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Quantum Mechanical Formulation of Boltzmann Transport Equation

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A quantum mechanical formulation of the Boltzmann transport equation by using a density matrix is described. The relaxation time is not included in an *ad hoc* manner but is obtained in a natural way in the development of the transport equation. Starting from the formal manipulation of the density matrix, the theory emphasizes various approximations needed to formulate a transport equation of the Boltzmann type. This density matrix is then used to find the expectation value of the current operator and hence the electric conductivity. Some applications of the formalism are suggested.

Electronic transport in the absence of a magnetic field or in a low magnetic field is conveniently described by using the semi-classical Boltzmann transport equation (*see*, for example, Nag 1972). This transport equation is a familiar "gain–loss" equation for the distribution function f:

$$\left.\frac{\partial f}{\partial t}\right|_{\text{fields}} + \left.\frac{\partial f}{\partial t}\right|_{\text{collisions}} = 0 \qquad (1)$$

where the first term is the drift term and the second is the collision term. Classical arguments have been used to obtain explicit expressions for the two terms. Although successful, the Boltzmann transport equation has implicit in it many assumptions which are not always satisfied. A review paper by Dresden (1961) discusses in detail various assumptions and approximations implicit in the Boltzmann transport equation, including the relaxation time approximation, which are not always satisfied. Classical arguments are not valid in the domain where quantum effects are important (*see*, for example, Arora 1976). Arora and co-workers (Arora 1975; Arora

1976; Arora and Miller 1974; Arora and Peterson 1975) have shown the inadequacy of the Boltzmann transport equation for problems involving a magnetic field. Kohn and Luttinger (1956) emphasize that the familiar Boltzmann transport equation is valid in the limiting case of very weak or very dilute scatterers. They use the density matrix to investigate the electronic transport corrections which are of higher orders in the scattering interaction. Price (1966) has used the method of Kohn and Luttinger (1956) to obtain a generalized Boltzmann transport equation, for electrons in solids, when the driving field has nonzero wavevector as well as frequency. By means of this equation, the behaviour of the electrons in response to the field may be followed from the quasi-classical limit to the quantal limit at large rates of change. In the work of Arora and Qureshi (1976), a frequency dependent relaxation time is obtained and included in a generalized transport equation. These works suggest very strongly the need of a more basic approach starting from the basic principles of quantum and statistical mechanics.

Quantum statistical theory has been extensively used in the linear transport theory of Kubo (1956), Hubermann and Chester (1975), Edwards (1958, 1965), Greenwood (1958), Sigel and Argyres (1969, 1970), and Argyres (1961). Kohn and Luttinger (1956) and Greenwood (1958), have derived the linearized inhomogeneous equation from first principles as a consequence of the Liouville's equation for density matrix. Magnetic corrections to the Boltzmann transport equation have been derived by Thomas (1966). Theory of Kohn and Luttinger has been extended by Argyres (1961) to include inelastic electron scattering by absorption and emission of phonons. Sigel and Argyres (1969, 1970) consider the case of an electric field of arbitrary $\mathbf{q}$ and ω and derive the coefficients of the quantum transport equation in powers of the impurity density and for arbitrary strength of the one-impurity potential. No application of their formalism to the problems of physical interest is given.

The formal linear transport formula or the density matrix found in literature offer very little in the derivation of transport coefficients. The expansion of the linear response formula for the electric conductivity in terms of the strength of the scattering potential resulted in divergence. An alternative was thought to use a resistivity formula. This resulted in conflicting results. Huberman and Chester (1975) review in detail these quantum mechanical attempts. They have explicitly shown that the conflict between resistivity and conductivity formula could be resolved provided the infiinite number of divergent terms in the expansion are summed. In concluding the work, they strongly suggest the development of an alternative procedure similar to Van Hove's "V^2t limit" technique (1955).

Arora and Peterson (1975) by extending the scattering dynamics beyond the strict Born approximation have developed a formalism equivalent to Van Hove's technique. An application of this formalism to elastic electron acoustic phonon scattering

has already been communicated in a short note (Arora and Gomber 1976). The purpose in this paper is to formulate the theory of electric conductivity starting from the quantum statistical density matrix equation and exhibit clearly the approximations which are needed to derive the more complete Boltzmann transport equation.

Basic Formulation

The system under consideration consists of a number of independent mobile electrons in interaction with a scattering system, taken to be optical or acoustical phonons, or impurity interaction or any combination of them. The Hamiltonian of a single electron in the presence of a perturbing electric field **E**, turned on at time $t = -\infty$ can be written as

$$H = H_0 + H'(t), \tag{2}$$

with

$$H_0 = H_e + H_L, \tag{3}$$

$$H_0 = p^2/2m^*, \tag{4}$$

$$H' = V + Fe^{st} = V + e\mathbf{E} \cdot \mathbf{r}\, e^{st}, \tag{5}$$

where H_0 is the unperturbed Hamiltonian consisting of an electronic part H_e and a lattice part H_L; H' is the lattice Hamiltonian consisting of electron-lattice interaction V and electron-electric field interaction $F = e\mathbf{E} \cdot \mathbf{r}$ s is a small positive number ($s \to O^+$) which describes the slow switching on of the electric field at time $t = -\infty$. The steady state Hamiltonian is obtained by taking the limit $s \to O^+$. The electric field is assumed to be small in the Ohmic limit. This provides the convenience of making the electronic distribution uniform in the absence of a perturbation. At high fields when spatial distribution of carrier gas is non-uniform and electric field cannot be treated small, a different formulation is required (Weismann 1976).

For large samples and weak perturbation, **p** commutes with the Hamiltonian. Then, **p** or $\mathbf{k} = \mathbf{p}/\hbar$ can be taken as constants of motion. In that case, the electronic state can be well represented by a plane wave-function

$$|\mathbf{k}> = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{6}$$

where V is the volume of the crystal, and **k** stands for (k_x, k_y, k_z). For strong perturbations, *i.e.* large electric fields (hot electrons) and strong electron lattice interactions, (k_x, k_y, k_z) do not make a good set of quantum numbers. For example,

electronic wave functions are Bessel functions instead of plane waves for strong electric fields.

In the absence of perturbation, the electronic state is well characterized by a wave-function of the form given by (6). But, in the presence of perturbation, we loose the preciseness of the electronic state, necessitating an expansion of the wave-function Ψ^i of the ith electron in terms of an orthonormal set of wave-functions of the type given by (6):

$$\Psi^i(t) = \sum_{\mathbf{k}} a_k^i(t)|\mathbf{k}\rangle, \tag{7}$$

where $|a_k^i(t)|^2$ is the probability of finding an electron in electronic state $|\mathbf{k}\rangle$ after perturbation is switched on. The N-electron ensemble average $\langle \mathbf{J} \rangle$ of the electron current operator $\mathbf{J}_{\text{op}}$ can then be written as

$$\begin{aligned}\langle \mathbf{J} \rangle &= \frac{1}{N} \sum_i \langle \Psi^i | \mathbf{J}_{\text{op}} | \Psi^i \rangle, \\ &= \sum_{k,k'} \langle k|\rho|k'\rangle \langle k'|\mathbf{J}_{\text{op}}|\mathbf{k}\rangle = \text{Tr}\,(\rho \mathbf{J}_{\text{op}}),\end{aligned} \tag{8}$$

with

$$\langle k|\rho|k'\rangle \equiv \frac{1}{N} \sum_i a_k^i(t) a_{k'}^{i*}(t). \tag{9}$$

The time-dependence of $a_k^i(t)$ can be obtained from the time-dependent Schrodinger equation for $\Psi^i(t)$ by using the orthonormality of plane wave-functions k:

$$i\hbar \frac{\mathrm{d}a_k^i}{\mathrm{d}t} = \sum_{k'} \langle k|H'|k'\rangle a_{k'}^i(t). \tag{10}$$

The time-dependence of the density matrix of Eq. (9) then immediately follows:

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{i}{\hbar}(\rho H - H\rho) \equiv \frac{i}{\hbar}[\rho, H]. \tag{11}$$

In order to solve this equation, we separate the density matrix into an equilibrium part and a time-dependent non-equilibrium part:

$$\rho = \rho_0 + \rho' e^{st}, \tag{12}$$

where ρ_0 is the uniform density-matrix independent of an electric field. The matrix elements of ρ_0 are Fermi–Dirac distribution functions:

$$\langle k'|\rho_0|k\rangle = f_k \delta_{k'k} = [e^{(E_k - \zeta)/k_B T} + 1]^{-1} \delta_{k'k}, \tag{13}$$

where

$$E_k = \hbar^2 k^2 / 2m^* \tag{14}$$

are the unperturbed energy levels. ζ is the Fermi energy evaluated from the normaliz-

ation condition

$$\sum_k \langle k|\rho_0|k\rangle = N. \tag{15}$$

For an electric field applied in the x-direction, the substitution of Eq. (12) in Eq. (11) results in a coupled equation

$$\begin{aligned}(E_{k'k} - i\hbar s)\langle k'|\rho'|k''\rangle = &\frac{-i\hbar^2}{m^*}\frac{\mathrm{d}f}{\mathrm{d}E_k} eEk_x\delta_{k'k} \\ &+ f_{k'k}\langle k'|V|k\rangle\, e^{-st} \\ &+ \langle k'|[\rho', H']|k\rangle,\end{aligned} \tag{16}$$

with

$$E_{k'k} = E_{k'} - E_k, \tag{17}$$

$$f_{k'k} = f_{k'} - f_k. \tag{18}$$

This equation is usually solved by a linearization procedure (*see*, for example, discussion by Huberman and Chester 1975). According to this procedure, $[\rho', H']$ is neglected on the basis that this contains higher order terms. This linearizes ρ' in terms of F and V. The higher order terms are then generated by an iteration process giving an infinite series to be summed for $\langle k'|\rho'|k\rangle$. As discussed by Huberman and Chester (1975), this expansion is the cause of divergence difficulty encountered by several workers. To avoid this divergence difficulty and get the results for $\langle k'|\rho'|k\rangle$ in the summed form, we follow the procedure outlined earlier (Arora and Gomber 1976) and solve Eq. (16) formally as

$$\langle k'|\rho'|k\rangle = \frac{-i\hbar^2/m^*(\mathrm{d}f/\mathrm{d}E_k)eEk_x + f_{k'k}\langle k'|V|k\rangle\, e^{-st} + \langle k'|[\rho', H']|k\rangle}{E_{k'k} - i\hbar s}, \tag{19}$$

which can be used in the last term of Eq. (16) to get an expanded form of the coupled equation for matrix elements of ρ':

$$\begin{aligned}&(E_{k'k} - i\hbar s)\langle k'|\rho'|k\rangle \\ &\quad = -\frac{i\hbar^2}{m^*}\frac{\mathrm{d}f}{dE_k} eEk_x\delta_{k'k} + f_{k'k}\langle k'|V|k\rangle\, e^{st} \\ &\qquad + \sum_{k''}\frac{(-i\hbar^2/m^*)(\mathrm{d}f/\mathrm{d}E_{k'})eEk'_x\delta_{k'k''} + f_{k'k''}\langle k'|V|k''\rangle e^{-st} + \langle k'|[\rho', H']|k''\rangle}{E_{k'k''} - i\hbar s} \\ &\qquad \times\langle k''|H'|k\rangle - \sum_{k''}\langle k'|H'|k''\rangle \\ &\qquad \times\frac{(-i\hbar^2/m^*)(\mathrm{d}f/\mathrm{d}E_k)eEk_x\delta_{kk''} + f_{k''k}\langle k''|V|k\rangle e^{-st} + \langle k''|[\rho', H']|k\rangle}{E_{k''k} - i\hbar s}.\end{aligned} \tag{20}$$

This iteration procedure can be continued further. But at this iteration we see the terms of the form $\rho' VV$-type in Eq. (20), which describe the collision effect with the lattice. If we use the Fourier expansion $V = \sum_q V_q \, e^{iq \cdot r}$ of the scattering potential, in taking the ensemble average, all first order terms in V drop out. Thus, only the electric field part of H' drives the non-equilibrium density matrix elements of interest. Secondly, for the large class of scattering interactions we can use the property:

$$\sum_{k''} g(k, k', k'')\langle k|V|k''\rangle\langle k''|V|k'\rangle = 0, \quad \text{unless } k = k', \tag{21}$$

where $g(k, k', k'')$ is an arbitrary function. In those terms, where the matrix elements of ρ' are sandwiched between those for V, *i.e.* the terms of the type $\langle k'|V|k''\rangle \langle k''|\rho'|k'''\rangle\langle k'''|V|k\rangle$, we can use the fact that $\langle k''|\rho'|k'''\rangle \alpha k_x'' \delta_{k''k'''}$ in the lowest order approximation. Since we are dealing with currents in the Ohmic limit linear in an electric field, we neglect all the higher order terms in the electric field interaction. Finally we use the identity

$$\lim_{s \to 0} 1/(x - is) = P(1/x) + i\pi\delta(x), \tag{22}$$

where P is the principal part. For elastic scattering process, the contribution of the principal part to the electronic current vanishes. But, for inelastic scattering process, the principal part provides a small second order perturbation correction to energy levels E_k. If this correction is neglected, the use of the procedure outlined above results in a simplified expression for $\langle k'|\rho'|k\rangle$:

$$E_{k'k}\langle k'|\rho'|k\rangle = -\frac{i\hbar^2}{m^*}\frac{df}{dE_k} eEk_x\delta_{k'k} + \frac{i\hbar}{\tau_k}\langle k'|\rho'|k\rangle, \tag{23}$$

$$\tau_k^{-1} = \frac{2\pi}{\hbar}\sum_{k''}(1 - k_x''/k_x)|\langle k|V|k''\rangle|^2\delta(E_{kk''}). \tag{24}$$

The last term in Eq. (23) is equivalent to summing an infinite series and is equivalent to the technique mentioned earlier (Van Hove 1955; Hubermann and Chester 1975). The presence of $(1 - k_x''/k_x)$ in (24) describes the anisotropic nature of the scattering and is important, especially for impurity scattering. For any scattering interaction which is an even function of k'', the anisotropic part involving k_x'' in Eq. (24) vanishes. Eq. (23) can be easily solved for the matrix elements $\langle k'|\rho'|k\rangle$ to give

$$\langle k'|\rho'|k\rangle = \frac{\hbar e}{m^*}\frac{df}{dE_k} Ek_x\tau_k\delta_{k'k}. \tag{25}$$

This non-equilibrium part of the density matrix which is diagonal in plane-wave representation is equivalent to the non-equilibrium Boltzmann transport function.

Applications

As an application of the above formalism, we evaluate the expectation value of the current operator $\mathbf{J}_{op} = -e\mathbf{p}/m^*$ using the recipe given by Eq. (8). The matrix elements of $\mathbf{J}_{op}$ in the plane-wave representation are diagonal:

$$\langle k'|\mathbf{J}_{op}|k\rangle = -\frac{e\hbar\mathbf{k}}{m^*}\,\delta_{k'k}. \tag{26}$$

The ensemble average of the electric current is then given by

$$\langle \mathbf{J}\rangle = -e^2 \sum_{\mathbf{k}} \frac{df}{dE_k}\,\frac{\hbar^2 k_x^2}{m^{*2}}\,\tau_k E. \tag{27}$$

The electric conductivity σ in the Ohmic limit is then the coefficient of E on the left-hand side of Eq. (27):

$$\sigma = -e^2 \sum_{\mathbf{k}} \frac{df}{dE_k}\left(\frac{\hbar k_x}{m^*}\right)^2 \tau_k. \tag{28}$$

For isotropic crystals, since $\langle k_x^2\rangle = \langle k_y^2\rangle = \langle k_z^2\rangle = \frac{1}{3}\,k^2$, we can rewrite this expression as

$$\sigma = -\frac{e^2}{3} \sum_{\mathbf{k}} \frac{df}{dE_k}\left(\frac{\hbar k}{m^*}\right)^2 \tau_k. \tag{29}$$

For strongly degenerate electrons df/dE_k behaves like a delta function:

$$\frac{df}{dE_k} = -\delta(E_k - \zeta). \tag{30}$$

In that case, expression (29) becomes

$$\sigma = N e^2 \tau / m^*, \tag{31}$$

which is the classical result.

For non-degenerate electons, the derivative of f with respect to energy is given by

$$\frac{df}{dE_k} = -e^{(\zeta - E_k)/k_B T}/k_B T, \tag{32}$$

where ζ could be found from Eq. (15).

Converting summation to integration by $\sum_{\mathbf{k}} \to \frac{V}{(2\pi)^3}\int dk_x\, dk_y\, dk_z$, and using Eq. (15), we get the familiar result (*see*, for example, Conwell 1967)

$$\sigma = Ne^2\pi\hbar^4\rho u^2/3(2\pi m^* k_B T)^{1/2} m^{*2} E_1^2 k_B T, \tag{33}$$

for elastic acoustic-phonon scattering for which

$$\tau_k^{-1} = (\sqrt{2}\, E_1^2 m^{*3/2} k_B T / \pi \rho u^2 \hbar^4) E_k^{1/2}, \tag{34}$$

where E_1 is the deformation-potential constant. This is in agreement with the result obtained from the Boltzmann transport equation with *ad hoc* insertion of τ_k.

As another application, we suggest the inelastic acoustic-phonon scattering, where energy of the phonon is not neglected compared to the energy of an application. In that case, even the principal term of Eq. (22) will also contribute to conductivity. This is especially important in electronic transport at low temperature and will be discussed in a separate communication.

For non-linear effects, where electron electric field interaction cannot be treated small, as has been discussed in the previous section, plane wave representation cannot be used, as **k** is not a constant of motion. Moreover, the term involving $[\rho', F]$ in Eq. (20) cannot be neglected. This interesting area of "hot electron effects" can also be studied in the framework of the above formalism.

For polar semiconductors, where the selection rule of Eq. (21) is not valid, the decoupling of Eq. (20) for matrix elements $\langle k'|\rho'|k\rangle$ warrants special attention. These are some of a few suggested applications where the above formalism may be successfully applied.

Conclusion

A quantum-mechanical formulation of the density matrix for studying the electronic transport properties is described. For the special case of elastic acoustic-phonon scattering, the theory is found to be equivalent to the Boltzmann transport equation approach. No *ad hoc* insertion of relaxation time was made in the theory. No divergence difficulty (*see*, for example, Huberman and Chester 1975 and references therein) is encountered because by avoiding the linearization procedure, we have summed the perturbation series in a natural way. Some application of theory are suggested.

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الصياغة الكمومية لمعادلة بولتزمان للنقل

فيجي أرورا

قسم الفيزياء ـ كلية العلوم ـ جامعة الملك سعود ، الرياض ، المملكة العربية السعودية

نصف في هذا البحث صياغة كوانتومية لمعادلة بولتزمات النقلية وذلك باستخدام مصفوفة الكثافة . يمكننا الحصول على زمن « الاسترخاء » بطريقة طبيعية من تطوير معادلة النقل . ابتداءا بالمعالجة الشكلية لمصفوفة الكثافة تعتني نظريتنا بدراسة وسائل تقريبية مختلفة للحصول على معادلات نقل من نوع بولتزمان . نستخدم مصفوفة الكثافة لايجاد القيمة المتوقعة لمؤثر التيار ومن ثم التوصيلية الكهربائية ثم نقترح بعد ذلك عددا من التطبيقات لصياغتنا هذه .