim. i Teor. Fiz. **17**, 614 (1947).
[7] I. G. Lang, Fiz. Tverd. Tela **2**, 2330 (1960) [translation: Soviet Phys.—Solid State **2**, 2077 (1961)].
[8] P. N. Argyres, J. Phys. Chem. Solids **19**, 66 (1961).
[9] O. V. Konstantinov and V. I. Perel', Zh. Eksperim. i Teor. Fiz. **39**, 197 (1960) [translation: Soviet Phys.—JETP **12**, 142 (1961)].
[10] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).
[11] M. Lax, Phys. Rev. **109**, 1921 (1958).
[12] L. E. Gurevich and G. M. Nedlin, Zh. Eksperim. i Teor. Fiz. **40**, 809 (1961) [translation: Soviet Phys.—JETP **13**, 568 (1961)].
[13] N. J. Horing and P. N. Argyres, in *Proceedings of the International Conference on Physics of Semiconductors* (Institute of Physics and Physical Society, London, 1962), p. 58.
[14] K. Yamada, Progr. Theoret. Phys. (Kyoto) **28**, 299 (1962). I am indebted to E. E. H. Shin for bringing this paper to my attention.
[15] Solid State Research Report, Lincoln Laboratory, MIT, No. 3, 1962, DDC 291546 (unpublished), p. 19.

and it is not of the Markoffian type. For the steady state this results in a collision operator that depends on the frequency of the driving field. Specifically, we consider in the next section the case of dynamically independent electrons under the action of a weak but arbitrarily space-time-varying dynamical disturbance. From the equation of motion for the density matrix for the system of electrons+phonons, we derive an equation for the time development of a one-electron density matrix, linear in the disturbance. A kinetic equation for the steady state, if it exists, is also derived, valid in an arbitrary one-electron representation. Arbitrary static external fields are included in the "unperturbed" motion of the electrons, i.e., are treated without approximations. The effects of the exclusion principle are treated rigorously. The quantum-mechanical nature of the various electronic processes is fully described by the kinetic equation. The effects of the scattering by the phonons are studied only for normal substances and in the first Born approximation. The effect of the driving disturbance on the scattering is derived without any additional assumptions and for arbitrary space-time variations. The application of this method to more general situations is discussed briefly in the last section and will be reported in another publication.

In Sec. 3 we discuss the general iterative solution of the kinetic equation and use it to compute the power absorption from the driving field of force. Both direct and so-called indirect processes are automatically described in this way. The special case of a uniform and oscillating electric field is discussed in Sec. 4, where from the general theory more specialized kinetic equations are derived for free, Landau and Bloch electrons. In Sec. 5 we define a one-electron *local* matrix (i.e., depending *parametrically* on position as well as time) which can be used in the evaluation of local densities of physical observables like the density operator, and derive a kinetic equation for it (or rather its Fourier components) in an arbitrary one-electron representation and for variations of arbitrary wavelength. We apply this to the special cases of free and Landau electrons.

All these kinetic equations have a fairly large field of applicability in the study of semiconductors and metals.

2. EQUATION FOR THE ONE-ELECTRON DENSITY OPERATOR

We consider the total system of electrons+phonons under the influence of an external dynamical disturbance, and are interested in the linear response of the system of electrons.

The statistical density operator of the total system $\mathfrak{R}_T$ satisfies the Liouville equation ($\hbar=1$)

$$d\mathfrak{R}_T/dt=i[\mathfrak{R}_T,\mathfrak{H}_T], \tag{2.1}$$

$[\ ,\ ]$ denoting, as usual, the commutator. $\mathfrak{H}_T$ is the total Hamiltonian

$$\mathfrak{H}_T=\mathfrak{H}+\mathfrak{F}(t), \tag{2.2}$$

where $\mathfrak{H}$ is the Hamiltonian of the system of electrons+phonons including any external *static* fields of force and $\mathfrak{F}(t)$ denotes the interaction of the electrons with the external, in general time-dependent, disturbance. In order to obtain the linear response of the system, we assume that just before the external disturbance is turned on, say at $t=0$, the system is in thermodynamic equilibrium at temperature $T=(k\beta)^{-1}$, i.e.,

$$\mathfrak{R}_T(0)=f(\tilde{\mathfrak{H}})\equiv\exp(-\beta\tilde{\mathfrak{H}})/\mathrm{Tr}\{\exp(-\beta\tilde{\mathfrak{H}})\};\quad \tilde{\mathfrak{H}}\equiv\mathfrak{H}-\zeta\mathfrak{N}. \tag{2.3}$$

$\mathfrak{N}$ is the operator for the total number of electrons in the system and ζ is the Fermi energy in the presence of the electron-phonon interaction, determined from $\mathrm{Tr}\{\mathfrak{N}f(\tilde{\mathfrak{H}})\}=N_e=$ total number of electrons. It is then clear that the linear response of the system is described by

$$\mathfrak{R}(t)=\mathfrak{R}_T(t)-f(\tilde{\mathfrak{H}}), \tag{2.4}$$

which satisfies, to the first order in the external disturbance, the inhomogeneous equation

$$d\mathfrak{R}(t)/dt=i[\mathfrak{R}(t),\mathfrak{H}]+i\mathfrak{A}(t),\quad \mathfrak{R}(0)=0, \tag{2.5}$$

with $\mathfrak{A}$ given by, since $\mathfrak{N}$ commutes with $\mathfrak{H}$,

$$\mathfrak{A}(t)=[f(\tilde{\mathfrak{H}}),\mathfrak{F}(t)]. \tag{2.6}$$

The system in the absence of the external disturbance is described by the Hamiltonian

$$\mathfrak{H}=\mathfrak{H}_0+\mathfrak{V}=\mathfrak{H}_e+\mathfrak{H}_p+\mathfrak{V}. \tag{2.7}$$

$\mathfrak{H}_e$ is the Hamiltonian for the dynamically independent electrons, each one of which moves in accordance with the Hamiltonian H that includes any external static fields of force. In the occupation number representation, which proves convenient for our purposes, we have

$$\mathfrak{H}_e=\sum_i H(i)=\sum_\mu \omega_\mu a_\mu^\dagger a_\mu. \tag{2.8}$$

The one-electron representation is chosen here for convenience to be that which diagonalizes H, i.e., $H|\mu\rangle=\omega_\mu|\mu\rangle$. $a_\mu^\dagger$, a_μ are the creation and annihilation operators, respectively, for the electrons in the state $|\mu\rangle$ and satisfy the fermion anticommutation relations, $\{a_\mu,a_\nu\}=0$, $\{a_\mu,a_\nu^\dagger\}=\delta_{\mu\nu}$. The phonon field is described by

$$\mathfrak{H}_p=\textstyle\sum_q \omega_q(b_q^\dagger b_q+\frac{1}{2}), \tag{2.9}$$

$b_q^\dagger$, b_q being the creation and annihilation operators, respectively, for the phonon q with energy ω_q, and obey the boson commutation relations, $[b_q,b_{q'}]=0$, $[b_q,b_{q'}^\dagger]=\delta_{qq'}$. Here $q=(j,\mathbf{q})$ stands for both the polarization index j and the wave vector $\mathbf{q}$, covering the first Brillouin zone, of the normal modes of oscillation of the lattice. The electron-phonon interaction can be taken quite generally to be, in the usual approximation of small lattice displacements from the equilibrium

configuration,

$$\mathcal{U}=\sum_{\mu\nu}\sum_{q} c_{\mu\nu}(q)a_\mu^\dagger a_\nu(b_q+b_{-q}^\dagger), \tag{2.10}$$

where $c_{\mu\nu}(q)=\langle\mu|c(q)|\nu\rangle$ are the matrix elements of the one-electron operator $c(q)$, which describes in a self-consistent approximation scheme the interaction of an electron with the vibrating lattice. Since $\mathcal{U}$ is Hermitian, $c(-q)=c^\dagger(q)$, where $-q=(j,-\mathbf{q})$. The interaction with the external disturbance can be written in this representation in terms of the self-consistent one-electron operator $F(t)$ as

$$\mathcal{F}(t)=\sum_i F(i)=\sum_{\mu\nu} F_{\mu\nu}(t)a_\mu^\dagger a_\nu, \tag{2.11}$$

provided the matrix elements $F_{\mu\nu}$ exist.

The expectation value of an observable $\mathcal{J}$ of the electronic system that is a sum of one-electron observables J, i.e.,

$$\mathcal{J}=\sum_i J(i)=\sum_{\mu\nu} J_{\mu\nu}a_\mu^\dagger a_\nu, \tag{2.12}$$

can be calculated from the one-electron operator $\rho_T(t)$, defined in the $|\mu\rangle$-representation by the matrix

$$(\rho_T)_{\mu\nu}=\mathrm{Tr}\{a_\nu^\dagger a_\mu\mathcal{R}_T\}. \tag{2.13}$$

The expectation value of $\mathcal{J}$ is then

$$\langle\mathcal{J}\rangle\equiv\mathrm{Tr}\{\mathcal{J}\mathcal{R}_T(t)\}=\sum_{\mu\nu}J_{\mu\nu}[\rho_T(t)]_{\nu\mu}\equiv\mathrm{tr}\{J\rho_T(t)\}, \tag{2.14}$$

where tr denotes the trace operation in the space of one-electron operators. For such observables the linear response is accordingly described by

$$\rho(t)=\rho_T(t)-\rho_0, \tag{2.15}$$

where

$$\rho_{\mu\nu}=\mathrm{Tr}\{a_\nu^\dagger a_\mu\mathcal{R}\},\quad (\rho_0)_{\mu\nu}=\mathrm{Tr}\{a_\nu^\dagger a_\mu f(\mathcal{H})\}. \tag{2.16}$$

It is clear from the definitions that ρ_T, ρ, and ρ_0 are Hermitian operators. In addition, since the total number of electrons is a constant of the motion, we have

$$\mathrm{tr}\rho_T(t)=\mathrm{tr}\rho_0=N_e,\quad \mathrm{tr}\rho(t)=0. \tag{2.17}$$

The first equation determines the Fermi energy ζ in the presence of the electron-phonon interaction. Finally, from the definition (2.13) it is seen immediately that the diagonal elements of $\rho_T(t)$ in any one-electron representation are non-negative. These properties characterize ρ_T as a one-electron density operator.

The object of this section is then to derive an equation of motion for the one-electron density operator $\rho(t)$ from the corresponding equation (2.5) for $\mathcal{R}(t)$. It is convenient to carry this out in the $|\mu\rangle$-representation first and then generalize it to an arbitrary one-electron representation. This equation must preserve, of course, the Hermitian nature of $\rho(t)$ and its traceless property, Eq. (2.17), so that the total number of electrons be conserved.

Since we shall be interested only in the case of small electron-phonon interaction, it is convenient to work in the interaction picture. That is, we put

$$\mathcal{R}'(t)=\exp(i\mathcal{H}_0t)\mathcal{R}(t)\exp(-i\mathcal{H}_0t), \tag{2.18}$$

and similarly for $\mathcal{U}'(t)$ and $\mathcal{A}'(t)$. Equation (2.5) then reads

$$d\mathcal{R}'(t)/dt=i[\mathcal{R}'(t),\mathcal{U}'(t)]+i\mathcal{A}'(t);\quad \mathcal{R}'(0)=0. \tag{2.19}$$

In this picture the one-electron density matrix is

$$\rho_{\mu\nu}'(t)\equiv\mathrm{Tr}\{a_\nu^\dagger a_\mu\mathcal{R}'(t)\}=\exp(i\omega_{\mu\nu}t)\rho_{\mu\nu}(t), \tag{2.20}$$

where $\omega_{\mu\nu}\equiv\omega_\mu-\omega_\nu$. The electron-phonon interaction takes the form

$$\mathcal{U}'(t)=\sum_{\mu\nu}\sum_q[c_{\mu\nu}(qt)b_q+c_{\mu\nu}^\dagger(qt)b_q^\dagger]a_\mu^\dagger a_\nu, \tag{2.21}$$

where

$$c_{\mu\nu}(qt)=\exp[i(\omega_{\mu\nu}-\omega_q)t]c_{\mu\nu}(q). \tag{2.21a}$$

An equation for $d\rho_{\mu\nu}'(t)/dt$ is easily obtained from the definition of $\rho_{\mu\nu}'(t)$ and the equation of motion for $\mathcal{R}'(t)$. In carrying out the operation (2.20), and the similar operations to follow, with the commutator $[\mathcal{R}',\mathcal{U}']$, we note that, because of the invariance property of the trace under cyclic permutations, we can write $\mathrm{Tr}\{a_\mu^\dagger a_\nu[\mathcal{R}',\mathcal{U}']\}=\mathrm{Tr}\{[\mathcal{U}',a_\mu^\dagger a_\nu]\mathcal{R}'\}$. Since $\mathcal{U}'$ is quadratic in the fermion operators, we can make use of the commutation relations

$$[a_\kappa^\dagger a_\lambda,a_\mu^\dagger a_\nu]=a_\kappa^\dagger a_\nu\delta_{\lambda\mu}-a_\mu^\dagger a_\lambda\delta_{\kappa\nu},$$

and thus find

$$\frac{d}{dt}\rho_{\mu\nu}'(t)=iA_{\mu\nu}'(t)+i\sum_{\kappa q}\{c_{\kappa\nu}(qt)\rho_{\kappa\mu q}'(t)+c_{\kappa\nu}^\dagger(qt)\rho_{\kappa\mu\bar{q}}'(t)-c_{\mu\kappa}(qt)\rho_{\nu\kappa q}'(t)-c_{\mu\kappa}^\dagger(qt)\rho_{\nu\kappa\bar{q}}'(t)\}, \tag{2.22}$$

with the initial condition $\rho_{\mu\nu}'(0)=0$. Here

$$A_{\mu\nu}'(t)=\exp(i\omega_{\mu\nu}t)A_{\mu\nu}(t)\equiv\exp(i\omega_{\mu\nu}t)\,\mathrm{Tr}\{a_\nu^\dagger a_\mu\mathcal{A}(t)\}, \tag{2.23}$$

and the 3-indexed quantities are other reduced density matrices of higher order defined by

$$\rho_{\kappa\lambda q}'=\mathrm{Tr}\{a_\kappa^\dagger a_\lambda b_q\mathcal{R}'\},\quad \rho_{\kappa\lambda\bar{q}}'=\mathrm{Tr}\{a_\kappa^\dagger a_\lambda b_q^\dagger\mathcal{R}'\}. \tag{2.24}$$

It is clear that in this picture the coupling of $d\rho_{\mu\nu}'/dt$ to the higher order density matrices comes from the commutator $[\mathcal{R}',\mathcal{U}']$ and is therefore proportional to the strength of the electron-phonon interaction (to be denoted from now on by the dimensionless parameter λ).

An equation of motion for the higher order density matrices can be obtained in the same manner from

(2.19). We thus find, for example,

$$\frac{d}{dt}\rho_{\mu\nu q}'(t)=iA_{\mu\nu q}'(t)-i\sum_{\kappa\lambda}c_{\kappa\lambda}^{\dagger}(qt)\rho_{\kappa\lambda\mu\nu}'(t)$$
$$+i\sum_{\kappa q'}\{c_{\kappa\mu}(q't)\rho_{\kappa\nu qq'}'(t)+c_{\kappa\mu}^{\dagger}(q't)\rho_{\kappa\nu q\bar{q}'}'(t)$$
$$-c_{\nu\kappa}(q't)\rho_{\mu\kappa qq'}'(t)-c_{\nu\kappa}^{\dagger}(q't)\rho_{\mu\kappa q\bar{q}'}'(t)\},\quad(2.25)$$

again with the initial condition $\rho_{\mu\nu q}'(0)=0$. Here

$$A_{\mu\nu q}'(t)=\mathrm{Tr}\{a_\mu^{\dagger}a_\nu b_q\mathfrak{R}'(t)\},\qquad(2.25a)$$
$$\rho_{\kappa\lambda\mu\nu}'=\mathrm{Tr}\{a_\kappa^{\dagger}a_\lambda a_\mu^{\dagger}a_\nu\mathfrak{R}'\},$$

$$\rho_{\kappa\lambda q'q}'=\mathrm{Tr}\{a_\kappa^{\dagger}a_\lambda b_{q'}b_q\mathfrak{R}'\},\qquad(2.25b)$$
$$\rho_{\kappa\lambda q'\bar{q}}'=\mathrm{Tr}\{a_\kappa^{\dagger}a_\lambda b_{q'}b_q^{\dagger}\mathfrak{R}'\}.$$

A similar equation can be written for $d\rho_{\mu\nu\bar{q}}'/dt$, since $\rho_{\mu\nu\bar{q}}'=\rho_{\nu\mu q}'^{*}$. The new matrices that enter this equation, e.g., $\rho_{\mu\nu\bar{q}q'}'$, $\rho_{\mu\nu\bar{q}\bar{q}'}'$, are defined in an obvious way: the fermion indices always appear in pairs denoting creation and annihilation operators in this order, whereas the boson indices appear in any number and sequence, the creation operators being indicated by a bar over the corresponding boson index.

It is now clear that in this manner we can write down a system of coupled equations, each one giving the time derivative of a reduced density matrix in terms of other reduced density matrices of higher order. Such a system of equations is characteristic of a number of many-body theories. We shall be interested here exclusively in normal substances and seek to obtain an approximate equation for $\rho_{\mu\nu}(t)$ valid for sufficiently small λ. Such an equation with the effects of the electron-phonon interaction taken into account in the lowest order, i.e., λ^2, can be obtained in the following way.

We first seek to express the 4-indexed density matrices defined by (2.25a) and (2.25b) in terms of the one-electron density matrix $\rho_{\mu\nu}'(t)$, in an approximation valid for small λ. We accomplish this by examining both in the absence of electron-phonon interaction. We thus find that we may approximate for $\lambda\neq 0$

$$\rho_{\kappa\lambda qq'}'(t)=\rho_{\kappa\lambda\bar{q}\bar{q}'}'(t)=O(\lambda),\qquad(2.26a)$$
$$\rho_{\kappa\lambda q\bar{q}'}'(t)=\delta_{qq'}(N_q+1)\rho_{\lambda\kappa}'(t)+O(\lambda),\qquad(2.26b)$$
$$\rho_{\kappa\lambda\bar{q}q'}'(t)=\delta_{qq'}N_q\rho_{\lambda\kappa}'(t)+O(\lambda),\qquad(2.26c)$$
$$\rho_{\kappa\lambda\mu\nu}'(t)=n_\kappa\delta_{\kappa\lambda}\rho_{\nu\mu}'(t)-n_\kappa\delta_{\kappa\nu}\rho_{\lambda\mu}'(t)+n_\mu\delta_{\mu\nu}\rho_{\lambda\kappa}'(t)$$
$$+(1-n_\mu)\delta_{\mu\lambda}\rho_{\nu\kappa}'(t)+O(\lambda).\qquad(2.26d)$$

Here we have put

$$N_q\equiv\mathrm{Tr}_p\{b_q^{\dagger}b_q f(\mathcal{H}_p)\}=[\exp(\beta\omega_q)-1]^{-1},\qquad(2.27)$$

i.e., the Planck distribution function for phonons in thermal equilibrium, and

$$n_\kappa=n(\omega_\kappa)\equiv\mathrm{Tr}_e\{a_\kappa^{\dagger}a_\kappa f(\mathcal{H}_e-\zeta_0\mathfrak{N})\}$$
$$=[\exp\beta(\omega_\kappa-\zeta_0)+1]^{-1},\qquad(2.28)$$

the Fermi distribution function for the electrons. It should be noticed that ζ_0 is the value of the Fermi energy in the case of $\lambda=0$ and is determined from $\sum_\kappa n_\kappa=\mathrm{tr}\rho_0^{(0)}=N_e$ [compare (2.17)]. In arriving at (2.26d) we have made use of the relation

$$\mathrm{Tr}_e\{a_\kappa^{\dagger}a_\lambda a_\mu^{\dagger}a_\nu f(\mathcal{H}_e-\zeta_0\mathfrak{N})\}$$
$$=\delta_{\kappa\lambda}\delta_{\mu\nu}n_\kappa n_\mu+\delta_{\kappa\nu}\delta_{\lambda\mu}n_\kappa(1-n_\mu).$$

The symbol $O(\lambda)$ indicates that the additional terms vanish for $\lambda=0$.

Using expressions (2.26) in (2.25) for $d\rho_{\mu\nu q}'(t)/dt$ and integrating with the use of the initial condition, we obtain $\rho_{\mu\nu q}'(t)$ as a functional of $\rho_{\mu\nu}'(t)$, with coefficients correct up to order λ. An analogous functional is obtained for $\rho_{\mu\nu\bar{q}}'(t)$.

When these functional expressions are substituted in (2.22) an equation is obtained for the one-electron density matrix $\rho_{\mu\nu}'(t)$ with coefficients correct up to order λ^2. This can be written after rearrangement as

$$\frac{d}{dt}\rho_{\mu\nu}'(t)=(\mathcal{S}'\{t,\rho'(t)\})_{\mu\nu}+iA_{\mu\nu}'(t)+B_{\mu\nu}'(t).\qquad(2.29)$$

$A_{\mu\nu}'(t)$ is given by (2.23) and

$$B_{\mu\nu}'(t)=\sum_{\kappa q}\Big\{c_{\mu\kappa}(qt)\int_0^t d\tau A_{\nu\kappa q}'(\tau)$$
$$+c_{\mu\kappa}^{\dagger}(qt)\int_0^t d\tau A_{\nu\kappa\bar{q}}'(\tau)-c_{\kappa\nu}(qt)\int_0^t d\tau A_{\kappa\mu q}'(\tau)$$
$$-c_{\kappa\nu}^{\dagger}(qt)\int_0^t d\tau A_{\kappa\mu\bar{q}}'(\tau)\Big\},\qquad(2.30)$$

where $A_{\nu\kappa q}'$ should for consistency be taken only up to order λ, as given through (2.25a). The operator $\mathcal{S}'\{t,\rho'(t)\}$ can be expressed in terms of the corresponding operator $\mathcal{S}$ in the Schrödinger picture operating on $\rho(t)$ as

$$(\mathcal{S}'\{t,\rho'(t)\})_{\mu\nu}=e^{i\omega_{\mu\nu}t}(\mathcal{S}\{t,\rho(t)\})_{\mu\nu}\qquad(2.31)$$

with

$$(\mathcal{S}\{t,\rho(t)\})_{\mu\nu}=\sum_{\kappa\lambda}\int_0^t d\tau\{\rho_{\kappa\lambda}(t-\tau)$$
$$\times[e^{-i\omega_{\mu\lambda}\tau}W_{\mu\nu}{}^{\kappa\lambda}(\tau)+e^{-i\omega_{\kappa\nu}\tau}W_{\nu\mu}{}^{\lambda\kappa*}(\tau)]$$
$$-\rho_{\mu\kappa}(t-\tau)e^{-i\omega_{\mu\lambda}\tau}W_{\lambda\lambda}{}^{\kappa\nu*}(\tau)$$
$$-\rho_{\lambda\nu}(t-\tau)e^{-i\omega_{\kappa\nu}\tau}W_{\kappa\kappa}{}^{\lambda\mu}(\tau)\},\qquad(2.32)$$

the W's being given by

$$W_{\mu\nu}{}^{\kappa\lambda}(\tau)=\sum_q c_{\mu\kappa}^{\dagger}(q)c_{\lambda\nu}(q)[(N_q+1-n_\mu)e^{-i\omega_q\tau}$$
$$+(N_q+n_\mu)e^{i\omega_q\tau}].\qquad(2.32a)$$

Here we have made use of the relations $c(-q)=c^{\dagger}(q)$, $N_{-q}=N_q$ and $\omega_{-q}=\omega_q$. Also we have not written down a

few terms associated with the zero-point oscillations of the lattice which are of no consequence in all the applications we have investigated. (Note that the operator $\mathcal{S}$ operates in the space of one-electron operators rather than state vectors.)

In the Schrödinger picture (2.29) reads

$$\frac{d}{dt}\rho_{\mu\nu}(t)=-i\omega_{\mu\nu}\rho_{\mu\nu}(t)+(\mathcal{S}\{t,\rho(t)\})_{\mu\nu}+iA_{\mu\nu}(t)+B_{\mu\nu}(t). \quad (2.33)$$

This is the equation of motion for the one-electron density matrix $\rho_{\mu\nu}(t)$, valid for *all* t in conjunction with the initial condition $\rho_{\mu\nu}(0)=0$. The meaning of the various terms is clear. The first term, which can be written as $-i[H,\rho(t)]_{\mu\nu}$, describes the effects of the unperturbed motion of the electron as an independent particle. The second gives the effects of the electron-phonon interaction alone to second order and, as it is seen from (2.32), it shows "memory," i.e., it makes $d\rho(t)/dt$ depend on all previous values of $\rho(t)$. $A_{\mu\nu}(t)$ is the "driving" term, and it should be kept up to order λ^2 for consistency. It is found from (2.23), (2.6), and (2.16) that

$$A_{\mu\nu}(t)=[\rho_0,F(t)]_{\mu\nu}. \quad (2.34)$$

Upon expanding $f(\mathfrak{H})$ in powers of λ up to λ^2, we find $A=A^{(0)}+A^{(2)}$, where

$$A_{\mu\nu}{}^{(0)}(t)=(n_\mu-n_\nu)F_{\mu\nu}(t)=[n(H),F(t)]_{\mu\nu} \quad (2.35)$$

describes the effect of the external disturbance alone; $A_{\mu\nu}{}^{(2)}(t)$ is its correction to order λ^2 due to the fact that the electrons were in thermal equilibrium in the presence of the vibrating lattice before the external disturbance was turned on, and therefore their energies were shifted from their unperturbed values. Since we shall not be interested in the energy shifts in any detail, we shall not write down the explicit expression for $A_{\mu\nu}{}^{(2)}(t)$. $B_{\mu\nu}(t)=\exp(-i\omega_{\mu\nu}t)B_{\mu\nu}{}'(t)$ is proportional to the driving disturbance and to λ^2 and it is found from (2.30) to be

$$B_{\mu\nu}(t)=\sum_{\kappa\lambda}\int_0^t d\tau\{F_{\kappa\lambda}(t-\tau)\times[e^{-i\omega_{\mu\lambda}\tau}V_{\mu\nu}{}^{\kappa\lambda}(\tau)+e^{-i\omega_{\kappa\nu}\tau}V_{\lambda\kappa}{}^{\nu\mu}(\tau)]-F_{\mu\kappa}(t-\tau)e^{-i\omega_{\mu\lambda}\tau}V_{\kappa\nu}{}^{\lambda\lambda}(\tau)-F_{\lambda\nu}(t-\tau)e^{-i\omega_{\kappa\nu}\tau}V_{\kappa\kappa}{}^{\lambda\mu}(\tau)\}, \quad (2.36)$$

where

$$V_{\mu\nu}{}^{\kappa\lambda}(\tau)=n_\mu(1-n_\kappa)\sum_q c_{\mu\kappa}{}^\dagger(q)c_{\lambda\nu}(q)\times\left[N_q e^{-i\omega_q\tau}\int_0^\beta dz e^{(\omega_{\mu\kappa}+\omega_q)z}+(N_q+1)e^{i\omega_q\tau}\int_0^\beta dz e^{(\omega_{\mu\kappa}-\omega_q)z}\right]. \quad (2.36a)$$

[We have not written down in (2.36) a couple of terms of the same type as those we ignored in (2.32).] It describes the effects due to the interference between the external disturbance and the electron-phonon interaction. In contrast to $A^{(2)}(t)$, however, it not only gives the consequences of the shifts of the electronic energy levels but also describes the effects of the external field on the scattering.

It should be pointed out that it can be easily verified from the structure of the operators $\mathcal{S}$, A, and B that the solution of (2.33) is indeed a Hermitian operator, as it should be. The kinetic equation (2.33) must also preserve the property $\mathrm{Tr}\rho(t)=0$, Eq. (2.17), which guarantees that the total number of electrons is conserved. This indeed is true, since $\mathrm{Tr}\rho(0)=0$ and $d\,\mathrm{Tr}\rho(t)/dt=0$, as it can easily be proved from (2.33).

The solution of the kinetic equation (2.33) describes the complete time development of $\rho(t)$ from $t=0$ to very large times, where presumably a steady state is attained. A kinetic equation for the steady state itself, when it exists, can be obtained from (2.33) on the basis of the following argument. We take $F(t)$ to be given quite generally by

$$F(t)=\sum_\omega e^{i\omega t}F(\omega), \quad (2.37)$$

where for each ω the summation $\sum_\omega$ goes over ω and $-\omega$. Thus, since $F(t)$ is Hermitian, we must have $F(-\omega)=F^\dagger(\omega)$, which serves to define the operator $F(-\omega)$ in case $F(\omega)$ is independent of ω. Now we seek a solution of (2.33) of the form

$$\rho(t)=\sum_\omega e^{i\omega t}\rho(\omega,t);\quad \rho(\omega,t)\underset{t\to\infty}{\longrightarrow}\rho(\omega), \quad (2.38)$$

where $\sum_\omega$ goes over the same frequencies as in (2.37). Thus (2.38) describes for very long times a steady state $\rho^{(s)}(t)=\sum_\omega e^{i\omega t}\rho(\omega)$. In order to find an equation for $\rho(\omega)$, we substitute (2.38) and (2.37) into (2.33) and study it in the limit $t\to\infty$. The inhomogeneous terms are found to be simply

$$A(t)=\sum_\omega e^{i\omega t}A(\omega),\quad B(t)=\sum_\omega e^{i\omega t}B(\omega). \quad (2.39)$$

Here $A(\omega)=A^{(0)}(\omega)+A^{(2)}(\omega)$ with

$$A(\omega)=[\rho_0,F(\omega)] \quad \text{and} \quad A^{(0)}(\omega)=[n(H),F(\omega)]. \quad (2.40)$$

Similarly from (2.36)

$$B_{\mu\nu}(\omega)=\sum_{\kappa\lambda}\{F_{\kappa\lambda}(\omega)[v_{\mu\nu}{}^{\kappa\lambda}(\omega_{\mu\lambda}+\omega)+v_{\lambda\kappa}{}^{\nu\mu}(\omega_{\kappa\nu}+\omega)]-F_{\mu\kappa}(\omega)v_{\kappa\nu}{}^{\lambda\lambda}(\omega_{\mu\lambda}+\omega)-F_{\lambda\nu}(\omega)v_{\kappa\kappa}{}^{\lambda\mu}(\omega_{\kappa\nu}+\omega)\}, \quad (2.41)$$

where

$$v_{\mu\nu}{}^{\kappa\lambda}(x)=\int_0^\infty d\tau e^{-ix\tau}V_{\mu\nu}{}^{\kappa\lambda}(\tau)=n_\mu(1-n_\kappa)\sum_q c_{\mu\kappa}{}^\dagger(q)c_{\lambda\nu}(q)\times\left[N_q\theta(x+\omega_q)\int_0^\beta dz e^{z(\omega_{\mu\kappa}+\omega_q)}+(N_q+1)\theta(x-\omega_q)\int_0^\beta dz e^{z(\omega_{\mu\kappa}-\omega_q)}\right] \quad (2.41a)$$

and

$$\theta(x)=\int_0^\infty d\tau e^{-ix\tau}=\pi\delta(x)-i\left(\frac{1}{x}\right)_p. \quad (2.42)$$

The expression for $\mathcal{S}\{t,\rho(t)\}$ for long times is evaluated by noting that for an *infinite* lattice $W_{\mu\nu}{}^{\kappa\lambda}(\tau)$, as given by (2.32a) (or at least after the summations over $\kappa\lambda$ have been carried out), tends to zero for large values of τ. More specifically, we have

$$W_{\mu\nu}{}^{\kappa\lambda}(\tau)\cong 0 \quad \text{for} \quad \tau>\tau_c, \quad (2.43)$$

where τ_c is some correlation time for the vibrating lattice. Therefore, for $t>\tau_c$ the upper limit of the integral in (2.32) can be put equal to τ_c. Thus the values of $\rho(\omega,t)$ that enter the integral are from $\rho(\omega, t-\tau_c)$ to $\rho(\omega,t)$, which for $t\to\infty$ can be taken, in accordance with (2.38), to be equal to $\rho(\omega)$. Therefore, we have

$$\mathcal{S}\{t,\sum_\omega e^{i\omega t}\rho(\omega,t)\}\underset{t\to\infty}{\to}\sum_\omega e^{i\omega t}\mathcal{S}(\omega)\rho(\omega), \quad (2.44)$$

where

$$\begin{aligned}(\mathcal{S}(\omega)\rho(\omega))_{\mu\nu}&=\sum_{\kappa\lambda}\{\rho_{\kappa\lambda}(\omega)[w_{\mu\nu}{}^{\kappa\lambda}(\omega_{\mu\lambda}+\omega)+w_{\nu\mu}{}^{\lambda\kappa*}(\omega_{\nu\kappa}-\omega)]\\&\quad-\rho_{\mu\kappa}(\omega)w_{\lambda\lambda}{}^{\kappa\nu*}(\omega_{\lambda\mu}-\omega)\\&\quad-\rho_{\lambda\nu}(\omega)w_{\kappa\kappa}{}^{\lambda\mu}(\omega_{\kappa\nu}+\omega)\}, \quad (2.45)\end{aligned}$$

the w's being given by

$$\begin{aligned}w_{\mu\nu}{}^{\kappa\lambda}(x)&=\int_0^\infty d\tau e^{-ix\tau}W_{\mu\nu}{}^{\kappa\lambda}(\tau)\\&=\sum_q c_{\mu\kappa}{}^\dagger(q)c_{\lambda\nu}(q)[(N_q+1-n_\mu)\theta(x+\omega_q)\\&\quad+(N_q+n_\mu)\theta(x-\omega_q)]. \quad (2.45a)\end{aligned}$$

The singular part of $\theta(x)$ may be interpreted to give in (2.45) the effects of scattering in the usual form of "scattering-in" minus "scattering-out" due to the emission and absorption of phonons, with due consideration of the exclusion principle for the electrons and the conservation of energy in the various collision processes. It should be noted that the presence of the driving frequency ω in $\mathcal{S}(\omega)$ is due to the "memory" of $\mathcal{S}\{t,\rho(t)\}$. The regular part of $\theta(x)$ may be taken to describe in (2.45) the "renormalization" of the unperturbed electronic energy levels due to electron-phonon interaction (to order λ^2). It should be noted, however, that these terms depend on ω and thus they are not simply shifts of the resonance frequencies, but they contribute to the shape of the absorption line, just as the scattering terms do. The other terms of (2.33) after the substitution of (2.38) are quite simple. Thus, if a steady-state solution $\rho^{(s)}(t)=\sum_\omega e^{i\omega t}\rho(\omega)$ of (2.33) exists, $\rho(\omega)$ satisfies the equation

$$i\omega\rho(\omega)=-i[H,\rho(\omega)]+\mathcal{S}(\omega)\rho(\omega)+iA(\omega)+B(\omega). \quad (2.46)$$

The correctness of this equation is substantiated in Appendix A, where it is obtained by the method of Fourier transforms.

As (2.46) indicates, it is desirable to write the kinetic equations for $\rho(\omega)$ and $\rho(t)$ as operator equations, valid in any one-electron representation. We shall exhibit this only for $\rho(\omega)$, the case of (2.33) for $\rho(t)$ being entirely analogous. $A(\omega)$ has already been expressed in that form, as given by (2.40). From (2.41) we find that we may write

$$\begin{aligned}B(\omega)=\sum_q\int_0^\infty d\tau e^{-i\omega\tau}&\times\int_0^\beta dz\{N_q e^{-\omega_q(i\tau-z)}+(N_q+1)e^{\omega_q(i\tau-z)}\}\\&\times[c(q),e^{-iH\tau}[F(\omega),n(H)e^{zH}c^\dagger(q)\\&\quad\times e^{-zH}(1-n(H))]e^{iH\tau}]. \quad (2.47)\end{aligned}$$

Similarly, (2.45) can be put in the form

$$\begin{aligned}\mathcal{S}(\omega)\rho(\omega)=\sum_q\Big[c(q),\int_0^\infty d\tau e^{-i\omega\tau}e^{-iH\tau}\{\rho(\omega)c^\dagger(q)g_q{}^\dagger(H,\tau)\\-g_q(H,\tau)c^\dagger(q)\rho(\omega)\}e^{iH\tau}\Big], \quad (2.48)\end{aligned}$$

where

$$\begin{aligned}g_q(H,\tau)&=(N_q+1-n(H))e^{-i\omega_q\tau}\\&\quad+(N_q+n(H))e^{i\omega_q\tau}. \quad (2.48a)\end{aligned}$$

These operator expressions for $B(\omega)$ and $\mathcal{S}(\omega)\rho(\omega)$ are very useful in various applications and in particular will be used in Sec. 5.

From the definitions it is clear that we must have $\rho(-\omega)=\rho^\dagger(\omega)$, $A(-\omega)=-A^\dagger(\omega)$ and $B(-\omega)=B^\dagger(\omega)$, which are, strictly speaking, the definitions of these operators for $-\omega$. From the structure of the operators entering (2.46), it can be verified that the solutions of (2.46) do satisfy the relation $\rho(-\omega)=\rho^\dagger(\omega)$. Also the relation $\mathrm{tr}\rho(\omega)=0$, which expresses the conservation of the total number of electrons, is obvious from the operator expressions of $\mathcal{S}(\omega)\rho(\omega)$, $A(\omega)$ and $B(\omega)$ as commutators.

In order to gain some insight into the meaning of the various terms of $B(\omega)$ and to facilitate later applications, it proves useful to observe that

$$B(\omega)=-\mathcal{S}(\omega)r(\omega)+D(\omega), \quad (2.49)$$

where

$$r_{\mu\nu}(\omega)=A_{\mu\nu}{}^{(0)}(\omega)/(\omega+\omega_{\mu\nu})_p \quad (2.49a)$$

is the nonsingular part of the one-electron steady-state density matrix in the absence of any electron-phonon

interaction, as it can be seen immediately from (2.46). In $D(\omega)$ there are two kinds of terms that are associated respectively with the singular and nonsingular parts of $\theta(x)$. The latter terms result from the electronic energy shifts, and as such they should be combined with $A_{\mu\nu}^{(2)}(\omega)$. If we ignore them, $D(\omega)$ is found to be

$$D_{\mu\nu}(\omega)=(e^{\beta\omega}-1)\sum_{\kappa\lambda}\Big\{\frac{F_{\kappa\lambda}(\omega)}{(\omega_{\kappa\lambda}+\omega)_p}[n_\lambda(1-n_\mu)u_{\mu\nu}{}^{\kappa\lambda}(\omega_{\mu\lambda}+\omega)+n_\nu(1-n_\kappa)u_{\mu\nu}{}^{\kappa\lambda}(\omega_{\kappa\nu}+\omega)]$$
$$-\frac{F_{\mu\kappa}(\omega)}{(\omega_{\mu\kappa}+\omega)_p}n_\lambda(1-n_\mu)u_{\kappa\nu}{}^{\lambda\lambda}(\omega_{\mu\lambda}+\omega)-\frac{F_{\lambda\nu}(\omega)}{(\omega_{\lambda\nu}+\omega)_p}n_\nu(1-n_\kappa)u_{\mu\lambda}{}^{\kappa\kappa}(\omega_{\kappa\nu}+\omega)\Big\}$$
$$+\beta\sum_{\kappa\lambda}\{\bar{F}_{\kappa\lambda}(\omega)[n_\mu(1-n_\kappa)u_{\mu\nu}{}^{\kappa\lambda}(\omega_{\lambda\mu}-\omega)+n_\lambda(1-n_\nu)u_{\mu\nu}{}^{\kappa\lambda}(\omega_{\nu\kappa}-\omega)]$$
$$-n_\kappa(1-n_\lambda)[\bar{F}_{\mu\kappa}(\omega)u_{\kappa\nu}{}^{\lambda\lambda}(\omega_{\lambda\mu}-\omega)+\bar{F}_{\lambda\nu}(\omega)u_{\mu\lambda}{}^{\kappa\kappa}(\omega_{\nu\kappa}-\omega)]\}\,, \tag{2.50}$$

where

$$u_{\mu\nu}{}^{\kappa\lambda}(x)=\pi\sum_q c_{\mu\kappa}{}^\dagger(q)c_{\lambda\nu}(q)[(N_q+1)\delta(x+\omega_q)+N_q\delta(x-\omega_q)] \tag{2.50a}$$

$$\bar{F}_{\kappa\lambda}(\omega)=F_{\kappa\lambda}(\omega)\delta_{\omega,\omega\lambda\kappa}\,. \tag{2.50b}$$

The second term in (2.50) that is proportional to β arises from the terms of (2.41a) with vanishing exponents, and it can make a finite contribution in special cases. It is worth pointing out that for a static external disturbance, i.e., $\omega=0$, the first term of $D(\omega)$ vanishes in general and the second term combines with $(\mathcal{S}(0)r(0))_{\mu\nu}$ to just give, as far as the relaxation effects are concerned,

$$B(0)=-\mathcal{S}(0)[n(H+F)-n(H)], \tag{2.51}$$

where $n(H+F)$ is to be taken up to terms linear in F. That is, in the case of a steady external disturbance the collisions have in general the effect of forcing the electrons to relax to a state characteristic of thermodynamic equilibrium for fermions in the presence of the external field, as it is expected on physical grounds. For disturbances oscillating in time this is clearly *not* true; the process of relaxation is disturbed by the finite frequency of oscillation of the external field, the end result thus depending on ω and the "collision frequency" as given by $B_{\mu\nu}(\omega)$ without any assumptions. The situations for which $F(\omega)$ is not a regular function of ω should be examined individually. The physical meaning of the various terms of $D_{\mu\nu}(\omega)$ is not entirely obvious in (2.50). We shall see, however, that in the calculation of the power absorbed (see next section) away from direct resonance they assume the clear physical interpretation of describing the indirect processes of absorption or emission of the quanta of energy of the external disturbance through the simultaneous emission or absorption of phonons.

We note that with (2.49) the steady-state kinetic equation (2.46) can be written as

$$i\omega\rho(\omega)=-i[H,\rho(\omega)]+\mathcal{S}(\omega)[\rho(\omega)-r(\omega)]+iA(\omega)+D(\omega). \tag{2.52}$$

For the case of a time-independent driving field the kinetic equation for the steady state is

$$0=-i[H,\rho]+\mathcal{S}(0)[\rho-n(H+F)]+i[n(H),F], \tag{2.53}$$

since $\mathcal{S}(0)n(H)=0$, where only the relaxation effects of the electron-phonon interaction are included.

The "memory" effects of the kinetic equation (2.33) for the time dependence of $\rho(t)$ can be approximated so as to yield a Markoffian equation for $d\rho(t)/dt$ for *long* times involving only the instantaneous value of $\rho(t)$. We consider this in Appendix B.

3. ITERATIVE SOLUTION AND POWER ABSORPTION

A general solution for the steady-state equation (2.46) is too difficult due to the complexity of the scattering operator $\mathcal{S}(\omega)$. For special systems (2.46) simplifies somewhat, as we shall see in the next section. Here we are interested in the case of a general one-electron Hamiltonian H and interaction $F(t)$ under circumstances that a solution in powers of the electron-phonon interaction exists. Insight into the meaning of the various terms is obtained by studying the rate at which energy is absorbed from the driving field.

We seek a solution of the steady-state equation (2.46) in powers of the electron-phonon interaction,

$$\rho(\omega)=\rho^{(0)}(\omega)+\rho^{(2)}(\omega)+\cdots. \tag{3.1}$$

The solution for $\lambda=0$ is clearly

$$\rho_{\mu\nu}{}^{(0)}(\omega)=iA_{\mu\nu}{}^{(0)}(\omega)\theta(\omega_{\mu\nu}+\omega)$$
$$=r_{\mu\nu}(\omega)+i\pi A_{\mu\nu}{}^{(0)}(\omega)\delta(\omega_{\mu\nu}+\omega)\,, \tag{3.2}$$

where $r(\omega)$ is given by (2.49a). We note that in case $\omega_{\mu\nu}+\omega=0$, division by $i(\omega_{\mu\nu}+\omega)$ should be interpreted as multiplication by $\pi\delta(\omega_{\mu\nu}+\omega)$. This can be verified directly from (2.33) for $d\rho(t)/dt$ for $\lambda=0$, or from Appendix A. Thus, in the case of direct resonance, i.e., for $\omega_{\mu\nu}+\omega=0$ with $A_{\mu\nu}{}^{(0)}(\omega)\neq 0$, the density matrix in

the absence of electron-phonon interaction is partly singular. However, the induced current, and consequently the absorption, can be finite in many cases of interest. There are special cases where this is *not* true and then a more accurate solution of (2.46) is required for these sharp frequencies. The regular part of (3.2) gives rise to the unperturbed "reversible" current.

$\rho^{(2)}(\omega)$ can be found from (2.46) by iteration. Thus

$$\rho_{\mu\nu}{}^{(2)}(\omega)=G_{\mu\nu}(\omega)\theta(\omega_{\mu\nu}+\omega)\,, \tag{3.3}$$

where

$$G(\omega)=\mathcal{S}(\omega)\rho^{(0)}(\omega)+iA^{(2)}(\omega)+B(\omega)\,. \tag{3.3a}$$

This iterative solution is clearly a poor one for ω close to direct resonance, where a nonperturbative solution is appropriate.

In the following, we shall be interested in $\rho^{(2)}(\omega)$ for ω away from direct resonance. In such a case, we note that $\rho^{(0)}(\omega)=r(\omega)$. As a consequence we have $G(\omega)=D(\omega)$, if we ignore the terms describing the effects due to energy "shifts," and thus

$$\rho_{\mu\nu}{}^{(2)}(\omega)=(-i)D_{\mu\nu}(\omega)/(\omega_{\mu\nu}+\omega)_p\,. \tag{3.4}$$

It is easy to see from Appendix B, Eq. (B8), that in this case the Markoffian approximation yields an identical expression for $\rho_M{}^{(2)}(\omega)$, as it should, since the Markoffian approximation is valid for sufficiently small λ. It should be noticed that for ω away from direct resonance the second term of $D_{\mu\nu}(\omega)$ vanishes except possibly for $\omega=0$. This case arises when $F_{\mu\nu}(0)\neq 0$ for states $|\mu\rangle$, $|\nu\rangle$ on the same energy shell; this is *not*, according to our definition, a case of direct resonance, since although $F_{\mu\nu}(0)\neq 0$ we have $A_{\mu\nu}{}^{(0)}(0)=0$.

It should be evident that the perturbative solution (3.2) and (3.3) can be derived, and thus its correctness checked, directly by solving the equation of motion of $\mathcal{R}(t)$, (2.5), in power series of λ and then performing the operation (2.16) to obtain the corresponding $\rho(t)$.

A slightly better solution of (2.46) is obtained by first combining all the terms of $(\mathcal{S}(\omega)\rho(\omega))_{\mu\nu}$ that involve $\rho_{\mu\nu}(\omega)$ with the first two terms of (2.46) and iterating afterwards. It is then found that instead of the sharp resonances at the unperturbed differences $\omega_\mu-\omega_\nu$, resonances are obtained at slightly displaced energy differences due to the energy shifts and somewhat broadened by the life times of these states due to electron-phonon interaction. The appropriate expressions are easily obtainable from (2.46) and shall not be written down here.

The rate at which the electron+phonon system absorbs energy at time t from the driving field can be taken as

$$P(t)=\left\langle \frac{d}{dt}\mathcal{H}\right\rangle=\mathrm{Tr}\left\{\mathcal{R}_T(t)\frac{d}{dt}\mathcal{H}\right\}\,. \tag{3.5}$$

Since $d\mathcal{H}/dt=i[\mathcal{F}(t),\mathcal{H}]$ it is clear that

$$P(t)=i\,\mathrm{Tr}\{\mathcal{R}(t)[\mathcal{F}(t),\mathcal{H}]\}\,. \tag{3.6}$$

For the system under consideration here this can be evaluated in terms of the one-particle operators. In the steady state the *mean* power absorbed from an external field of single frequency ω is then

$$P=P_1+P_2\,, \tag{3.7}$$

where

$$P_1=i\sum_\omega \mathrm{tr}\{\rho(\omega)[F(-\omega),H]\}\,, \tag{3.7a}$$

$$P_2=i\sum_\omega\sum_{\mu\nu q}\{\rho_{\mu\nu q}(\omega)+\rho_{\mu\nu-\bar{q}}(\omega)\}[F(-\omega),c(q)]_{\mu\nu}\,, \tag{3.7b}$$

$\sum_\omega$ indicating a sum over ω and $-\omega$ and $\rho_{\mu\nu q}$ being determined from (2.25).

We shall evaluate (3.7) using the perturbative solution (3.2) and (3.4), and thus obtain expressions for the direct and indirect power absorption.

From (3.2) and (3.7a) we get, after some rearrangement, for the direct power absorption

$$P^{(0)}=\sum_{\mu\nu} n_\mu(\omega_\nu-\omega_\mu)W_{\mu\nu}{}^{(0)}\,, \tag{3.8}$$

where

$$W_{\mu\nu}{}^{(0)}=W_{\mu\nu}{}^{(0)}(\omega)+W_{\mu\nu}{}^{(0)}(-\omega)\,, \tag{3.8a}$$

$$W_{\mu\nu}{}^{(0)}(\omega)=2\pi|F_{\mu\nu}(\omega)|^2\delta(\omega_{\mu\nu}+\omega)\,. \tag{3.8b}$$

Thus $W_{\mu\nu}{}^{(0)}$ has the physical significance of a direct transition probability rate from state $|\mu\rangle$ to $|\nu\rangle$ due to absorption ($W_{\mu\nu}{}^{(0)}(\omega)$) or emission ($W_{\mu\nu}{}^{(0)}(-\omega)$) of quanta of energy ω. Intuitively, the exclusion principle would have indicated the presence of the factor $(1-n_\nu)$ in (3.8). It is easy to see that indeed (3.8) can be written with this factor, since $W_{\mu\nu}{}^{(0)}=W_{\nu\mu}{}^{(0)}$. The direct power absorption can also be written as a balance between absorption and emission of quanta ω, i.e.,

$$P^{(0)}=\omega\sum_{\mu\nu} n_\mu(1-n_\nu)[W_{\mu\nu}{}^{(0)}(\omega)-W_{\mu\nu}{}^{(0)}(-\omega)]\,. \tag{3.9}$$

When this diverges the iterative solution of the kinetic equation is meaningless.

For the indirect power absorption we get, to begin with, from (3.4) and (3.7a)

$$P_1{}^{(2)}=\sum_\omega\sum_{\mu\nu}\frac{\omega_{\mu\nu}}{(\omega_{\mu\nu}+\omega)_p}D_{\mu\nu}(\omega)F_{\nu\mu}(-\omega)\,. \tag{3.10}$$

Clearly P_2 makes a contribution of the same order. The determination of $\rho_{\mu\nu q}(\omega)$ to the desired order in λ from (2.25) and (2.26) proceeds as in the previous section. The result when combined with (3.7b) is simply

$$P_2{}^{(2)}=-\sum_\omega\sum_{\mu\nu}D_{\mu\nu}(\omega)F_{\nu\mu}(-\omega)\,. \tag{3.11}$$

Thus, for the indirect power absorption we get

$$P^{(2)}=-\sum_{\omega}\sum_{\mu\nu}\left[\frac{\omega}{(\omega+\omega_{\mu\nu})_p}+\delta_{\omega,\omega_{\nu\mu}}\right]\times D_{\mu\nu}(\omega)F_{\nu\mu}(-\omega). \quad (3.12)$$

According to our previous discussion of $D_{\mu\nu}(\omega)$ for ω away from direct resonance, the second term in (3.12) can possibly make a contribution only for $\omega=0$. Using the expression (2.50) for $D_{\mu\nu}(\omega)$, rearranging terms here and there and making use of the nature of the equilibrium distribution functions n_μ and N_q, we can write for the indirect power absorption

$$P^{(2)}=P_\omega{}^{(2)}+\delta_{\omega,0}P_0{}^{(2)}. \quad (3.13)$$

$P_\omega{}^{(2)}$ is the power absorption for $\omega\neq 0$ and it is

$$P_\omega{}^{(2)}=\omega\sum_{\mu\nu}n_\mu(1-n_\nu)[W_{\mu\nu}{}^{(2)}(\omega)-W_{\mu\nu}{}^{(2)}(-\omega)] \quad (3.14)$$

with

$$W_{\mu\nu}{}^{(2)}(\omega)=2\pi\sum_q|M_{\mu\nu}(q\omega)|^2[N_q\delta(\omega_{\mu\nu}+\omega_q+\omega)+(N_q+1)\delta(\omega_{\mu\nu}-\omega_q+\omega)], \quad (3.14a)$$

where the matrix element is

$$M_{\mu\nu}(q\omega)=\sum_\kappa\left\{\frac{F_{\mu\kappa}(\omega)c_{\kappa\nu}(q)}{(\omega_{\mu\kappa}+\omega)_p}-\frac{c_{\mu\kappa}(q)F_{\kappa\nu}(\omega)}{(\omega_{\kappa\nu}+\omega)_p}\right\}. \quad (3.14b)$$

$P_\omega{}^{(2)}$ clearly represents the indirect power absorption due to electronic jumps from state $|\mu\rangle$ to $|\nu\rangle$ due to absorption (or emission) of quanta of energy ω with the simultaneous absorption or emission of phonons.[16] The $W_{\mu\nu}{}^{(2)}(\pm\omega)$ have the physical significance of transition probability rates for these processes, and they should be compared with $W_{\mu\nu}{}^{(0)}(\pm\omega)$. They are in agreement with the usual formulas of second-order time-dependent perturbation theory. $P_0{}^{(2)}$ is the power absorption for $\omega=0$, for the case where the iterative solution exists. From (3.12) and (2.50) we have

$$P_0{}^{(2)}=\beta\sum_{\mu\nu}n_\mu(1-n_\nu)\times\sum_q 2\pi\{N_q\delta(\omega_{\mu\nu}+\omega_q)+(N_q+1)\delta(\omega_{\mu\nu}-\omega_q)\}\times c_{\nu\mu}{}^\dagger(q)\{\bar{F}(0),[\bar{F}(0),c(q)]\}_{\nu\mu}, \quad (3.15)$$

where $\bar{F}(0)$ is given by (2.50b). In the particular case where the selection rules on $F_{\kappa\lambda}(0)$ are such that only the diagonal elements $F_{\lambda\lambda}(0)=F_{\lambda\lambda}$ are nonvanishing on the same energy shell, (3.15) assumes the simple form

$$P_0{}^{(2)}=\beta\sum_{\mu\nu}n_\mu(1-n_\nu)W_{\mu\nu}(F_{\mu\mu}-F_{\nu\nu})^2, \quad (3.16)$$

where

$$W_{\mu\nu}=2\pi\sum_q|c_{\mu\nu}(q)|^2[N_q\delta(\omega_{\mu\nu}+\omega_q)+(N_q+1)\delta(\omega_{\mu\nu}-\omega_q)] \quad (3.16a)$$

has the obvious physical significance of a transition probability rate from state $|\mu\rangle$ to $|\nu\rangle$ due to absorption or emission of phonons. In the following section we shall discuss such a system.

4. THE CASE OF A UNIFORM ELECTRIC FIELD IN SIMPLE SYSTEMS

In this section we make the first application of the equation for the one-electron density operator (2.46) to the case where the driving field is an oscillating, uniform electric field. We shall take it to be oscillating with a single frequency ω, and thus we may write

$$F(t)=-e\mathbf{E}\cdot\mathbf{r}\cos\omega t. \quad (4.1)$$

A number of physical situations of interest are encompassed in this case; e.g., the electromagnetic properties of semiconductors and some of the properties of metals can be studied on the basis of this model. In these cases the physical observable of interest is the induced current. The one-electron current operator is

$$\mathbf{J}=e\mathbf{v}=ei[H,\mathbf{r}], \quad (4.2)$$

since both the electron-phonon interaction and the driving disturbance (4.1) are taken to be independent of the momentum of the electron.

In most cases of interest it happens that only a subset of the matrix elements $\mathbf{J}_{\mu\nu}$ in a representation that diagonalizes H is different from zero. For the calculation of the macroscopic current it is then sufficient, according to (2.14), to know only a corresponding subset of the density matrix $\rho_{\mu\nu}$. It is then of interest to inquire whether and under what conditions it is possible to derive an equation for the desired subset of the density matrix from (2.46) for the whole matrix. We investigate this below considering three special cases of interest.

A. Free Electrons

For free electrons $H=\mathbf{p}^2/2m$, where $\mathbf{p}$ is the momentum operator. For basic one-electron representation we take running plane waves, $\langle\mathbf{r}|\mathbf{k}\rangle=\Omega^{-1/2}\times\exp(i\mathbf{k}\cdot\mathbf{r})$, with periodic boundary conditions, characterized by the wave vector $\mathbf{k}$ and energies $\omega_\mathbf{k}=\mathbf{k}^2/2m$. The current operator $\mathbf{J}=(e/m)\mathbf{p}$ is then diagonal in $\mathbf{k}$, and we are thus interested in the occupation probabilities $\rho_{kk}(\omega)\equiv f_k(\omega)$. (The vector character of $\mathbf{k}$ and $\mathbf{q}$ will not be denoted explicitly when used as subscripts.)

In finding an equation for $f_k(\omega)$ from (2.46), we note that the only term that could bring in other matrix elements of $\rho(\omega)$ is, obviously, the scattering term (2.45). Since the matrix elements of $c(q)$ in the running wave representation for the phonons are $c_{kk'}(q)\propto\delta_{k,q+k'}$,

[16] The contribution to $P_\omega{}^{(2)}$ of the terms of $B(\omega)$ and $\mathbb{S}(\omega)$ that were ignored is $\omega\sum_q 2\pi|\mathrm{tr}\{r(\omega)c(q)\}|^2\delta(\omega-\omega_q)$.

from (2.45a) it is clear that the quantities $w_{\mu\nu}{}^{\kappa\lambda}$, that enter the expression (2.45) for $(\mathcal{S}(\omega)\rho(\omega))_{kk}$, obey the selection rules

$$w_{kk}{}^{k'k''}=w_{kk}{}^{k'k'}\delta_{k'k''},\quad w_{k'k'}{}^{k''k}=w_{k'k'}{}^{kk}\delta_{k''k}. \tag{4.3}$$

Thus, the effect of the electron-phonon interaction alone on the rate of change of the steady-state occupation probability $f_k(\omega)$ is described solely in terms of all other occupation probabilities $f_{k'}(\omega)$. Explicitly, we find

$$(\mathcal{S}(\omega)\rho(\omega))_{kk}=\sum_{k'}[f_{k'}(\omega)w_{k'k}(\omega)-f_k(\omega)w_{kk'}(\omega)]\equiv\sum_{k'}S_{kk'}(\omega)f_{k'}(\omega), \tag{4.4}$$

where

$$w_{k'k}(\omega)=\pi\sum_q|c_{k'k}(q)|^2\{(N_q+1-n_k)[\delta(\omega_{kk'}+\omega_q+\omega)+\delta(\omega_{kk'}+\omega_q-\omega)]+(N_q+n_k)[\delta(\omega_{kk'}-\omega_q+\omega)+\delta(\omega_{kk'}-\omega_q-\omega)]\} \tag{4.4a}$$

plays the role of a transition probability rate from state $|\mathbf{k}'\rangle$ to $|\mathbf{k}\rangle$ due to absorption and emission of phonons with due consideration of the exclusion principle for the electrons.[17] In (4.4a) we have written only the terms that describe the relaxation effects of the electron-phonon interaction; the terms for the energy "shifts" can easily be obtained.

Of the remaining terms of (2.46) the homogeneous one is $[H,\rho(\omega)]_{kk}=0$. The inhomogeneous term that describes only the accelerating effect of the electric field is, according to (2.40),

$$iA_{kk}{}^{(0)}(\omega)=-\frac{ie}{2}\mathbf{E}\cdot[n(\mathbf{p}^2/2m),\mathbf{r}]_{kk}=-\frac{e}{2}\mathbf{E}\cdot\nabla_k n(\omega_k). \tag{4.5}$$

The use of (2.40) in evaluating $A_{kk}{}^{(0)}(\omega)$ for the driving interaction energy (4.1) in the plane-wave representation may be considered objectionable, since (2.40) was derived for the case of an F with regular matrix elements in the chosen representation. Although this is not true in the case under consideration here, it can be proved[18] independently that (4.5) is correct. The last term $B_{kk}(\omega)$, that describes the effect of the electric field on the scattering, can be proven[18] to be, in analogy to (2.49) and (2.50),

$$B_{kk}(\omega)=-\sum_{k'}S_{kk'}(\omega)\frac{ie}{2\omega}\mathbf{E}\cdot\nabla_{k'}n_{k'}+D_k(\omega), \tag{4.6}$$

where

$$D_k(\omega)=\frac{ie}{2m}\frac{e^{\beta\omega}-1}{\omega^2}\mathbf{E}\cdot\sum_{k'}(\mathbf{k}-\mathbf{k}')\times\{n_{k'}(1-n_k)u_{kk}{}^{k'k'}(\omega_{kk'}+\omega)+n_k(1-n_{k'})u_{kk}{}^{k'k'}(\omega_{k'k}+\omega)\}. \tag{4.6a}$$

Here again, only the singular part of $\theta(x)$ has been written down. For $\omega=0$ (4.6) can be proven to give $B_{kk}(0)=0$. Thus, the steady-state occupation probability $f_k(\omega)$ satisfies the kinetic equation

$$i\omega f_k(\omega)=\sum_{k'}S_{kk'}(\omega)\left\{f_{k'}(\omega)-\frac{ie}{2\omega}\mathbf{E}\cdot\nabla_{k'}n_{k'}\right\}-\frac{e}{2}\mathbf{E}\cdot\nabla_k n_k+D_k(\omega). \tag{4.7}$$

The summation over k' in (4.7) and (4.6a) can be carried out trivially due to the selection rule $c_{kk'}(q)\propto\delta_{k,k'+q}$.

For sufficiently high frequencies, i.e., for $\omega\tau_r\gg1$, where τ_r denotes the order of magnitude of the relaxation effects of the electron-phonon interaction, (4.7) has an iterative solution, namely,

$$f_k(\omega)=(ie\mathbf{E}\cdot\nabla_k n_k/2\omega)+(D_k(\omega)/i\omega). \tag{4.8}$$

The first term gives rise to the unperturbed polarization current, whereas the second yields the irreversible current oscillating in phase with the electric field. Using it to evaluate the mean rate of energy absorption from the electric field we find, corresponding to (3.14),

$$P_\omega{}^{(2)}=\omega\sum_{kk'}n_k(1-n_{k'})\times[W_{kk'}{}^{(2)}(\omega)-W_{kk'}{}^{(2)}(-\omega)], \tag{4.9}$$

where

$$W_{kk'}{}^{(2)}(\omega)=\left(\frac{e}{m}\right)^2\frac{[\mathbf{E}\cdot(\mathbf{k}-\mathbf{k}')]^2}{\omega^4}u_{kk}{}^{k'k'}(\omega_{k'k}-\omega). \tag{4.9a}$$

For lower frequencies, i.e., for $\omega\tau_r\lesssim1$, these expressions are not applicable and a better solution of (4.7) is required. It is easy to see that (4.9a) is identical to (3.15a) for $F(\omega)=-(e/mc)\mathbf{A}(\omega)\cdot\mathbf{p}=(-ie/2m\omega)\mathbf{E}\cdot\mathbf{p}$. This is just the description of the interaction Hamiltonian in a different gauge for the electric field. Since it has well-defined matrix elements, the formulas of the previous section are directly applicable.

The form of the scattering operator (4.4), and in general the kinetic equation (4.7), for the case $\omega=0$ was established independently by Lang[7] and the author.[8] Apart from the narrowness of scope of these works,

[17] Since we have restricted ourselves from the start to the response linear in the external field, the exclusion factors are not given here in their usual form (Ref. 8). It can easily be verified, however, that for $\omega=0$ (4.4a) is just the linear in the electric field part of the usual (Ref. 8) scattering operator.

[18] The method of proof consists in arranging first the operator $\mathbf{r}$ in a commutator with some function of H, and then taking matrix elements. This gives well-defined results since $[\mathbf{r},f(H)]_{kk'}$ are regular. (See Refs. 1 and 8.) The calculation of (4.6) is somewhat lengthy and will not be given here. An alternative way to obtain these results is to consider an inhomogeneous electric field and find the limit as the wavelength goes to infinity (see Sec. 5A).

however, additional assumptions were made which are avoided in the present treatment. The case of an oscillating electric field has been treated by Gurzhi[5] and more recently (after this work was finished) by Yamada.[14] They have derived kinetic equations identical to (4.7) by entirely different methods, special to the case of free electrons. The expression (4.9) for the indirect power absorption was first arrived at, and its importance for the understanding of the volume absorptivity of metals at low temperatures was emphasized, in the well-known work of Holstein[19] by use of second-order time-dependent perturbation theory and an intuitive introduction of the exclusion principle.

B. Electrons in a Magnetic Field

For electrons in a uniform magnetic field $\mathbf{B}$ in the z direction, the Hamiltonian can be taken to be $H=(1/2m)(\mathbf{p}-e\mathbf{A}_0/c)^2$, where $\mathbf{A}_0=(0,Bx,0)$ is the vector potential. Its eigenfunctions can be characterized by the quantum number $l=0, 1, 2, \cdots$, and the two-dimensional wave vector $\mathbf{k}(k_y,k_z)$, namely,

$$\langle \mathbf{r}|l\mathbf{k}\rangle=\phi_l(x-X_k)\exp(ik_y y+ik_z z), \qquad (4.10)$$

where ϕ_l are the harmonic oscillator eigenfunctions and $X_k=-k_y/m\omega_0$ with $\omega_0=|e|B/mc=$ cyclotron frequency. The energy eigenvalues are $\omega_{lk}=(l+\frac{1}{2})\omega_0+k_z^2/2m$. The current operator $\mathbf{J}=(e/m)(\mathbf{p}-e\mathbf{A}_0/c)$ is then diagonal in $\mathbf{k}$; in particular, the transverse components $J_{x,y}$ obey the selection rule $\langle l'\mathbf{k}'|J_{x,y}|l\mathbf{k}\rangle\propto\delta_{l',l\pm1}\delta_{k'k}$, whereas the longitudinal one is totally diagonal, i.e., $\langle l'\mathbf{k}'|J_z|l\mathbf{k}\rangle\propto\delta_{l'l}\delta_{k'k}$. We are thus interested in the subset of density matrix elements diagonal in $\mathbf{k}$.

As in the case of free electrons, it is easily seen that this subset satisfies a kinetic equation, i.e., the scattering operator (2.45) couples matrix elements only of the same subset. This is again a consequence of the selection rule for the electron-phonon interaction in this representation, $c_{lk,l'k'}(q)\propto\delta_{k,q+k'}$. In fact, in many cases stricter selection rules exist for the w's, (2.45a). For example, in Appendix A of Ref. 4 it was proved that for a large class of $c(q)$, $w_{ll'}{}^{mm'}=0$ unless $m-m'=l-l'$. This enables one to find kinetic equations for even "smaller" subsets of the density matrix. In particular, for a longitudinal geometry, i.e., $\mathbf{E}\|\mathbf{B}$, the subset consists merely of the occupation probabilities $\rho_{lk,lk}(\omega)\equiv f_{lk}(\omega)$, which is sufficient for the evaluation of $\langle \mathcal{J}_z\rangle$. For a transverse geometry, i.e., $\mathbf{E}\perp\mathbf{B}$, the subset consists of $\rho_{lk,l'k}(\omega)$ with $l'=l\pm1$, which again is sufficient for the determination of $\langle \mathcal{J}_{x,y}\rangle$. More generally, however, we can derive from the kinetic equation (2.46) for the density matrix $\rho_{\mu\nu}(\omega)$ an equation for the desired subset by eliminating the undesired subset, as in the case of elastic scattering.[4] We shall only state below the final results.

For the case of a longitudinal electric field $\mathbf{E}=(0,0,E_z)$, the kinetic equation for $f_{lk}(\omega)$ is entirely analogous to that of free electrons, on account of the selection rule $z_{lk,l'k'}\propto\delta_{ll'}\delta_{kk'}$. Thus, all equations from (4.4) to (4.9) are valid in this case, if we replace $\mathbf{k}$ by $(l\mathbf{k})$, $\mathbf{k}'$ by $(l'\mathbf{k}')$ and $\mathbf{E}\cdot\mathbf{k}$ by $E_z k_z$.

For a transverse geometry we may take $\mathbf{E}=(E_x,0,0)$. Denoting the desired subset by

$$f_{\mu\nu}(\omega)=\rho_{\mu\nu}(\omega)(\delta_{l',l+1}+\delta_{l',l-1})\delta_{k'k}, \qquad (4.11)$$

where $\mu=(l\mathbf{k})$, $\nu=(l'\mathbf{k}')$, we find for $l'=l\pm1$ (dropping the common $\mathbf{k}$)

$$0=-i(\omega+\omega_{ll'})f_{ll'}(\omega)+(\mathcal{S}(\omega)[f(\omega)-r(\omega)])_{ll'}+iA_{ll'}{}^{(0)}(\omega)+D_{ll'}(\omega), \qquad (4.12)$$

on account of the selection rule $x_{\mu\nu}\propto\delta_{l',l\pm1}\delta_{kk'}$. The matrix elements of $F(\omega)=(-e/2)E_x x$ are now regular in the representation $|l\mathbf{k}\rangle$ and thus all formulas of Sec. 2 are directly applicable. Thus, (2.40) gives in this case

$$A_{ll'}{}^{(0)}(\omega)=(-e/2)E_x(2m\omega_0)^{-1/2}(n_l-n_{l'})\times[(l+1)^{1/2}\delta_{l',l+1}+l^{1/2}\delta_{l',l-1}]. \qquad (4.12a)$$

We note that it is independent of k_y, the quantum number that determines the center of localization of the wave function $\langle \mathbf{r}|l\mathbf{k}\rangle$ in the x direction. This is also true of the other inhomogeneous terms of (4.12). This raises the possibility of a solution $f_{lk,l'k}$ of (4.12) that is independent of k_y, i.e., representing a spatially uniform distribution of electrons, which is the solution of interest for the calculation of the usual conductivity. This is indeed possible, since, with the ansatz of a k_y-independent $f(\omega)$, it is easily proved from the structure of $\mathcal{S}(\omega)$ and $\langle \mathbf{r}|l\mathbf{k}\rangle$ that

$$(\mathcal{S}(\omega)f(\omega))_{ll'}=\sum_{\kappa\lambda}\{f_{\kappa\lambda}(\omega)[w_{ll'}{}^{\kappa\lambda}(\omega_{l\lambda}+\omega)+w_{l'l}{}^{\lambda\kappa*}(\omega_{l'\kappa}-\omega)]-f_{l\kappa}(\omega)w_{\lambda\lambda}{}^{\kappa l'*}(\omega_{\lambda l}-\omega)-f_{\lambda l'}(\omega)w_{kk}{}^{\lambda l}(\omega_{kl'}+\omega)\} \qquad (4.12b)$$

is also independent of k_y. $D_{ll'}(\omega)$ is given by (2.50) and $r(\omega)$ can be obtained from (2.49a) and (4.12a), and both are independent of k_y.

For the special case of $\omega=0$ a kinetic equation for the one-electron density matrix has been derived before by Gurevich and Nedlin[12] and Horing and the author[13] by different methods. The equation of Gurevich *et al.* is in complete agreement with (4.12) for $\omega=0$, whereas that of Horing *et al.* differs slightly in the structure of the scattering operator; the difference stems from the fact that in the latter work the Markoffian approximation (see Appendix B) was made. Equation (4.12) is valid for arbitrary frequencies ω and thus it gives a quantum-mechanical description for the well-known phenomena of cyclotron resonance, Faraday rotation, etc., of conduction electrons in semiconductors, in the temperature region where scattering by phonons is the dominant mechanism.

[19] T. D. Holstein, Phys. Rev. **96**, 535 (1954).

For frequencies ω sufficiently away from the cyclotron frequency ω_0 a perturbative solution of (4.12) exists, and it is given by (3.2) and (3.4). From (3.2) it is easy to obtain the steady-state unperturbed "reversible" current. The irreversible current due to collisions can be calculated from (3.4), or directly from the indirect power absorption given by (3.13). For $\omega\neq 0$, this is determined from 3.14. For $\omega=0$ it is easily checked that the selection rules for $F_{\kappa\lambda}(0)$ are such that the simple expression (3.16) is applicable, in accordance with other works[4,20,21] for this particular case.

C. Electrons in a Periodic Potential

For electrons in crystalline solids the one-electron Hamiltonian is $H=(\mathbf{p}^2/2m)+V(\mathbf{r})$, where $V(\mathbf{r})$ is a periodic potential with the periodicity of the crystal. Its eigenfunctions can be written in the well-known Bloch form

$$\langle \mathbf{r}\,|\,s\mathbf{k}\rangle = u_{s\mathbf{k}}(\mathbf{r})\exp(i\mathbf{k}\cdot\mathbf{r}), \tag{4.13}$$

where s is the band index, $\mathbf{k}$ the wave vector restricted in the first Brillouin zone, and $u(\mathbf{r})$ has the periodicity of the lattice; its eigenvalues are denoted by ω_{sk}. The current operator $\mathbf{J}=(e/m)\mathbf{p}$ is again diagonal in $\mathbf{k}$, although it has in general both intraband and interband matrix elements. We are thus interested in the subset

$$f_{\mu\nu}(\omega)=\rho_{sk,s'k}(\omega)\delta_{k'k}, \tag{4.14}$$

where $\mu=(s\mathbf{k})$, $\nu=(s'\mathbf{k}')$.

As in the previous two cases, this subset satisfies a kinetic equation. The scattering operator (2.45) couples matrix elements only of the same subset, since for a quite general electron-phonon interaction we have[22] $c_{sk,s'k'}(q)\propto\delta_{k,k'+q+K}$, where $\mathbf{K}$ is a vector of the reciprocal lattice. This is a consequence of the lattice periodicity. Since $\mathbf{k}$, $\mathbf{k}'$, and $\mathbf{q}$ are all restricted in the first Brillouin zone, there is only one $\mathbf{K}$ which satisfies the selection rule. This in turn guarantees that the w's of (2.45a) combine matrix elements only of the subset $f_{\mu\nu}(\omega)$. Thus, $f_{ss'}(\omega)$ (dropping the common $\mathbf{k}$) satisfies the kinetic equation

$$0=-i(\omega+\omega_{ss'})f_{ss'}(\omega)+(\mathcal{S}(\omega)[f(\omega)-r(\omega)])_{ss'}+iA_{ss'}{}^{(0)}(\omega)+D_{ss'}(\omega), \tag{4.15}$$

where

$$(\mathcal{S}(\omega)f(\omega))_{ss'}=\sum_{\kappa\lambda}\{f_{\kappa\lambda}(\omega)[w_{ss'}{}^{\kappa\lambda}(\omega_{s\lambda}+\omega)+w_{s's}{}^{\lambda\kappa*}(\omega_{s'\kappa}-\omega)]-f_{s\kappa}(\omega)w_{\lambda\lambda}{}^{\kappa s'*}(\omega_{\lambda s}-\omega)-f_{\lambda s'}(\omega)w_{\kappa\kappa}{}^{\lambda s}(\omega_{\kappa s'}+\omega)\}. \tag{4.15a}$$

From (2.40) and the well-known relationship between matrix elements of position and conjugate momentum operators we get

$$iA_{ss}{}^{(0)}(\omega)=(-e/2m)\mathbf{E}\cdot\mathbf{p}_{ss'}(n_s-n_{s'}/\omega_s-\omega_{s'}), \tag{4.15b}$$

where $\mathbf{p}_{ss'}=\langle s\mathbf{k}\,|\,\mathbf{p}\,|\,s'\mathbf{k}\rangle$. For the intraband matrix elements, i.e., $s'=s$, it can be proved that (4.15b) holds if it is understood that the ratio $n_s-n_{s'}/\omega_s-\omega_{s'}$ assumes its limiting value as the denominator approaches zero smoothly, i.e., it becomes $n_s'\equiv dn(\omega_{sk})/d\omega_{sk}$. The operator $r(\omega)$ is given by (2.49a) and (4.15b). The operator $D(\omega)$ is more complicated in this case. The complication arises from the fact that while the interband matrix elements $F_{ss'}(\omega)(s'\neq s)$ are regular, the intraband elements $F_{ss}(\omega)$ are irregular and should be treated as in the case of plane waves. Denoting their respective contributions to $D(\omega)$ by $D^{(r)}(\omega)$ and $D^{(i)}(\omega)$, we have $D=D^{(r)}+D^{(i)}$, where $D_{ss'}{}^{(r)}(\omega)$ is given by (2.50) with the understanding that only the interband elements $F_{rr'}(\omega)(r'\neq r)$ are to be summed over in (2.50). It is worth noting that in this case the last term that is proportional to β contributes nothing. By a calculation analogous to that in the case of plane waves, $D_{ss'}{}^{(i)}(\omega)$ is found to be, since $[n(H),\mathbf{r}]_{ss}=(1/im)\mathbf{p}_{ss}n_s'$,

$$D_{ss'}{}^{(i)}(\omega)=\frac{ie}{2m}\frac{e^{\beta\omega}-1}{\omega^2}\mathbf{E}\cdot\sum_{\kappa}[(\mathbf{p}_{ss}-\mathbf{p}_{\kappa\kappa})n_\kappa(1-n_s)u_{ss'}{}^{\kappa\kappa}(\omega_{s\kappa}+\omega)+(\mathbf{p}_{s's'}-\mathbf{p}_{\kappa\kappa})n_{s'}(1-n_\kappa)u_{ss'}{}^{\kappa\kappa}(\omega_{\kappa s'}+\omega)]. \tag{4.16}$$

All these expressions are valid for arbitrary ω. For $\omega=0$ we note that all expressions are regular except for $\mathcal{S}(0)r^{(i)}(0)$ and $D^{(i)}(0)$, which, however, when combined give $B^{(i)}(0)=-\mathcal{S}(0)r^{(i)}(0)+D^{(i)}(0)$ a well-defined value. It is worth noting that for the diagonal elements we have $B_{ss}{}^{(i)}(0)=0$, as in the case of plane waves. For this case of a static electric field, one may further reduce the subset $f_{ss'}(0)$ by considering only the occupation probabilities $f_{ss}(0)$. A kinetic equation for $f_{ss}(0)$ can now be found from (4.15), as in the work of Kohn and Luttinger,[1] by expressing the interband elements $f_{ss'}(s'\neq s)$ in terms of the diagonal ones. One thus finds, again in the second order for the electron-phonon interaction, the transport equation

$$0=\sum_{\kappa}[f_{\kappa\kappa}(0)W_{\kappa s}-f_{ss}(0)W_{s\kappa}]-\frac{e}{2}\mathbf{E}\cdot\nabla_{\mathbf{k}}n(\omega_{s\mathbf{k}}), \tag{4.17}$$

where $W_{\kappa s}\equiv 2w_{ss}{}^{\kappa\kappa}(\omega_{s\kappa})$ is the commonly conjectured[23] transition probability rate. The factor $\frac{1}{2}$ in (4.17) is due to the fact that, according to our definitions, the steady-state density matrix for this case is $f^{(s)}=f(\omega=0)+f(-\omega=0)=2f(0)$. Finally, it should be borne in mind that the elimination of the interband matrix

[20] R. Kubo, H. Hasegawa, and N. Hashitsume, J. Phys. Soc. Japan **14**, 56 (1959).
[21] P. N. Argyres and L. M. Roth, J. Phys. Chem. Solids **12**, 89 (1959).
[22] See, for example, R. E. Peierls, *Quantum Theory of Solids* (Clarendon Press, Oxford, 1956), p. 126.
[23] See, for example, E. H. Wilson, *Theory of Metals* (Cambridge University Press Cambridge, 1953).

elements from the kinetic equation brings in additional restrictions about the "smallness" of the electron-phonon interaction.

In the absence of electron-phonon interaction and for $\omega\neq 0$ the direct power absorption is, according to (3.9),

$$P^{(0)}=4\pi\omega\sum_{s\neq s'}\sum_{\mathbf{k}} n_s|F_{ss'}(\omega)|^2 \times[\delta(\omega_{ss'}+\omega)-\delta(\omega_{ss'}-\omega)], \quad (4.18)$$

which clearly converges. (The extra factor 2 is for the spin.) It should be observed that in (4.18) we could use the vector potential gauge, i.e., $F(\omega)=(-ie/2m\omega)\mathbf{E}\cdot\mathbf{p}$. In fact, for the power absorption due to indirect transitions it is expedient to use this gauge, since then $F(\omega)$ has regular intraband and interband matrix elements and thus the expressions of the previous section are directly applicable. Thus, the indirect power absorption, either intraband or interband, is given by (3.14).

5. EQUATION FOR THE LOCAL DENSITY OPERATOR AND APPLICATIONS

In many instances we require the expectation value of the density of an electronic observable at the point $\mathbf{x}$. For observables of the form $\mathcal{J}=\sum_i J_i$ we have for their densities at $\mathbf{x}$

$$\mathcal{J}(\mathbf{x})=\tfrac{1}{2}\sum_i\{J_i\delta(\mathbf{x}-\mathbf{x}_i)+\delta(\mathbf{x}-\mathbf{r}_i)J_i\} =\tfrac{1}{2}\sum_{\mu\nu}\langle\mu|J\delta(\mathbf{x}-\mathbf{r})+\delta(\mathbf{x}-\mathbf{r})J|\nu\rangle a_\mu^\dagger a_\nu, \quad (5.1)$$

where $\mathbf{r}$ is the position *operator* and $\mathbf{x}$ is a c number. [In (5.1) we restrict our attention to operators J that are linear functions of the momentum operator $\mathbf{p}$ plus arbitrary functions of $\mathbf{r}$. The current operator is of this type. For arbitrary one-electron operators J, we need a more general "symmetrization" procedure than that indicated in (5.1).] The expectation value of $\mathcal{J}(\mathbf{x})$ can be expressed as

$$j(\mathbf{x}t)\equiv\mathrm{Tr}\{\mathcal{J}(\mathbf{x})\mathcal{R}_T(t)\}=\mathrm{tr}\{J\rho_T(\mathbf{x}t)\}, \quad (5.2)$$

where

$$\rho_T(\mathbf{x}t)\equiv\tfrac{1}{2}\{\rho_T(t)\delta(\mathbf{x}-\mathbf{r})+\delta(\mathbf{x}-\mathbf{r})\rho_T(t)\}, \quad (5.3)$$

this is, the symmetrized product of $\rho_T(t)$ and the projection operator $\delta(\mathbf{x}-\mathbf{r})=|\mathbf{x}\rangle\langle\mathbf{x}|$ at the point $\mathbf{x}$. We note that $\rho_T(\mathbf{x},t)$ is a Hermitian operator. Although it does not have all the properties of a density operator, e.g., its eigenvalues are not non-negative, we shall refer to it as a *local* one-electron density operator, because of its property (5.2). For the linear response we are interested in $\rho(\mathbf{x}t)=\rho_T(\mathbf{x}t)-\rho_0(\mathbf{x})$, where $\rho(\mathbf{x}t)$ and $\rho_0(\mathbf{x})$ are defined by (5.3) with $\rho(t)$ and ρ_0 replacing $\rho_T(t)$.

It is of interest to inquire whether we can find a kinetic equation for $\rho(\mathbf{x}t)$. It is more convenient to work with its Fourier components. Thus, for the *steady state* we write

$$\rho(\mathbf{x}t)=\Omega^{-1}\sum_{\sigma}\sum_{\omega}\exp[-i(\boldsymbol{\sigma}\cdot\mathbf{x}-\omega t)]\rho(\boldsymbol{\sigma}\omega), \quad (5.4)$$

where

$$\rho(\boldsymbol{\sigma}\omega)=\tfrac{1}{2}\{R(\boldsymbol{\sigma}\omega)+R^\dagger(-\boldsymbol{\sigma}-\omega)\} \quad (5.4a)$$

and

$$R(\boldsymbol{\sigma}\omega)=\rho(\omega)\exp(i\boldsymbol{\sigma}\cdot\mathbf{r})\equiv\rho(\omega)\epsilon(\boldsymbol{\sigma}). \quad (5.5)$$

A kinetic equation for $R(\boldsymbol{\sigma}\omega)$ is obtained from the corresponding one for $\rho(\omega)$, Eq. (2.46), by operating on it with $\epsilon(\boldsymbol{\sigma})$ from the left. The abstract expressions (2.47) and (2.48) for $B(\omega)$ and $\mathcal{S}(\omega)\rho(\omega)$ are most convenient for this operation. In commuting $\epsilon(\boldsymbol{\sigma})$ with the various operators, we only need to notice that it commutes with any function of the position operator $\mathbf{r}$, whereas for the momentum operator $\mathbf{p}$ we have $\mathbf{p}\epsilon(\boldsymbol{\sigma})=\epsilon(\boldsymbol{\sigma})(\mathbf{p}+\boldsymbol{\sigma})$. Thus, for any operator, say $H=H(\mathbf{p},\mathbf{r})$, we have

$$H\epsilon(\boldsymbol{\sigma})=\epsilon(\boldsymbol{\sigma})H(\mathbf{p}+\boldsymbol{\sigma},\mathbf{r})\equiv\epsilon(\boldsymbol{\sigma})H_\sigma. \quad (5.6)$$

In general, the self-consistent electron-phonon interaction operator $c(q)$ could depend on the momentum $\mathbf{p}$. Although there is no basic difficulty with this general case, we shall restrict ourselves for economy to the usually adopted approximation of a $c(q)$ independent of $\mathbf{p}$. It is then clear that the kinetic equation for $R(\boldsymbol{\sigma}\omega)$ is

$$i\omega R(\boldsymbol{\sigma}\omega)=-i\{HR(\boldsymbol{\sigma}\omega)-R(\boldsymbol{\sigma}\omega)H_\sigma\}+\mathcal{S}(\boldsymbol{\sigma}\omega)R(\boldsymbol{\sigma}\omega) +i\{n(H)F(\boldsymbol{\sigma}\omega)-F(\boldsymbol{\sigma}\omega)n(H_\sigma)\}+B(\boldsymbol{\sigma}\omega), \quad (5.7)$$

where H_σ is defined by (5.6) and

$$\mathcal{S}(\boldsymbol{\sigma}\omega)R(\boldsymbol{\sigma}\omega) =\sum_q\Big[c(q),\int_0^\infty d\tau e^{-i\omega\tau}e^{-iH\tau}\{R(\boldsymbol{\sigma}\omega)c^\dagger(q)g_q^\dagger(H_\sigma,\tau) -g_q(H,\tau)c^\dagger(q)R(\boldsymbol{\sigma}\omega)\}e^{iH_\sigma\tau}\Big], \quad (5.7a)$$

$$B(\boldsymbol{\sigma}\omega)=\sum_q\int_0^\infty d\tau e^{-i\omega\tau} \times\int_0^\beta dz\{N_q e^{-\omega_q(i\tau-z)}+(N_q+1)e^{\omega_q(i\tau-z)}\} \times[c(q),e^{-iH\tau}\{F(\boldsymbol{\sigma}\omega)n(H_\sigma)e^{zH_\sigma}c^\dagger(q) \times e^{-zH_\sigma}(1-n(H_\sigma))-n(H)e^{zH}c^\dagger(q) \times e^{-zH}(1-n(H))F(\boldsymbol{\sigma}\omega)\}e^{iH_\sigma\tau}], \quad (5.7b)$$

$$F(\boldsymbol{\sigma}\omega)=F(\omega)\epsilon(\boldsymbol{\sigma}). \quad (5.7c)$$

In writing (5.7) we have ignored the term $A^{(2)}(\omega)\epsilon(\boldsymbol{\sigma})$. Note that no restriction on the magnitude of $\boldsymbol{\sigma}$ has been made above. Particular applications of this kinetic equation to simple cases will be made below.

A kinetic equation for the corresponding quantity

in the $\mathbf{x}$ space, namely $R(\mathbf{x},\omega)=\rho(\omega)\delta(\mathbf{x}-\mathbf{r})$, can be obtained either by taking the Fourier transform of (5.7), or directly from (2.46) with the observation that $H(\mathbf{p},\mathbf{r})\delta(\mathbf{x}-\mathbf{r})=\delta(\mathbf{x}-\mathbf{r})H(\mathbf{p}+i\nabla_x,\mathbf{r})$, ∇_x operating to its left. Similarly, an equation can be obtained for $\rho(\mathbf{x}t)$.

It is of importance to prove that the approximations made in deriving the kinetic equation (5.7) have not destroyed the principle of the local conservation of electrons. This states that for the Fourier components we must have

$$\omega n(\sigma\omega)=\sigma\cdot\mathbf{i}(\sigma\omega), \tag{5.8}$$

where $n(\sigma\omega)$ and $\mathbf{i}(\sigma\omega)$ are, respectively, the particle and particle-current densities. Considering only the parts linear in the external disturbance, we have from (5.2)

$$n(\sigma\omega)=\mathrm{tr}\{\rho(\sigma\omega)\}, \tag{5.9}$$

$$\mathbf{i}(\sigma\omega)=\mathrm{tr}\{\mathbf{v}_0\rho(\sigma\omega)+\mathbf{v}_1(\omega)\rho_0(\sigma)\}, \tag{5.10}$$

where $\mathbf{v}_0+\mathbf{v}_1(\omega)=i[H+F(\omega),\mathbf{r}]$ is the velocity operator. Now (5.8) is proved to follow from the kinetic equation (5.7) for $R(\sigma\omega)$ and the corresponding one for $R^\dagger(-\sigma-\omega)$ by simply taking the trace of their average. From the structure of $\$(\sigma\omega)R(\sigma\omega)$ and $B(\sigma\omega)$ as commutators, it is clear that these two terms contribute nothing to the trace. Thus, we may write, making use of the invariance property of the trace,

$$\omega n(\sigma\omega)=\mathrm{tr}\{\rho(\omega)[H,\epsilon(\sigma)]+\rho_0[F(\omega),\epsilon(\sigma)]\}. \tag{5.11}$$

For a general one-electron Hamiltonian of the form $H=(1/2m)[\mathbf{p}+\mathbf{A}_0(\mathbf{r})]^2+V(\mathbf{r})=(\frac{1}{2})m\mathbf{v}_0^2+V(\mathbf{r})$, we can easily see with the help of (5.6) that

$$[H,\epsilon(\sigma)]=\epsilon(\sigma)\{(1/2m)\sigma^2+\sigma\cdot\mathbf{v}_0\}$$
$$=\tfrac{1}{2}\{\epsilon(\sigma)\sigma\cdot\mathbf{v}_0+\sigma\cdot\mathbf{v}_0\epsilon(\sigma)\}.$$

Thus, the first term of (5.11) gives $\mathrm{tr}\{\rho(\sigma\omega)\sigma\cdot\mathbf{v}_0\}$. Similarly, for a general interaction of the form $F(\omega)=\mathbf{a}(\mathbf{r}\omega)\cdot\mathbf{p}+\phi(\mathbf{r})$, we find that the second term of (5.11) yields $\mathrm{tr}\{\rho_0(\sigma)\sigma\cdot\mathbf{v}_1(\omega)\}$. Substituting these two results in (5.11) we obtain a proof of (5.8). The restriction to an electron-phonon interaction independent of the momentum of the electron was made only for simplicity. The general case is more involved.

In the following we shall apply the kinetic equation (5.7) to some simple systems of interest. We take the external disturbance to be a general electromagnetic field with potentials $\mathbf{A}(\mathbf{r}t)$ and $\Phi(\mathbf{r}t)$, so that

$$F(t)=(-1/2c)\{\mathbf{J}\cdot\mathbf{A}(\mathbf{r}t)+\mathbf{A}(\mathbf{r}t)\cdot\mathbf{J}\}+e\Phi(\mathbf{r}t), \tag{5.12}$$

where $\mathbf{J}=ei[H,\mathbf{r}]$. A physical observable of interest is then the induced current density, since this constitutive equation in conjunction with Maxwell's equations determines the electromagnetic properties of the system. The one-electron current operator is

$$\mathbf{J}_T=\mathbf{J}+\mathbf{J}_1=ei\left\{[H,\mathbf{r}]+\frac{ei}{mc}\mathbf{A}\right\}. \tag{5.13}$$

The second term $\mathbf{J}_1$ gives rise to part of the polarization current density $\mathbf{j}_1(\mathbf{x}t)=(-e^2/mc)\mathbf{A}(\mathbf{x}t)n_0(\mathbf{x})$, where $n_0(\mathbf{x})=\mathrm{tr}\{\rho_0\delta(\mathbf{x}-\mathbf{r})\}$ is the equilibrium electron density. We shall concern ourselves from here on with the evaluation of the more interesting part of the current density $\mathbf{j}(\mathbf{x}t)=\mathrm{tr}\{\mathbf{J}\rho(\mathbf{x}t)\}$. As in the previous section, we shall seek kinetic equations for the subset of the local density matrix sufficient for the evaluation of the current density $\mathbf{j}(\mathbf{x}t)$ in a convenient representation for some simple systems.

A. Free Electrons

For free electrons $\mathbf{J}=(e/m)\mathbf{p}$ and thus the macroscopic current density, when evaluated in the representation of plane waves $|\mathbf{k}\rangle$, is

$$\mathbf{j}(\sigma\omega)=(2e/m)\textstyle\sum_k(\mathbf{k}+\frac{1}{2}\sigma)f_k(\sigma\omega), \tag{5.14}$$

where $f_k(\sigma\omega)\equiv\langle\mathbf{k}|R(\sigma\omega)|\mathbf{k}\rangle$ plays the role of a "distribution function." The extra factor of 2 is due to the spin and the second term arises from expressing the contribution of $R_{kk}^\dagger(-\sigma-\omega)$ in terms $f_k(\sigma\omega)$.

A kinetic equation for $f_k(\sigma\omega)$ is obtained from (5.7) by simply considering its diagonal matrix elements in the $|\mathbf{k}\rangle$-representation. It is important to note that in this case $H_\sigma=(\mathbf{p}+\sigma)^2/2m$ and thus the plane-wave-state vector $|\mathbf{k}\rangle$ is an eigenvector not only of H, $H|\mathbf{k}\rangle=\omega_k|\mathbf{k}\rangle$, but also of H_σ, i.e., $H_\sigma|\mathbf{k}\rangle=\omega_{k+\sigma}|\mathbf{k}\rangle$. It is then clear that the first two homogeneous terms of (5.7) for $i\omega f_k(\sigma\omega)$ are simply $(-i)(\omega_k-\omega_{k+\sigma})f_k(\sigma\omega)$. For the same reason, the scattering term $\langle\mathbf{k}|\$(\sigma\omega)\times R(\sigma\omega)|\mathbf{k}\rangle$, as given by (5.7a), can be expressed in terms of $f_{k'}(\sigma\omega)$, because, as in the previous section, $c_{kk'}^\dagger(q)c_{k''k}(q)\propto\delta_{k'k''}$. Thus we find

$$(\$(\sigma\omega)R(\sigma\omega))_{kk}$$
$$=\sum_{\mathbf{k}'}\{f_{k'}(\sigma\omega)w_{k'k}(\sigma\omega)-f_k(\sigma\omega)w_{kk'}(\sigma\omega)\}$$
$$\equiv\sum_{k'}S_{kk'}(\sigma\omega)f_{k'}(\sigma\omega), \tag{5.15}$$

where

$$w_{k'k}(\sigma\omega)$$
$$=\sum_q|c_{k'k}(q)|^2[(N_q+1-n_{k+\sigma})\theta(\omega_{k',k+\sigma}-\omega_q+\omega)$$
$$+(N_q+n_{k+\sigma})\theta(\omega_{k',k+\sigma}+\omega_q+\omega)$$
$$+(N_q+1-n_k)\theta(\omega_{k,k'+\sigma}+\omega_q+\omega)$$
$$+(N_q+n_k)\theta(\omega_{k,k'+\sigma}-\omega_q+\omega)]. \tag{5.15a}$$

[Actually the summation over $\mathbf{k}'$ in (5.15) can be carried out trivially if we make use of the selection rule $c_{k'k}(q)\propto\delta_{k',k+q}$; we shall not, however, indicate this explicitly.] Similarly, the inhomogeneous terms of (5.7) can be expressed in terms of the matrix elements $\langle\mathbf{k}|F(\sigma\omega)|\mathbf{k}\rangle\equiv F_k(\sigma\omega)$, which from (5.7c) and (5.12)

are found to be

$$F_k(\sigma\omega)=(-e/\Omega)\{(1/mc)(\mathbf{k}+\tfrac{1}{2}\sigma)\cdot\mathbf{A}(\sigma\omega)-\Phi(\sigma\omega)\}, \quad (5.16)$$

where $\mathbf{A}(\sigma\omega)$, $\Phi(\sigma\omega)$ are the Fourier components of the external potentials. Thus the kinetic equation for $f_k(\sigma\omega)$ reads

$$0=-i(\omega+\omega_{k,k+\sigma})f_k(\sigma\omega)+\sum_{k'}S_{kk'}(\sigma\omega)\{f_{k'}(\sigma\omega)-f_{k'}{}^{(0)}(\sigma\omega)\}+i(n_k-n_{k+\sigma})F_k(\sigma\omega)+D_k(\sigma\omega). \quad (5.17)$$

As before, we have written

$$\langle\mathbf{k}|B(\sigma\omega)|\mathbf{k}\rangle=-\sum_{k'}S_{kk'}(\sigma\omega)f_{k'}{}^{(0)}(\sigma\omega)+D_k(\sigma\omega),$$

where

$$f_k{}^{(0)}(\sigma\omega)=F_k(\sigma\omega)(n_k-n_{k+\sigma})/(\omega+\omega_{k,k+\sigma}) \quad (5.17a)$$

$$D_k(\sigma\omega)=(e^{\beta\omega}-1)\sum_{k'}\left\{\frac{F_{k'}(\sigma\omega)}{\omega+\omega_{k',k'+\sigma}}-\frac{F_k(\sigma\omega)}{\omega+\omega_{k,k+\sigma}}\right\}\times\{u_{kk'}(\sigma\omega)+u_{k'k}(\sigma\omega)\}, \quad (5.17b)$$

with

$$u_{kk'}(\sigma\omega)=n_{k+\sigma}(1-n_{k'})\pi\sum_q|c_{kk'}(q)|^2[N_q\delta(\omega_{k',k+\sigma}-\omega_q+\omega)+(N_q+1)\delta(\omega_{k',k+\sigma}+\omega_q+\omega)]. \quad (5.17c)$$

In (5.17b) we have exhibited only the terms that come from the singular part of $\theta(x)$. An equation similar to (5.17) has been derived by Yamada.[14]

A kinetic equation for the semiclassical distribution function $f(\mathbf{k},\mathbf{x},t)$ is obtained from (5.17) by expanding the coefficients of $f_k(\sigma\omega)$ and $F_k(\sigma\omega)$ in powers of σ, keeping the leading terms and then taking Fourier transforms. The second term of (5.17) yields then the usual "drift" term $\mathbf{v}\cdot\nabla_x f$. Such a kinetic equation is thus correct for disturbances of long wavelength, namely $\sigma\ll k$, where $\mathbf{k}$ is the wave vector of the electrons of importance in the evaluation of the current density.

In the limit $\sigma\to 0$, one recovers the results of Sec. 4A.

B. Electrons in a Magnetic Field

For electrons in a uniform magnetic field $\mathbf{B}$ in the z direction, it is convenient to use the vector potential $\mathbf{A}_0=(0,Bx,0)$, where now the x axis is taken to be, without loss of generality, perpendicular to the plane of $\mathbf{B}$ and the wave vector σ. Thus σ lies in the same plane as the $\mathbf{k}$ of the $|l\mathbf{k}\rangle$ representation. For the calculation of the current density in this representation, it is sufficient to consider, according to the discussion in the previous section, the reduced local density matrix

$$f_{\mu\nu}(\sigma\omega)=R_{\mu\nu}(\sigma\omega)\delta_{kk'}, \quad (5.18)$$

where $\mu=(l\mathbf{k})$ and $\nu=(l'\mathbf{k}')$.

A kinetic equation for $f_{ll'}(\sigma\omega)$ (dropping the common $\mathbf{k}$) is easily obtained from (5.7), if it is noticed that, on account of the arrangement of the coordinate axes, $H_\sigma|\mu\rangle=H_\sigma|l\mathbf{k}\rangle=\omega_{l,k+\sigma}|l\mathbf{k}\rangle\equiv\omega_{\mu+\sigma}|\mu\rangle$, where the last equality defines $\omega_{\mu+\sigma}$. This, along with the selection rule $c_{kk'}{}^\dagger(q)c_{k''k}(q)\propto\delta_{k'k''}$ (the integral quantum numbers are not indicated here) gives

$$0=-i(\omega+\omega_{l,l'+\sigma})f_{ll'}(\sigma\omega)+(\mathcal{S}(\sigma\omega)f(\sigma\omega))_{ll'}+i(n_l-n_{l'+\sigma})F_{ll'}(\sigma\omega)+B_{ll'}(\sigma\omega). \quad (5.19)$$

Here

$$(\mathcal{S}(\sigma\omega)f(\sigma\omega))_{ll'}=\sum_{\kappa\lambda}\{f_{\kappa\lambda}(\sigma\omega)[w_{ll'}{}^{\kappa\lambda}(\omega_{l,\lambda+\sigma}+\omega)+w_{l'l}{}^{\lambda\kappa*}(\sigma,\omega_{l'+\sigma,\kappa}-\omega)]-f_{l\kappa}(\sigma\omega)w_{\lambda\lambda}{}^{\kappa l'*}(\sigma,\omega_{\lambda+\sigma,l}-\omega)-f_{\lambda l'}(\sigma\omega)w_{\kappa\kappa}{}^{\lambda l}(\omega_{\kappa,l'+\sigma}+\omega)\}, \quad (5.19a)$$

where $w_{ll'}{}^{\kappa\lambda}(x)$ is given by (2.45a) and $w_{ll'}{}^{\kappa\lambda}(\sigma,x)$ is obtained from $w_{ll'}{}^{\kappa\lambda}(x)$ (for the same x) by the substitution $\omega_\mu\to\omega_{\mu+\sigma}$, μ denoting any state. Similarly,

$$B_{ll'}(\sigma\omega)=\sum_{\kappa\lambda}\{F_{\kappa\lambda}(\sigma\omega)[v_{ll'}{}^{\kappa\lambda}(\omega_{l,\lambda+\sigma}+\omega)+v_{\lambda\kappa}{}^{l'l}(\sigma,\omega_{\kappa,l'+\sigma}+\omega)]-F_{l\kappa}(\sigma\omega)v_{\kappa l'}{}^{\lambda\lambda}(\sigma,\omega_{l,\lambda+\sigma}+\omega)-F_{\lambda l'}(\sigma\omega)v_{\kappa\kappa}{}^{\lambda l}(\omega_{\kappa,l'+\sigma}+\omega)\}, \quad (5.19b)$$

where $v_{ll'}{}^{\kappa\lambda}(x)$ is given by (2.41a) and $v_{ll'}{}^{\kappa\lambda}(\sigma,x)$ is obtained from $v_{ll'}{}^{\kappa\lambda}(x)$ by the substitution $\omega_\mu\to\omega_{\mu+\sigma}$. Note that in (5.19b) as well as in (5.19) only the diagonal in $\mathbf{k}$ matrix elements of $F(\sigma\omega)$ enter. These can be found from (5.12) and $\mathbf{J}=(e/m)[\mathbf{p}-(e/c)\mathbf{A}_0(\mathbf{r})]$ in terms of the Fourier components of $\mathbf{A}$ and Φ, and shall not be exhibited here.

The case of electrons in a periodic potential is more complicated. In the Bloch representation the kinetic equation cannot be simplified as in the previous two cases, due to the fact that the Bloch state is not an eigenfunction of H_σ.

6. REMARKS

It is well to emphasize that the kinetic equation (2.33), or (2.46), has been derived for an arbitrary one-electron Hamiltonian H. Thus it presents a sufficiently general and convenient starting point for further applications to more interesting physical situations, e.g., the hopping process, the mixed-scattering case, etc.

The major restrictions of the theory presented here are that the electron-phonon collisions are de-

scribed only in their lowest Born approximation and that only the response linear in the external disturbance is given by the kinetic equation (2.33). With regard to the first limitation, it is of course of extreme importance to have a systematic approximation scheme to replace (2.26), so that higher order in λ effects can be described and the dimensionless "parameters of expansion" deduced. Furthermore, nonperturbative approximation schemes are required for non-normal substances. It is also of fundamental and practical interest to have a theory for a more general response than the linear response to the external disturbance. It is not difficult to see that the approach of this paper can be generalized in these directions.

It should also be pointed out that in this paper we have been interested in the response only of the electrons. The response of the phonons, however, is equally important. In the basic approximation (2.26) we have effectively expanded the response of the phonons in powers of λ, which in the lowest approximation amounts to keeping the phonons in thermal equilibrium. It should, however, be evident that we can introduce the phonon density matrix $\mathrm{Tr}\{b_q^\dagger b_{q'} \mathcal{R}(t)\}$ and find a system of coupled kinetic equations for it and $\rho_{\mu\nu}(t)$ by the appropriate generalizations of (2.26). This, however, is most naturally and economically done in conjunction with the extension of the theory to disturbances of arbitrary strength.

Finally, another restriction of the theory is the one-electron approximation. Dynamical correlations among the electrons can, however, be treated along similar lines.

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APPENDIX A

The complete solution of the kinetic equation (2.33) for $\rho(t)$ can be obtained by the method of Fourier transforms. Introducing the transform

$$\tilde{\rho}(\epsilon)=\int_0^\infty dt\rho(t)e^{-i\epsilon t}, \tag{A1}$$

with ϵ in the lower half of the complex ϵ plane, and similarly for $\bar{A}_{\mu\nu}(\epsilon)$ and $\bar{B}_{\mu\nu}(\epsilon)$ we obtain from (2.33) and the initial condition $\rho(0)=0$ the following equation for $\tilde{\rho}(\epsilon)$:

$$i(\epsilon+\omega_{\mu\nu})\tilde{\rho}_{\mu\nu}(\epsilon)=(\mathcal{S}(\epsilon)\tilde{\rho}(\epsilon))_{\mu\nu}+i\bar{A}_{\mu\nu}(\epsilon)+\bar{B}_{\mu\nu}(\epsilon) \tag{A2}$$

with $\tilde{\rho}(\epsilon)$ analytic in the lower half-plane below a line parallel to the real axis, since $\rho(t)=0$ for $t\leq 0$. Here use has been made of the faltung theorem in the evaluation of both $\mathcal{S}(\epsilon)$ and $\bar{B}_{\mu\nu}(\epsilon)$. $\mathcal{S}(\epsilon)$ is given by (2.45) with the substitution of $\theta(\omega)$ by $\theta(\epsilon)=1/i\epsilon$. From (2.30) it is found that

$$\bar{B}_{\mu\nu}(\epsilon)=\sum_\omega \frac{1}{i(\epsilon-\omega)}\sum_{\kappa q}\left\{\frac{c_{\mu\kappa}(q)A_{\nu\kappa q}(\omega)}{i(\epsilon+\omega_{\kappa\nu}+\omega_q)}+\cdots\right\}$$

$$=\sum_\omega \frac{1}{i(\epsilon-\omega)}B_{\mu\nu}'(\epsilon;\omega), \tag{A3}$$

where $B_{\mu\nu}'(\epsilon;\omega)$ is given by (2.41) with the substitution of $\theta(\omega)$ by $\theta(\epsilon)=1/i\epsilon$. From (2.34) and (2.40) it is also evident that

$$\bar{A}_{\mu\nu}(\epsilon)=\sum_\omega \frac{1}{i(\epsilon-\omega)}A_{\mu\nu}(\omega). \tag{A4}$$

From their definitions it is clear that $\bar{A}_{\mu\nu}(\epsilon)$ and $\bar{B}_{\mu\nu}(\epsilon)$ are analytic functions everywhere except on the real axis, where both have poles at $\epsilon=\omega$ and $\bar{B}_{\mu\nu}(\epsilon)$ has additional poles at $\epsilon=\omega_{\nu\kappa}-\omega_q$, etc. The solution of (A2), which can be written formally as

$$\tilde{\rho}(\epsilon)=[i(\epsilon+\mathcal{L})-\mathcal{S}(\epsilon)]^{-1}[i\bar{A}(\epsilon)+\bar{B}(\epsilon)] \tag{A5}$$

with $\mathcal{L}\rho\equiv[H,\rho]$, will then have the same singularities on the real axis plus additional ones (such as branch lines along the real axis) arising from $[i(\epsilon+\mathcal{L})-\mathcal{S}(\epsilon)]^{-1}$. Since now

$$\rho(t)=\frac{1}{2\pi}\int_{-\infty-i\eta}^{+\infty-i\eta} d\epsilon\tilde{\rho}(\epsilon)e^{i\epsilon t}, \tag{A6}$$

with $\eta>0$, the time evolution of $\rho(t)$ for $t>0$ can be obtained by analytically continuing $\tilde{\rho}(\epsilon)$ in the appropriately cut ϵ plane and deforming the contour in (A6) in the upper half-plane, so that we may use the techniques of complex integration. In the limit of an infinite lattice the contribution of the poles at $\omega_{\nu\kappa}-\omega_q$, etc., vanishes at $t\to\infty$ and the steady-state solution is obtained from the contribution of the poles ω, *if we assume* that the contribution of the singularities of $[i(\epsilon+\mathcal{L})-\mathcal{S}(\epsilon)]^{-1}$ vanishes at $t\to\infty$. We thus find

$$\rho(t)\underset{t\to\infty}{\to}\sum_\omega e^{i\omega t}\rho(\omega) \tag{A7}$$

with

$$\rho(\omega)=[i(\omega+\mathcal{L})-\mathcal{S}(\omega)]^{-1}[iA(\omega)+B(\omega)]. \tag{A7a}$$

Thus $\rho(\omega)$ satisfies the kinetic equation (2.46). Knowledge of the analytic properties of $[i(\epsilon+\mathcal{L})-\mathcal{S}(\epsilon)]^{-1}$ gives not only the steady state but also the approach to it; it shall not be studied here.

APPENDIX B

For sufficiently small λ we can find a Markoffian approximation to the kinetic equation (2.33) by the following suggestive argument.

It is observed that for $t\gg\tau_c$ the upper limit of the integrals in (2.32) can be taken as infinity, on account

of (2.43). It is then clear from (2.29) that for $t\gg\tau_c$

$$\frac{d}{dt}\left[\rho'(t)-i\int_0^t d\tau A^{(0)\prime}(\tau)\right]=O(\lambda^2). \tag{B1}$$

An integration yields in the Schrödinger representation

$$\rho_{\mu\nu}(t-\tau)=e^{i\omega_{\mu\nu}\tau}\rho_{\mu\nu}(t)-i\int_0^\tau d\tau' e^{-i\omega_{\mu\nu}\tau'} \times A_{\mu\nu}{}^{(0)}(t-\tau')+O(\lambda^2), \tag{B2}$$

which upon substitution into (2.32) gives

$$\mathcal{S}\{t,\rho(t)\}=\mathcal{S}_M\rho(t)+C(t) \tag{B3}$$

plus terms that can be ignored if $\tau_c/\tau_r\ll 1$, where τ_r is a measure of the effects of collisions and is of order λ^{-2}. Here $\mathcal{S}_M$ is the scattering operator in the Markoffian approximation, namely,

$$(\mathcal{S}_M\rho(t))_{\mu\nu}=\sum_{\kappa\lambda}\{\rho_{\kappa\lambda}(t)[w_{\mu\nu}{}^{\kappa\lambda}(\omega_{\mu\kappa})+w_{\nu\mu}{}^{\lambda\kappa*}(\omega_{\nu\lambda})] -\rho_{\mu\kappa}(t)w_{\lambda\lambda}{}^{\kappa\nu*}(\omega_{\lambda\kappa})-\rho_{\lambda\nu}(t)w_{\kappa\kappa}{}^{\lambda\mu}(\omega_{\kappa\lambda})\} \tag{B4}$$

the w's being given by (2.45a). $C(t)$ is found to be

$$C(t)=\sum_\omega e^{i\omega t}C(\omega), \tag{B5}$$

where

$$C(\omega)=(\mathcal{S}(\omega)-\mathcal{S}_M)\bar{r}(\omega), \tag{B5a}$$

$\mathcal{S}(\omega)$ being given by (2.45) while

$$\bar{r}_{\mu\nu}(\omega)=A_{\mu\nu}{}^{(0)}(\omega)/(\omega_{\mu\nu}+\omega). \tag{B5b}$$

$\bar{r}_{\mu\nu}(\omega)$ differs from $r_{\mu\nu}(\omega)$, (2.49a), in that there is no principal part in $\bar{r}_{\mu\nu}(\omega)$. When the denominator of $\bar{r}_{\mu\nu}(\omega)$ vanishes, $C(\omega)$ is understood to equal its limiting value as the denominator approaches zero smoothly; $C(\omega)$ is regular, as it can be verified from its original expression. Note that away from direct resonance, i.e., for $\omega\neq\omega_{\nu\mu}$ with $A_{\mu\nu}{}^{(0)}(\omega)\neq 0$, we have $\bar{r}(\omega)=r(\omega)$. If we denote the density operator in the Markoffian approximation by $\rho_M(t)$, it obeys for $t\gg\tau_c$ the equation

$$\frac{d}{dt}\rho_M(t)=-i[H,\rho_M(t)]+\mathcal{S}_M\rho_M(t) +iA(t)+B(t)+C(t). \tag{B6}$$

The corresponding equation for the steady-state solution $\rho_M{}^{(s)}(t)=\sum_\omega \rho_M(\omega)\exp(i\omega t)$ can now be found immediately to be

$$i\omega\rho_M(\omega)=-i[H,\rho_M(\omega)]+\mathcal{S}_M\rho_M(\omega) +iA(\omega)+B(\omega)+C(\omega). \tag{B7}$$

The method of derivation of (B6) and (B7) indicates that, in addition to the other conditions on the smallness of λ which are also necessary for the more accurate equation (2.46), they are valid if $\tau_c/\tau_r\ll 1$. More quantitative criteria are obtained by comparing the solution $\rho_M(\omega)$ with $\rho(\omega)$ of (2.46).

Note that because of (B5a) and (2.49) we can write

$$i\omega\rho_M(\omega) =-i[H,\rho_M(\omega)]+\mathcal{S}_M[\rho_M(\omega)-r(\omega)]+iA(\omega)+D(\omega) +[\mathcal{S}(\omega)-\mathcal{S}_M][\bar{r}(\omega)-r(\omega)]. \tag{B8}$$

Away from direct resonance the last term vanishes and (B8) differs from (2.46) only in the structure of the scattering operator. Note that $\mathcal{S}_M$ does not depend on ω.