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The Quantum Mechanical Extension of the Boltzmann Equation

Abstract: It is shown that the method of Kohn and Luttinger may be applied to obtain a generalized Boltzmann equation, for electrons in a solid, when the driving field has nonzero wavevector as well as frequency. By means of this equation, the behavior of the electrons in response to the field may be followed from the quasi-classical limit at small rates of change to the quantal limit at large rates of change.

Introduction

Many transport phenomena of electrons in solids are described by the quasi-classical Boltzmann equation[1]

$$\partial f(\mathbf{p})/\partial t + \mathbf{v}(\mathbf{p})\cdot(\partial f(\mathbf{p})/\partial \mathbf{r}) + g(\mathbf{p}) = \int d^3\mathbf{p}'[f(\mathbf{p}')\,W(\mathbf{p}', \mathbf{p}) - f(\mathbf{p})\,W(\mathbf{p}, \mathbf{p}')], \qquad (1)$$

where $\mathbf{p} = \hbar\mathbf{k}$ and $\mathbf{k}$ is the wavevector of a Bloch state, and $\mathbf{v}$ is its velocity; $f(\mathbf{p}, \mathbf{r}, t)$ is the distribution function of the system, whose disturbance due to the driving forces is to be found by solving (1); g represents these driving forces and is explicitly proportional to them; and g and f on the left refer to a particular band and spin direction, or spin-orbit combination of them. For an applied force $\mathbf{F}$ acting on each electron,

$$g = \mathbf{F}\cdot(\partial/\partial\mathbf{p})f. \qquad (2)$$

(In the linearized inhomogeneous equation with which we shall be concerned, f is the perturbed part of the distribution function proportional to $\mathbf{F}$ in (1) and is the equilibrium distribution function, independent of $\mathbf{F}$, in (2).)

The validity of this quasi-classical Boltzmann equation, and possible deviations from it, are important questions. Kohn and Luttinger[3] and Greenwood[4] have derived the linearized inhomogeneous equation from first principles as a consequence of the equation of motion

$$i\hbar\,\partial\rho/\partial t = H\rho - \rho H \qquad (3)$$

of the quantum density matrix of the electrons, ρ, in the case where the driving force is a uniform electric field ($\mathbf{F}$ in (2) equals the field strength times electron charge) and the scattering effect represented by $W(\mathbf{p}, \mathbf{p}')$ is due to randomly distributed defects or impurity atoms. Luttinger and Kohn showed, for these conditions, that the linearized equation is valid for localized scatterers of arbitrary strength and small concentration, and investigated the consequences of appreciable concentration. Kohn and Luttinger's and Greenwood's theory has been extended to include electron scattering by absorption and emission of lattice phonons, by Argyres;[5] nonlinear dependence of f on F ("hot electrons"), by Hasegawa and Yamashita;[6] and presence of a static magnetic field, by Thomas.[7]

A natural question is: what are the consequences of appreciable rates of change of the driving forces? So long as these are still small, we expect that (1) will hold and they will be represented by the first two terms on its left-hand side. For larger frequencies and space gradients, however, the quasi-classical domain must be transcended and quantal features will appear in the response of the system. If the driving field has angular frequency ω and wavevector $\mathbf{q}$, one expects this to happen when $\hbar\omega$ or $\hbar qv$, where v is an appropriate electron velocity, is no longer small compared to characteristic energies: such are κT and the energy scale of appreciable variation in the relevant properties (scattering matrix elements, energy density of states) of the Bloch states. For an ultrasonic field, $\hbar qv \sim (v/s)\hbar\omega$ where s is the velocity of sound. Since in practice one has $v \gg s$, the "spatial" quantum effects of appreciable q should predominate; and these should in fact be experimentally accessible. At higher ω and q the

response of the driven system should reach the familiar quantal domain (in which scattering effects may be neglected entirely or described by ordinary perturbation theory).

The purpose of the present communication is to show that the Kohn and Luttinger procedure may be readily extended to driving fields of nonvanishing q and ω;[8] that the result is still a Boltzmann equation of essentially the *form* of the quasi-classical equation, with the role of the distribution function performed by elements of the density matrix connecting Bloch states whose wavevectors differ by $\mathbf{q}$; and that the passage between the classical and quantal limits may be represented by the $\mathbf{q}$ and ω dependence of the solution of this equation. The analysis will be limited to the linear inhomogeneous equation in the absence of a magnetic field and to random elastic scatterers, as in Refs. 3 and 4; and in addition the calculation will be mainly limited to the lowest significant order in the scattering matrix elements, for each term of the equation. Thus no attempt is made here to carry out the equivalent, for nonzero q and ω, of Luttinger and Kohn's treatment of scatterers of arbitrary strength and effects of interference between scattered Schrödinger waves, or to approach the classic question of the permissible magnitude of the scattering frequency times Planck's constant.

We first need to reduce Eq. (3) to an appropriate form. Let

$$H(t) = H^{(0)} + (H^{\omega}e^{i\omega t} + H^{-\omega}e^{-i\omega t})e^{\chi t} \tag{4}$$

and

$$\rho(t) = \rho^{(0)} + (\rho^{\omega}e^{i\omega t} + \rho^{-\omega}e^{-i\omega t})e^{\chi t} + \cdots, \tag{5}$$

where χ is real and as usual we shall eventually let

$$x \to +0 \tag{6}$$

(the positive sign corresponding to the thermodynamic "direction of time"). The electrons of the unperturbed (steady state) crystal are represented by $\rho^{(0)}$ and the Hamiltonian $H^{(0)}$. The $H^{\pm\omega}$ represent the driving force, and $\rho^{\pm\omega}$ the part of the system response which is linear in these. Then (3) gives

$$\hbar(\pm\omega - i\chi)\rho^{\pm\omega} + H^{(0)}\rho^{\pm\omega} - \rho^{\pm\omega}H^{(0)} = C^{\pm\omega} \tag{7}$$

where

$$C^{\pm\omega} \equiv \rho^{(0)}H^{\pm\omega} - H^{\pm\omega}\rho^{(0)}. \tag{8}$$

Since $H^{(0)}$ and $H^{\pm\omega}$, and the dynamical variables of interest, are taken to be (sums, over the electrons, of) single-electron functions, for the conditions of Boltzmann statistics ρ may be taken as the density matrix of a single representative electron; and its matrix elements will completely describe the system, apart from fluctuations. For the conditions of Fermi statistics, as Kohn and Luttinger showed,[9] an exactly equivalent formalism applies, with the reinterpretation of the elements of ρ given in Eq. (11) below. In this case the basis states have the form of Slater determinants and are specified by sets $\{n\}$ of occupation numbers, $n_l = 0$ or 1, of one-electron component states; and ρ is specified by its matrix elements between these basis states. The basis states may conveniently be manipulated by means of second-quantization annihilation and creation operators a_l, $a_l^{\dagger}$. Then H and other one-electron variables are given by expansions

$$Q = \sum_l \sum_m Q_{lm}a_l^{\dagger}a_m, \tag{9}$$

where the Q_{lm} are the one-electron matrix elements. If ρ^{α} stands for ρ or any component of ρ (such as $\rho^{(0)}$, $\rho^{\pm\omega}$), the corresponding expectation of Q is

$$\langle Q\rangle_{\alpha} = \mathrm{Tr}\ \rho^{\alpha}Q = \sum_l \sum_m Q_{lm}\rho^{\alpha}_{ml} \tag{10}$$

where

$$\rho^{\alpha}_{lm} \equiv \mathrm{Tr}\ a_l\rho^{\alpha}a_m^{\dagger} \tag{11}$$

and "Tr" means the trace in $\{n\}$ space. We similarly define

$$C^{\pm\omega}_{lm} \equiv \mathrm{Tr}\ a_l(\rho^{(0)}H^{\pm\omega} - H^{\pm\omega}\rho^{(0)})a_m^{\dagger}. \tag{12}$$

The essential theorem is[9]:

$$\mathrm{Tr}\ a_l(\rho^{\alpha}Q - Q\rho^{\alpha})a_m^{\dagger} = \sum_u(\rho^{\alpha}_{lu}Q_{um} - Q_{lu}\rho^{\alpha}_{um}), \tag{13}$$

which may be proved by using the anticommutation rules of the a's and $a^{\dagger}$'s to reduce the combinations of two a's and two $a^{\dagger}$'s, obtained on substituting (9), to zero or combinations of one of each. Then, on multiplying both sides of (7) by a_l on the left and $a_m^{\dagger}$ on the right, and taking the trace, by Eq. (13) applied to $\rho^{\pm\omega}$ we have

$$\hbar(\pm\omega - i\chi)\rho^{\pm\omega}_{lm} + \sum_u(H^{(0)}_{lu}\rho^{\pm\omega}_{um} - \rho^{\pm\omega}_{lu}H^{(0)}_{um}) = C^{\pm\omega}_{lm}. \tag{14}$$

Thus, everything may proceed as though there were only a single electron, and the arrays defined by (11) and (12) were matrix elements; accordingly we shall refer to them as "matrix elements" hereafter. One need only note that, in thermal equilibrium, the diagonal elements of $\rho^{(0)}$ equal the Fermi function of the eigenvalues of $H^{(0)}$.

Derivation of the generalized Boltzmann equation

The main part of $H^{(0)}$ is the crystal-lattice electron Hamiltonian, diagonal in the Bloch representation. The matrix elements of $H^{(0)}$ in this representation will be written

$$H^{(0)}_{\mathbf{k}\mathbf{k}'} \equiv \hbar\omega_{\mathbf{k}}\,\delta_{\mathbf{k},\mathbf{k}'} + H'_{\mathbf{k}\mathbf{k}'} \tag{15}$$

where H', representing the scatters, will be taken as having zero diagonal matrix elements.[10] The off-diagonal part of $\rho^{(0)}$ will similarly be denoted by $\rho^{(0)\prime}$, and the diagonal elements by $\rho^{(0)}_{\mathbf{k}}$, in the Bloch representation. Since $\rho^{(0)}$

represents a steady state it commutes with $H^{(0)}$; then $\rho^{(0)\prime}$ is small because H' is small. The driving terms of (4) will be taken as

$$H^{\pm\omega} = \phi^{\pm\omega,\mathbf{q}}\, e^{i\mathbf{q}\cdot\mathbf{r}} + \phi^{\pm\omega,-\mathbf{q}}\, e^{-i\mathbf{q}\cdot\mathbf{r}} \tag{16}$$

for a single electron, where the ϕ's are constants. The main part of $C^{\pm\omega}$ then has nonzero matrix elements between the pairs of Bloch states with wavevectors differing by $\mathbf{q}$:

$$C^{\pm\omega}_{\mathbf{k}\pm\mathbf{q},\mathbf{k}} = \phi^{\pm\omega,\pm\mathbf{q}}\,(\mathbf{k}\pm\mathbf{q}\mid\mathbf{k})\,(\rho^{(0)}_{\mathbf{k}\pm\mathbf{q}} - \rho^{(0)}_{\mathbf{k}}), \tag{17}$$

by (13), where

$$(\mathbf{k}\mid\mathbf{k}') \equiv \langle\mathbf{k}\,|e^{\,i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}|\,\mathbf{k}'\rangle = \int u^*_{\mathbf{k}}(\mathbf{r})u_{\mathbf{k}'}(\mathbf{r})\,d^3\mathbf{r}, \tag{18}$$

$u_{\mathbf{k}}(\mathbf{r})$ being the lattice-periodic part of the wavefunction of the Bloch state $|\mathbf{k}\rangle$. (A punctuation comma between matrix subscripts will be used where it is useful as a reading aid, omitted otherwise.)

For the case $q = 0$, $H^{(0)}$ and $C^{\pm\omega}$ are simultaneously almost diagonal—in the Bloch representation—and the perturbation $\rho^{\pm\omega}$ is almost diagonal in the same representation. The off-diagonal elements $\rho^{\pm\omega}_{\mathbf{k}\mathbf{k}'}$ are of one higher order in H' than the diagonal elements; and Kohn and Luttinger's procedure is based on this fact. When q is nonzero, $H^{(0)}$ and $C^{\pm\omega}$ are no longer simultaneously almost diagonal. Since the physical disturbance has the space variation of exp $(\pm i\mathbf{q}\cdot\mathbf{r})$, we would expect the "strong" matrix elements of $\rho^{\pm\omega}$ to be now between states with wavevectors differing by $\mathbf{q}$—i.e., the same pairs of states as those for which the main part of $C^{\pm\omega}$ has nonzero matrix elements. This is indeed the case; by making this division of $\rho^{\pm\omega}$ into "strong" and "weak" parts, one can obtain a solution for the "strong part" by the same procedure, in terms of powers of H', as for $q = 0$. We will use the notation[11]

$$Q^{\mathbf{q}}_{\mathbf{k}} \equiv Q_{\mathbf{k}+\mathbf{q}/2,\mathbf{k}-\mathbf{q}/2}, \qquad Q^{-\mathbf{q}}_{\mathbf{k}} \equiv Q_{\mathbf{k}-\mathbf{q}/2,\mathbf{k}+\mathbf{q}/2} \tag{19}$$

and

$$Q'_{\mathbf{k}\mathbf{k}'} \equiv Q_{\mathbf{k}\mathbf{k}'}(1-\delta_{\mathbf{k},\mathbf{k}'+\mathbf{q}})(1-\delta_{\mathbf{k},\mathbf{k}'-\mathbf{q}}) \tag{20}$$

for the matrix elements of the strong and weak parts of $\rho^{\pm\omega}$ and of $C^{\pm\omega}$ (but of course H' will still have the meaning given by Eq. (15)); and similarly

$$\omega^{\pm\mathbf{q}}_{\mathbf{k}} \equiv \omega_{\mathbf{k}\pm\mathbf{q}/2,\mathbf{k}\mp\mathbf{q}/2} \tag{21}$$

where

$$\omega_{\mathbf{k}\mathbf{k}'} \equiv \omega_{\mathbf{k}} - \omega_{\mathbf{k}'}. \tag{22}$$

Hereafter we deal with Eq. (14) for $+\omega$, in the Bloch representation, suppressing the superscript $+\omega$ and writing the strong elements of $\rho^{+\omega}$ and $C^{+\omega}$ as $\rho^{\pm\mathbf{q}}_{\mathbf{k}}$, $C^{\pm\mathbf{q}}_{\mathbf{k}}$ and the weak parts as ρ', C' with matrix elements $\rho'_{\mathbf{k}\mathbf{k}'}$, $C'_{\mathbf{k}\mathbf{k}'}$.

With the foregoing notation, Eq. (14) gives

$$\hbar(\omega + \omega^{\mathbf{q}}_{\mathbf{k}} - i\chi)\rho^{\mathbf{q}}_{\mathbf{k}} = C^{\mathbf{q}}_{\mathbf{k}} + H'_{\mathbf{k}+3\mathbf{q}/2,\mathbf{k}-\mathbf{q}/2}\,\rho^{-\mathbf{q}}_{\mathbf{k}+\mathbf{q}} - H'_{\mathbf{k}+\mathbf{q}/2,\mathbf{k}-3\mathbf{q}/2}\,\rho^{-\mathbf{q}}_{\mathbf{k}-\mathbf{q}} + \sum_{\mathbf{k}'}(\rho'_{\mathbf{k}+\mathbf{q}/2,\mathbf{k}'}\,H'_{\mathbf{k}',\mathbf{k}-\mathbf{q}/2} - H'_{\mathbf{k}+\mathbf{q}/2,\mathbf{k}'}\,\rho'_{\mathbf{k}',\mathbf{k}-\mathbf{q}/2}) \tag{23}$$

and

$$\hbar(\omega + \omega_{\mathbf{k}\mathbf{k}'} - i\chi)\rho'_{\mathbf{k}\mathbf{k}'} + \sum_{\mathbf{k}''}(H'_{\mathbf{k}\mathbf{k}''}\rho'_{\mathbf{k}''\mathbf{k}'} - \rho'_{\mathbf{k}\mathbf{k}''}H'_{\mathbf{k}''\mathbf{k}'}) = C'_{\mathbf{k}\mathbf{k}'} + H'_{\mathbf{k}-\mathbf{q},\mathbf{k}'}\,\rho^{\mathbf{q}}_{\mathbf{k}-\mathbf{q}/2} - H'_{\mathbf{k},\mathbf{k}'+\mathbf{q}}\,\rho^{\mathbf{q}}_{\mathbf{k}'+\mathbf{q}/2} + H'_{\mathbf{k}+\mathbf{q},\mathbf{k}'}\,\rho^{-\mathbf{q}}_{\mathbf{k}+\mathbf{q}/2} - H'_{\mathbf{k},\mathbf{k}'-\mathbf{q}}\,\rho^{-\mathbf{q}}_{\mathbf{k}'-\mathbf{q}/2}. \tag{24}$$

The $\rho^{-\mathbf{q}}$ terms of (23) and (24), separate from the summations, represent the system response proportional to $\phi^{-\mathbf{q}}$.

Now, the matrix elements of H' are sums over the contributions of the individual scattering defects or impurities:

$$H'_{\mathbf{k}\mathbf{k}'} = \sum_I H^I_{\mathbf{k}\mathbf{k}'}\exp\,(i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}_I) \tag{25}$$

where the $\mathbf{R}_I$ give the positions of the scatterers. If the latter are randomly distributed, as is assumed here, then the $\rho^{-\mathbf{q}}$ terms of (23) may be dropped because of the cancellation of the randomly phased exponentials exp $(-2i\mathbf{q}\cdot\mathbf{R}_I)$. In (24) we neglect the C' term, which is of order H'; it will be considered later as a correction. The remaining equation may be solved for $\rho'_{\mathbf{k}\mathbf{k}'}$, in terms of the $\rho^{\pm\mathbf{q}}_{\mathbf{k}}$, as a "perturbation" power series in the matrix elements of H'. We require only the lowest order in H', of this formal solution, given by dropping the summation term on the left of (24) and just dividing both sides of the remaining equation by the coefficient of $\rho'_{\mathbf{k}\mathbf{k}'}$ on the left. The generalized Boltzmann equation is obtained by substituting in (23) this lowest-order solution of (24) for the matrix elements of ρ'. The resulting $\rho^{-\mathbf{q}}$ terms coming from the separate $\rho^{-\mathbf{q}}$ terms of (24) have coefficients with products of pairs of matrix elements of H'. These products are such that the (I, I) contributions from a single scatterer are again proportional to exp $(-2i\mathbf{q}\cdot\mathbf{R}_I)$; and these $\rho^{-\mathbf{q}}$ terms may also be dropped because of random-phase cancellation. (The (I, J) contributions from pairs of scatterers essentially cancel regardless of the particular combination of $\mathbf{k}$'s.)[12]

The remaining equation may be written

$$[i\omega + \chi + i\omega^{\mathbf{q}}_{\mathbf{k}} + i\Omega^{\mathbf{q}}_{\mathbf{k}}(\omega)]\rho^{\mathbf{q}}_{\mathbf{k}} - (i/\hbar)C^{\mathbf{q}}_{\mathbf{k}} = \sum_{\mathbf{k}'}\Delta^{\mathbf{q}}_{\mathbf{k}\mathbf{k}'}(\omega)\,S^{\mathbf{q}}_{\mathbf{k}\mathbf{k}'}(\rho^{\mathbf{q}}_{\mathbf{k}'} - \rho^{\mathbf{q}}_{\mathbf{k}}) \tag{26}$$

where

$$S^{\mathbf{q}}_{\mathbf{k}\mathbf{k}'} \equiv (2\pi/\hbar)H'_{\mathbf{k}+\mathbf{q}/2,\mathbf{k}'+\mathbf{q}/2}H'_{\mathbf{k}'-\mathbf{q}/2,\mathbf{k}-\mathbf{q}/2}, \tag{27}$$

$$\Delta^{q}_{\mathbf{k}\mathbf{k}'}(\omega) \equiv \frac{1}{2\pi i\hbar}\left(\frac{1}{\omega + \omega_{\mathbf{k}+\mathbf{q}/2,\mathbf{k}'-\mathbf{q}/2} - i\chi} + \frac{1}{\omega + \omega_{\mathbf{k}'+\mathbf{q}/2,\mathbf{k}-\mathbf{q}/2} - i\chi}\right), \tag{28}$$

and

$$\Omega^{q}_{\mathbf{k}}(\omega) \equiv \sum_{\mathbf{k}'} \frac{1}{\hbar^2}\left[\frac{(H'_{\mathbf{k}-\mathbf{q}/2,\mathbf{k}'-\mathbf{q}/2} - H'_{\mathbf{k}+\mathbf{q}/2,\mathbf{k}'+\mathbf{q}/2})H'_{\mathbf{k}'-\mathbf{q}/2,\mathbf{k}-\mathbf{q}/2}}{\omega + \omega_{\mathbf{k}+\mathbf{q}/2,\mathbf{k}'-\mathbf{q}/2} - i\chi} + \frac{(H'_{\mathbf{k}'+\mathbf{q}/2,\mathbf{k}+\mathbf{q}/2} - H'_{\mathbf{k}'-\mathbf{q}/2,\mathbf{k}-\mathbf{q}/2})H'_{\mathbf{k}+\mathbf{q}/2,\mathbf{k}'+\mathbf{q}/2}}{\omega + \omega_{\mathbf{k}'+\mathbf{q}/2,\mathbf{k}-\mathbf{q}/2} - i\chi}\right]. \tag{29}$$

By (25), we may substitute in (26)

$$S^{q}_{\mathbf{k}\mathbf{k}'} \to (2\pi/\hbar)\sum_{l} H^{l}_{\mathbf{k}+\mathbf{q}/2,\mathbf{k}'+\mathbf{q}/2}H^{l}_{\mathbf{k}'-\mathbf{q}/2,\mathbf{k}-\mathbf{q}/2}, \tag{30}$$

again because of random-phase cancellation of the contributions of pairs of scatterers.[12]

Because of (6), in summations over $\mathbf{k}$ in which the summand has a factor $(\xi - i\chi)^{-1}$, where ξ is a real function of $\mathbf{k}$, when the summation includes a simple zero of ξ the substitution

$$\frac{1}{\xi - i\chi} \to \mathcal{P}\frac{1}{\xi} + i\pi\,\delta(\xi) \tag{31}$$

(where $\mathcal{P}$ means "take the principal part") gives the value of the sum. With this substitution in Δ on the right-hand side, Eq. (26) is our generalized Boltzmann equation.

Discussion

The Ω term of (26) may be disregarded here; it will be considered later. The remaining terms correspond one by one to those of Eq. (1), when we make the identification

$$\rho^{q}_{\mathbf{k}} \to f^{\omega,\mathbf{q}}(\hbar\mathbf{k}) \tag{32}$$

with the $\mathbf{q}$, ω Fourier component of $f(\mathbf{p}, \mathbf{r}, t)$. (Adjustment of the normalization in going from $\sum_{\mathbf{k}}$ to $\int d^3\mathbf{p}$ may be taken for granted.) We should also set

$$\rho^{(0)}_{\mathbf{k}} = f_0(\hbar\mathbf{k}) \tag{33}$$

where $f_0(\mathbf{p})$ is the unperturbed distribution function. Then by (17)

$$C^{q}_{\mathbf{k}} = \phi^{\omega,\mathbf{q}}(\mathbf{k} + \tfrac{1}{2}\mathbf{q} \mid \mathbf{k} - \tfrac{1}{2}\mathbf{q})\,[f_0(\hbar(\mathbf{k} + \tfrac{1}{2}\mathbf{q})) - f_0(\hbar(\mathbf{k} - \tfrac{1}{2}\mathbf{q}))]. \tag{34}$$

We first examine the limit of (26) when q becomes zero. Since in this limit

$$\omega^{q}_{\mathbf{k}} \to \mathbf{q}\cdot(\partial\omega_{\mathbf{k}}/\partial\mathbf{k}) = \mathbf{q}\cdot\mathbf{v}, \tag{35}$$

the corresponding term on the left of (26) becomes $\mathbf{v}(\hbar\mathbf{k})\cdot(\partial f/\partial\mathbf{r})^{\mathbf{q}}$ in agreement with the second term on the left of (1). With $q = 0$ from the beginning, this diffusion term of (1) would not have been obtained. Also, by (34),

$$-(i/\hbar)C^{q}_{\mathbf{k}} \to (-i\mathbf{q}\phi^{\omega,\mathbf{q}})\cdot(\partial/\partial\,\hbar\mathbf{k})f_0 \tag{36}$$

–in obvious agreement with (2) for the linear-inhomogeneous case. The right-hand sides of (1) and (26)—the collision terms—do *not* agree when $\omega \neq 0$. By (31), for $q = 0$ the right-hand side of (26) is equal to

$$\sum_{\mathbf{k}'} S^{0}_{\mathbf{k}\mathbf{k}'}\left\{\tfrac{1}{2}[\delta(\epsilon_{\mathbf{k}\mathbf{k}'} + \hbar\omega) + \delta(\epsilon_{\mathbf{k}\mathbf{k}'} - \hbar\omega)] + \frac{1}{2\pi i}\mathcal{P}\left[\frac{1}{\epsilon_{\mathbf{k}\mathbf{k}'} + \hbar\omega} - \frac{1}{\epsilon_{\mathbf{k}\mathbf{k}'} - \hbar\omega}\right]\right\}(f^{\omega}(\hbar\mathbf{k}') - f^{\omega}(\hbar\mathbf{k})), \tag{37}$$

where

$$\epsilon_{\mathbf{k}} \equiv \hbar\omega_{\mathbf{k}}, \qquad \epsilon_{\mathbf{k}\mathbf{k}'} \equiv \hbar\omega_{\mathbf{k}\mathbf{k}'} = \epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'}. \tag{38}$$

For $\omega = 0$, the factor $\{\ \}$ reduces to $\delta(\epsilon_{\mathbf{k}\mathbf{k}'})$; and (37) becomes equivalent to the right-hand side of (1), with the scattering probabilities reckoned in the Born approximation.

The quantum effect due to nonzero ω is given by the supplanting of $\delta(\epsilon_{\mathbf{k}\mathbf{k}'})$ by the first term of $\{\ \}$ in (37) *and* the addition of a "principal part" contribution given by the second term of $\{\ \}$. Since the latter is imaginary, it represents a non-dissipative effect.[13] Ordinarily, when $\hbar\omega$ is large enough for these effects to become significant the first term on the left of (1) will be already large compared with the rate of change of f due to collisions (unless we are in the "strong scattering" domain where, in the notation of Ref. 4 (§3) and other papers on that situation, $\hbar/\tau\eta$ is not small), so that the latter has only a small effect on the response to the driving forces. If, accordingly, one expresses the solution of the Boltzmann equation as a power series in $1/\omega$, the second term ($\sim 1/\omega^2$), proportional to the collision rate, is just what would be obtained by second-order perturbation theory.[14] For high enough symmetries in the summand of (37), just as for $\omega = 0$, the solution of the Boltzmann equation is given by a relaxation time.[15] However, the relaxation time is now a function of ω,[16] and is complex. We may, of course, rewrite (37) in terms of time by recombining the Fourier components f^{ω}: Then

$$\partial f/\partial t + \mathbf{F}(t)\cdot(\partial f/\partial\hbar\mathbf{k}) = \sum_{\mathbf{k}'} S^{0}_{\mathbf{k}\mathbf{k}'}\int_{-\infty}^{t} 2\cos[\omega_{\mathbf{k}\mathbf{k}'}(t - t')][f(\hbar\mathbf{k}', t') - f(\hbar\mathbf{k}, t')]\,dt'/h \tag{39}$$

so long as the time dependence of $\mathbf{F}$, and hence of f, includes a factor like $\exp(\chi t)$ ensuring convergence of the integral.

We return now to nonzero q. The electron variable whose expectation, for the driven system, one is most likely to require is a Fourier component of the velocity:

$$\mathbf{v}^{\mathbf{q}} \equiv \tfrac{1}{2}(\mathbf{v}e^{i\mathbf{q}\cdot\mathbf{r}} + e^{i\mathbf{q}\cdot\mathbf{r}}\mathbf{v}). \tag{40}$$

Then

$$N\langle \mathbf{v}^{-\mathbf{q}}\rangle = \sum_{\mathbf{k}} \rho_{\mathbf{k}}^{\mathbf{q}}(\mathbf{k} - \tfrac{1}{2}\mathbf{q} \mid \mathbf{k} + \tfrac{1}{2}\mathbf{q})\tfrac{1}{2}(\mathbf{v}_{\mathbf{k}+\mathbf{q}/2} + \mathbf{v}_{\mathbf{k}-\mathbf{q}/2}) \tag{41}$$

where N is the number of electrons in the normalization volume and $\mathbf{v}_{\mathbf{k}}$ is the diagonal element of $\mathbf{v}$, equal to $\partial\omega_{\mathbf{k}}/\partial\mathbf{k}$. With the interpretation (32) for the first factor of the summand, this becomes the conventional expression if q is small enough for the other two factors to reduce to $\mathbf{v}_{\mathbf{k}}$. For the final factor, the fractional deviation from $\mathbf{v}_{\mathbf{k}}$ is of order $(\hbar^2q^2/m^*)/\epsilon_F$, where ϵ_F is the Fermi energy measured to the band edge (replaced by κT in the nondegenerate case). The deviation of the middle factor from one may be estimated by "$\mathbf{k}\cdot\mathbf{p}$ theory":

$$(\mathbf{k} - \tfrac{1}{2}\mathbf{q} \mid \mathbf{k} + \tfrac{1}{2}\mathbf{q}) - 1 \sim (\hbar^2q^2/m^*)/\epsilon_m \tag{42}$$

where $\epsilon_m(\mathbf{k})$ is the "vertical" energy interval to the band with the most influence on the inverse effective mass $1/m^*$.

As q increases from zero the first term in (26) to deviate appreciably from its quasi-classical limit is evidently C, when $\hbar qv/\kappa T$ becomes appreciable. When the latter is still fairly small, the factor $\mathbf{q}\cdot(\partial f_0/\partial\mathbf{k})$ on the right of (36) may be replaced by the first two terms of the expansion

$$f_0(\mathbf{p} + \tfrac{1}{2}\hbar\mathbf{q}) - f_0(\mathbf{p} - \tfrac{1}{2}\hbar\mathbf{q}) = \left[\hbar\mathbf{q}\cdot\frac{\partial}{\partial\mathbf{p}} + \frac{1}{24}\left(\hbar\mathbf{q}\cdot\frac{\partial}{\partial\mathbf{p}}\right)^3 + \cdots\right]f_0. \tag{43}$$

The resulting fractional correction to the current calculated from the Boltzmann equation is found to be only $\sim(\hbar^2q^2/m^*)/\epsilon_F$, for the degenerate case, rather than $\sim(\hbar^2q^2/m^*)/\kappa T$. When $\hbar qv$ becomes large compared to κT, the final factor of (34) takes on a different character: There is a region around the Fermi surface within which $f_0(\mathbf{p} + \frac{1}{2}\hbar\mathbf{q}) - f_0(\mathbf{p} - \frac{1}{2}\hbar\mathbf{q})$ equals $+1$, and an opposite region within which it equals -1. However, one can show that so long as q is still small compared to the dimensions of the Fermi surface, and provided that the other quantities involved in (26) do not vary significantly over distances $\sim q$ from the Fermi surface, the deviation of the current, and similar quantities, from their values at the quasi-classical limit remains small. Thus κT is not the scale measure for such deviations.

When q and ω are large enough for the scattering term of (26) to be small compared to the other $\rho^{\mathbf{q}}$ terms, one again has an expansion in ascending powers of H':

$$\rho_{\mathbf{k}}^{\mathbf{q}} = \frac{C_{\mathbf{k}}^{\mathbf{q}}}{\hbar(\omega + \omega_{\mathbf{k}}^{\mathbf{q}} - i\chi)} + \cdots. \tag{44}$$

The first term of (44) gives the familiar quantal limit; the second term is obtained by substituting the first term into the scattering function (including Ω) of (26).[17] When q becomes comparable to the dimensions of the Fermi surface,[18] it may be necessary to take account of interband elements of C and of H'. The Boltzmann equation then generalizes to coupled equations for the intraband and interband $\rho_{\mathbf{k}}^{\mathbf{q}}$ elements.[19] These equations may be obtained by the obvious extension of the derivation of (26) from (14).

Because of the lower symmetry of the terms of (26) when q is appreciable, one does not have a relaxation-time solution with $\epsilon_{\mathbf{k}}$ and $H'_{\mathbf{k}\mathbf{k}'}$ functions such that one *would* have this when $q = 0$. However, if the matrix elements of H' are insensitive to $\mathbf{k}$, and therefore to $\mathbf{q}$, and if q is small enough for its effect on the denominators in (28) to be reckoned to first order only, then

$$\Delta_{\mathbf{k}\mathbf{k}'}^{\mathbf{q}}(\omega)\, S_{\mathbf{k}\mathbf{k}'}^{\mathbf{q}} \simeq \Delta_{\mathbf{k}\mathbf{k}'}^{0}(\omega + \tfrac{1}{2}(\mathbf{v}_{\mathbf{k}} + \mathbf{v}_{\mathbf{k}'})\cdot\mathbf{q})\, S_{\mathbf{k}\mathbf{k}'}^{0}. \tag{45}$$

To this approximation (39) is generalized, in terms of $f(\hbar\mathbf{k}, \mathbf{r}, t)$, by making the substitution

$$f(\hbar\mathbf{k}, \mathbf{r}, t') \rightarrow f(\hbar\mathbf{k}, \mathbf{r} + \tfrac{1}{2}(\mathbf{v}_{\mathbf{k}} + \mathbf{v}_{\mathbf{k}'})(t' - t), t'), \tag{46}$$

and similarly for $f(\hbar\mathbf{k}', \mathbf{r}, t')$, in the integral on its right-hand side. In so far as the $t - t'$ values $\lesssim 1/\omega_{\mathbf{k}}$ contribute significantly to this integral,[3,20] then the term added to $\mathbf{r}$ amounts to displacements of the order of magnitude of the electron de Broglie wavelengths in the Bloch scheme, and so is associated with the "wavepacket" uncertainty in the electron positions.[20]

Correction terms

The retention of the contribution from C' in (24) leads to additional terms in (26). When the matrix elements of C' are estimated from the formulas

$$(\rho^{(0)}e^{i\mathbf{q}\cdot\mathbf{r}} - e^{i\mathbf{q}\cdot\mathbf{r}}\rho^{(0)})_{\mathbf{k}\mathbf{k}'} = (\mathbf{k}' + \mathbf{q} \mid \mathbf{k}')\,\rho^{(0)}_{\mathbf{k},\mathbf{k}'-\mathbf{q}} - (\mathbf{k} \mid \mathbf{k} - \mathbf{q})\,\rho^{(0)}_{\mathbf{k}-\mathbf{q},\mathbf{k}'} \tag{47}$$

and

$$\rho^{(0)}_{\mathbf{k}\mathbf{k}'} \simeq (\rho^{(0)}_{\mathbf{k}} - \rho^{(0)}_{\mathbf{k}'})H'_{\mathbf{k}\mathbf{k}'}/\hbar\omega_{\mathbf{k}\mathbf{k}'}, \tag{48}$$

these additional terms are equal to $\phi^{\mathbf{q}}$ times a sum over $\rho^{(0)}_{\mathbf{k}}$ and the $\rho^{(0)}_{\mathbf{k}'}$. For simplicity, only the result for the limit $q \rightarrow 0$ is given here. In this limit the addition is just equivalent to a changed value of $C_{\mathbf{k}}^{\mathbf{q}}$, as follows:

$$C_{\mathbf{k}}^{\mathbf{q}} \rightarrow C_{\mathbf{k}}^{\mathbf{q}} - \frac{1}{\hbar^2}\sum_{\mathbf{k}'} H'_{\mathbf{k}\mathbf{k}'}H'_{\mathbf{k}'\mathbf{k}}\left(\frac{1}{\omega + \omega_{\mathbf{k}\mathbf{k}'} - i\chi} + \frac{1}{\omega + \omega_{\mathbf{k}'\mathbf{k}} - i\chi}\right)\frac{(C_{\mathbf{k}}^{\mathbf{q}} - C_{\mathbf{k}'}^{\mathbf{q}})}{\omega_{\mathbf{k}\mathbf{k}'}}. \tag{49}$$

Then the imaginary part of $\delta C/C$ is of order $(\hbar/\epsilon_{\mathbf{k}})$ times the scattering frequency. The real part is similarly small, and vanishes when $\omega \rightarrow 0$.

We have also overlooked Ω, in Eq. (26), so far. By

inspection of (29) it is evident that Ω is zero if the matrix elements $H'_{\mathbf{k}\mathbf{k}'}$ do not vary with $\mathbf{k}$, $\mathbf{k}'$, and otherwise is zero when $\mathbf{q} = 0$ and proportional to q when the latter is small compared to the dimensions of the Fermi surface; and that the components of Ω which cancel when $q = 0$ have imaginary parts like the scattering frequency and real parts like its principal-part companion in (26). Thus the real part of $\Omega^{\mathbf{q}}_{\mathbf{k}}$ is like a correction to $\omega^{\mathbf{q}}_{\mathbf{k}}$ from the $\mathbf{k}$ dependence of the perturbation of the Bloch state energy to second order in H', with its imaginary part representing the inverse lifetimes of the states to the same order.[21]

Note added in proof

Two current publications contain treatments of the Boltzmann equation for nonzero q and ω: S. Fujita, *Introduction to Non-Equilibrium Quantum Statistical Mechanics*, W. B. Saunders Co., Philadelphia, 1966 (see especially Section 7.5); the chapter by P. N. Argyres in *Lectures in Theoretical Physics*, Vol. 8a, University of Colorado Press, 1966, in press (see especially Section 6C). K. Yamada, *Prog. Theor. Phys.* 28, 299 (1962) gives a comparable analysis in terms of the two-electron correlation function.

Footnotes and references

1. Effects of a static or slowly varying magnetic field and of a weak space gradient of crystal lattice parameters are given by terms in the Boltzmann equation which have been omitted from (1).
2. In the general equation, $\mathbf{p}$ and $\mathbf{p}'$ wherever they occur in (1) are accompanied by band and spin indexes, and the integration on the right is accompanied by the corresponding summation. These are omitted here for simplicity, and may be restored to the analysis and results in the obvious way. The quantum generalization can involve other interband effects, as will be indicated.
3. W. Kohn and J. M. Luttinger, *Phys. Rev.* **108**, 590 (1957); J. M. Luttinger and W. Kohn, *Phys. Rev.* **109**, 1892 (1958).
4. D. A. Greenwood, *Proc. Phys. Soc.* **71**, 585 (1958).
5. P. N. Argyres, *J. Phys. Chem. Solids* **19**, 66 (1961).
6. A. Hasegawa and J. Yamashita, *J. Phys. Chem. Solids* **23**, 875 (1962).
7. R. B. Thomas, Jr., scheduled for publication in *Phys. Rev.* **151** (1966).
8. Time dependence is discussed in Appendix D of the first of Refs. 3. Equation (D6) is essentially Eq. (39) here. The final term of D(17) corresponds to, but does not agree with, Eq. (37) here.
9. See Appendix F of the first of Refs. 3.
10. We are omitting interband matrix elements of H.
11. This particular form is of course used because it corresponds to the formalism introduced by E. Wigner, *Phys. Rev.* **40**, 749 (1932), for the distribution in position and momentum. In the present connection see, for example, §4 of Ref. 20. The subscripts are to be read as $\mathbf{k} \pm \frac{1}{2}\mathbf{q}$.
12. The H^I matrix elements in $\Sigma H^I \exp(-2i\mathbf{q}\cdot\mathbf{R}_I)$ are of order $1/V$, and so their sum (without the exponential factors) is of order N_I/V, where V is the normalization volume and N_I is the number of scatterers. With the exponential factors included, the variance of the sum (that is, the squared modulus, averaged over a random distribution of scatterer positions) is only of order N_I/V^2–in effect, is zero: This fact provides assurance that we may drop the $\rho^{-\mathbf{q}}$ terms of (23). The corresponding coefficient of the $\rho^{-\mathbf{q}}$ term coming from (24) has a product of two H^I elements in the I'th term of the sum, and hence if it were summed without the exponential factors the result would be of order N_I/V^2, and therefore of order N_I/V after the accompanying summation over wavevector $\mathbf{k}'$. Then this contribution also effectively vanishes on account of random-phase cancellation of the exponential factors.

    The situation for the (I, J) contribution from products of two matrix elements of H', such as (27), is somewhat different. (See page 594 of Ref. 3, Appendix B of Ref. 4.) The sum of the (I, I) terms of the product of H' elements is of order N_I/V^2; and the sum of the (I, J) terms, discarded in (30), has a variance of order $(N_I/V^2)^2$. Thus, this product oscillates violently when the scatterers are, conceptually, moved around. However, the quantity which enters into (26) is a sum, over $\mathbf{k}'$, of this matrix-element product times a slowly varying function of $\mathbf{k}'$. For this sum, while the (I, I) contribution is of order N_I/V, the (I, J) contribution has a variance only of order N_I/V^2. (One may realize this reduction by a factor of $1/N_I$ in a simple way by averaging the summand over a sphere $k' = \text{const.}$, with factors other than the exponentials assumed constant on the sphere. Then $\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{IJ}]$ becomes $\exp(i\mathbf{k}\cdot\mathbf{R}_{IJ})[\sin(k'\cdot R_{IJ})/k'R_{IJ}]$ so only pairs of scatterers with $R_{IJ} \lesssim 1/k'$ contribute substantially.)

    If the (I, J) contribution were included in (26), the solution would depend slightly on the configuration of scatterer positions. The scatterer-pair addition to (26), in turn operating on this configuration-dependent part of $\rho^{\mathbf{q}}$, would give a result having a nonzero average over configurations. The requirement that this average be a negligible addition to (26)—a reasonable basis for discarding the (I, J) terms—is, obviously, essentially the same as the preceding variance criterion.
13. The analogs of these two contributions appear in the theory of the conductance of a tunnel junction at nonzero frequency; the principal-part term contributes to the capacitance.
14. This gives the general result for "free carrier" optical absorption $\sim\lambda^2$. See H. J. G. Meyer, *Phys. Rev.* **112**, 298 (1958); W. P. Dumke, *Phys. Rev.* **124**, 1813 (1961).
15. When the "diffusion" term of (1) is appreciable, then for the quasi-classical limit $\hbar\omega \to 0$ there is a solution in terms of the scattering time when the scattering matrix element depends on the energy only (though it is not of as simple a form as for $q = 0$). For appreciable $\hbar\omega$ a more complicated integral equation (with the energy as variable) is involved.
16. In this connection see A. Ron, *Phys. Rev.* **131**, 2041 (1963).
17. Compare the context of Footnote 14. For an ultrasonic wave the first term of Eq. (44) already gives a dissipative component of the current, contributed by its poles to the sum (41) through the second term of (31). This dissipation which exists for vanishing scattering frequency is the Landau damping. At appreciable scattering frequencies, the poles of $\rho^{\mathbf{q}}_{\mathbf{k}}$ are displaced from those of the first term of (44) (the expansion (44) is of course not valid in the neighborhood of the poles). The magnitude of the dissipation is changed by the scattering, in particular when q times the mean free path is not $\gg 1$.
18. This might be attained with an ultrasonic wave in bismuth or graphite, for example. In semimetals such as bismuth one set of intraband $C^{\mathbf{q}}$'s (for the completely full or completely empty band) will be zero.
19. For an optical driving field also, one may describe the response by such equations. The interband elements are "vertical" (q is virtually zero); and they will become dominant as the absorption-edge frequency is approached. Another application possibly is to magneto-conductivity in the Landau sub-bands.
20. G. V. Chester, *Proc. Phys. Soc.* **81**, 938 (1963).
21. Compare the discussion of Eq. (98) in the first of Refs. 3.

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