

Electrical Conductivity, Boltzmann Equation, Neumann Equation and Variation Principles

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Electrical conductivity (or transport coefficient) is formulated on the basis of the Boltzmann-Bloch equation and also of the Neumann equation. Concerning this a variation principle for each equation is presented, which illuminates the basis of irreversibility. Contraction of the irrelevant information on the even component of the density matrix as to time reversal operation converts the stationarity problem in the variation principle based on the Neumann equation into the extremum problem of the same type as in the variation principle based on the Boltzmann equation. For such a gas system as conduction electrons in solids, the former can be completely reduced to the latter, which are understandable from the chaos-theoretical viewpoint.

§1. Introduction

The formulae for electrical conductivity is obtained as time integral of the temporal auto-correlation of electric current density j expressed as an inner product $(j(t), j)$ based on the Boltzmann-Bloch equation (dynamical stage) and also on the Neumann equation (dynamical stage), in which $j(t)$ obeys the respective basic equations of motion. For the dynamical system

exhibiting the so-called sensitivity on initial condition, the formula in dynamical stage can be reduced to the type of that in kinetic stage. Variation principles are helpful for understanding this reduction.

In §2 the kinetic theory based on the Boltzmann-Bloch equation is developed to derive the formula. Similarly, in §3 the dynamical theory is presented on the basis of the Neumann equation. In §4 the variation principle in the kinetic theory is presented as an extremum problem, with its thermodynamical meaning. In §5 the variation principle in the dynamical theory is presented as a stationarity problem. In §6 this stationarity problem is converted into an extremum problem of the same type as in the kinetic case, by contracting irrelevant informations on the even component with respect to time reversal operation and some concluding remarks are given.

§2. Formula in the kinetic stage

In the traditional theory, the electrical conductivity of a conducting system is calculated on the basis of the Boltzmann-Bloch equation^{1) 2) 3) 4)}. The distribution function $f(p, r, t)$ for the conduction electrons with electric charge e and effective mass m obeys the so-called Boltzmann-Bloch equation as a function of the momentum p , space coordinate r and time t . In the presence of an applied electric field E it is expressed as

$$\frac{\partial f}{\partial t} = \left[\frac{\partial f}{\partial t} \right]_D + \left[\frac{\partial f}{\partial t} \right]_C. \quad (2.1)$$

The first contribution

$$\left(\frac{\partial f}{\partial t} \right)_D = -eE \cdot \frac{\partial f}{\partial p} - \frac{p}{m} \cdot \frac{\partial f}{\partial r}. \quad (2.2)$$

is the drift term giving a systematic change. In the linear approximation with external disturbance, f can be replaced with the Fermi distribution $f_0 = 1/[e^{\beta(\epsilon - \mu)} + 1]$, where β and μ are the inverse local temperature and the local chemical potential, respectively. Then the drift term (2.2) can be rewritten as

$$\left(\frac{\partial f}{\partial t} \right)_D = - \frac{\partial f_0}{\partial \epsilon} [j(k) \cdot X_1 + q(k) \cdot X_2], \quad (2.3)$$

where the currents and the generalized forces are given, respectively, by

$$j(k) = e\hbar k/m, \quad q(k) = \hbar(\epsilon_k - \mu)k/m, \quad (2.4)$$

$$X_1 = E + \nabla \mu / e, \quad X_2 = -(\nabla T)/T. \quad (2.5)$$

The second contribution in (2.1) is called the collision term which is due to the scattering processes experienced by the electrons. We confine ourselves to the electron-phonon system. By introducing an auxiliary distribution function $\phi(k, t)$ via

$$f = f_0 - \frac{\partial f_0}{\partial \epsilon} \phi \quad (2.6)$$

in the time-dependent perturbation theory, the collision term in the linear approximation as to ϕ is obtained as⁴⁾

$$\left(\frac{\partial f}{\partial t} \right)_C = \frac{\partial f_0}{\partial \epsilon} L\phi, \quad (2.7)$$

where L is the collision operator defined by

$$L\phi(k) = \sum_k \frac{2\pi}{\hbar} |\langle k|V|k' \rangle|^2 \delta(\varepsilon - \varepsilon') (\phi - \phi'), \quad (2.8)$$

$$L\phi(k) = \sum_k \frac{4\pi}{\hbar} \alpha^2 |q| n_0 \left[\frac{1-f_0'}{1-f_0} \delta(\varepsilon' - \varepsilon - \omega) + \frac{f_0'}{f_0} \delta(\varepsilon' - \varepsilon + \omega) \right] (\phi - \phi'), \quad (2.9)$$

for the scatterings of electrons due to impurities and to lattice phonons, respectively, where $\varepsilon \equiv \varepsilon_k$, $\varepsilon' \equiv \varepsilon_{k'}$, $f \equiv f(k, t)$, $f' \equiv f(k', t)$, $\phi \equiv \phi(k, t)$, $\phi' \equiv \phi(k', t)$ and $\langle k|V|k' \rangle$ is the matrix element of the perturbing potential V due to the impurities. The distribution function of phonon with wave number $q = k' - k$ in thermal equilibrium is represented as the Planck distribution function $n_0(\omega_q) = 1/[e^{\beta \hbar \omega} - 1]$. The parameter α is given in terms of the so-called Sommerfeld-Bethe constant C by

$$\alpha = \left(\frac{2\hbar}{9NM_s} \right)^{1/2} C, \quad (2.10)$$

where N is the number of lattice ions of mass M per unit volume. Inserting (2.3) and (2.7) in (2.1), we get

$$\partial\phi/\partial t + L\phi = X, \quad X \equiv j(k) \cdot X_1 + q(k) \cdot X_2. \quad (2.11)$$

Averaging (2.4) as to the distribution function (2.6), we get the electric and heat current densities, respectively, as

$$J = \sum_k f(k) j(k) = (\phi, j) = (j, \phi), \quad (2.12)$$

$$Q = \sum_k f(k) q(k) = (\phi, q) = (q, \phi), \quad (2.13)$$

where we have defined the inner product as

$$(\phi, \psi) = (\psi, \phi) = -\sum_k \frac{\partial f_0(\epsilon)}{\partial \epsilon} \phi(k) \psi(k). \quad (2.14)$$

The steady state solution of (2.11) can be expressed as

$$\phi = X_1 \cdot \phi_1 + X_2 \cdot \phi_2, \quad (2.15)$$

with the use of ϕ_1 and ϕ_2 satisfying

$$L\phi_1 = j_1, \quad L\phi_2 = j_2, \quad (j_1 \equiv j, j_2 \equiv q). \quad (2.16)$$

Substituting the solutions of (2.16) in (2.12,13), we get

$$J_m = \sum_n L_{mn} X_n, \quad (J_1 \equiv J, J_2 \equiv Q), \quad (2.17)$$

for an isotropic or cubic system, where

$$L_{mn} = (\phi_m, L\phi_n) = \int_0^\infty (j_m(t), j_n) dt = L_{nm} \quad (m, n=1, 2), \quad (2.18)$$

satisfies Onsager's reciprocity relation,⁶⁾ and

$$j_m(t) = \exp(-Lt) j_m. \quad (2.19)$$

As a special case, the electrical conductivity is written as

$$\sigma = \int_0^\infty (j(t), j) dt, \quad (2.20)$$

where for an orthogonal component of electric current density j

$$j(t) = \exp(-Lt) j. \quad (2.21)$$

§3. Formula in the the Dynamical Stage

The density matrix $\rho(t)$ for the system exposed to an external electric field $E(t)$ obeys the Neumann equation,^{4), 5)}

$$i\hbar \frac{\partial \rho}{\partial t} = [H - P \cdot E(t), \rho], \quad (3.1)$$

where H and P are the Hamiltonian and polarization operator, respectively. We solve this as

$$\rho(t) = \rho_0 + \rho_1(t). \quad (3.2)$$

to the first order in the external field where ρ_0 denotes the grand canonical distribution $\rho_0 = K \exp[-\beta(H - \mu N)]$ in terms of a normalization constant and of the total number N of conduction electrons.

Generalizing ϕ in (2.6), we define an operator Φ by

$$\rho_1(t) = \int_0^\beta d\lambda \rho_0 \exp(\lambda H) \Phi(t) \exp(-\lambda H). \quad (3.3)$$

Substituting (3.2) into (3.1) with (3.3), we obtain

$$\partial \Phi / \partial t + \hat{L} \Phi = j \cdot E(t), \quad (3.4)$$

where a superoperator $\hat{L}$ is defined on the operator Φ by

$$\hat{L} \Phi = -i[H, \Phi] / \hbar, \quad (3.5)$$

and $j = i[H, P] / \hbar$ is the electric current density. The solution of (3.5) is written as

$$\Phi(t) = \int_0^\infty \exp(-i\hat{L}t) j dt, \quad (3.6)$$

for the field with unity strength, where j denotes the current density operator parallel to the field.

We define the inner product between a pair Φ and Ψ as⁴⁾

$$(\Phi, \Psi) = (\Psi, \Phi) = \int_0^\beta \text{Tr} \{ \Phi \rho_0 \exp(\lambda H) \Psi \exp(-\lambda H) \} d\lambda, \quad (3.7)$$

which is reduced to (2.26) by neglecting the electron-impurity and electron-phonon interactions in H . Substituting (3.2) with (3.3) into the average $\text{Tr}(\rho(t)j)$ of j , we obtain (2.20) again, where j should be read as the operator, the inner product is defined by (3.7) and the time dependence of $j(t)$ is given by

$$j(t) = \exp(-Lt)j = \exp(iHt/\hbar)j\exp(-iHt/\hbar). \quad (3.8)$$

§4. Kinetic Variation principle

The variation principle provides a powerful method to clarify the theoretical basis as well as facilitate the computation. With respect to the inner product (2.14) the collision operator L defined by (2.7) satisfies the relations⁴⁾

$$(\phi, L\psi) = (\psi, L\phi), \quad (4.1)$$

$$(\phi, L\phi) \geq 0, \quad (4.2)$$

for any pair of functions ϕ and ψ . Thus, the kinetic variation principle is presented as follows:^{7) 8) 9) 2) 3) 4)}

[I] Maximize the functional

$$(\psi, L\psi), \quad (4.3)$$

with respect to ψ under the condition

$$(\psi, L\psi) = (\psi, X). \quad (4.4)$$

[II] Maximize the functional

$$2(\psi, X) - (\psi, L\psi). \quad (4.5)$$

[III] Maximize the functional

$$\frac{(\psi, X)^2}{(\psi, L\psi)}. \quad (4.6)$$

The last one can be restated as a minimum principle for the reciprocal of (4.6). The solutions of [I], [II] and [III] all satisfy the linearized Boltzmann-Bloch equation (2.11) in the steady state. If X is merely due to the electric field, they give the Joule heat generated. The electrical conductivity is obtained for the unity field strength, whereas the minimum of the reciprocal of (4.6) gives the resistivity. By assuming $\psi = c j_x$ for the field directed in the x -axis, the electrical conductivity is obtained as the maximum with respect to a constant parameter c :

$$\sigma = \frac{(j_x, j_x)^2}{(j_x, L j_x)} = \frac{\hbar^2}{\pi k_B T} \frac{\langle j_x^2 \rangle}{\sum_{\omega} \langle [j_x, H'_{\omega}] [H'_{\omega}, j_x] \rangle \delta(\omega)} = \langle j_x^2 \rangle \tau, \quad (4.7)$$

where τ gives the mean free time and H'_{ω} is the Fourier component of the perturbation H' causing the scattering of electrons in the so-called interaction representation: viz.

$$\exp(iH_0 t/\hbar) H' \exp(-iH_0 t/\hbar) = \sum_{\omega} H'_{\omega} \exp(i\omega t). \quad (4.8)$$

where H_0 denotes the unperturbed Hamiltonian. we can obtain the well-known Grüneisen formula from (4.7).

The time derivative of the entropy of the electron system,

$$S = -k_B \sum_k f_k \ln f_k - (1-f_k) \ln(1-f_k), \quad (4.9)$$

is written as

$$\frac{S}{k_B} = \sum_k \frac{\partial f_k}{\partial t} \ln \left(\frac{f_k}{1-f_k} \right). \quad (4.10)$$

By inserting (2.2) and next (2.1) for $\partial f / \partial t$ in (4.10) and

retaining the external disturbance to the lowest order, contributions from the collision and drift terms are obtained as

$$\left[\frac{\partial S}{\partial t} \right]_C = \frac{(\phi, L\phi)}{T}, \quad (4.11)$$

$$\left[\frac{\partial S}{\partial t} \right]_D = - \frac{(\phi, X)}{T}, \quad (4.12)$$

respectively. The former is intrinsic to the system and is called the entropy production. The relation (4.2) implies the non-negativity of the entropy production (4.11). The requirement [III] means the principle of maximum entropy production in the steady state, whereas (4.12) should be minimized as the principle of least energy dissipation.⁴⁾

§5. Dynamical variation principle^{4), 12)}

For the Neumann equation (3.1), we assume two situations:

$$E(t) = E \exp(st) \quad (t < 0), \quad (5.1)$$

$$E(t) = E \exp(-st) \quad (t > 0), \quad (5.2)$$

where E is a constant electric field and s is a positive infinitesimal. In conformity with these, we assume

$$\lim_{t \rightarrow -\infty} \rho(t) = \rho_C, \quad \phi(t) = \phi^{(+)} \exp(st), \quad (5.3)$$

$$\lim_{t \rightarrow \infty} \rho(t) = \rho_C, \quad \phi(t) = \phi^{(-)} \exp(-st). \quad (5.4)$$

We must take into account these two situations simultaneously, in contrast with the kinetic variation principle based on the Boltzmann-Bloch equation described in §3, where we can discuss confining to either one case of (5.1) and (5.2). By substituting (5.1) to (5.4) into (3.4), we obtain

$$L_s \Phi^{(+)} = j \cdot E, \quad (5.5)$$

$$L_{-s} \Phi^{(-)} = j \cdot E, \quad (5.6)$$

where a superoperator L_s is defined on an operator Φ by

$$L_s \Phi = s\Phi + \hat{L}\Phi = s\Phi + i[H, \Phi]/\hbar. \quad (5.7)$$

As to the inner product (3.7), L_s satisfies the relation

$$(\Phi, L_s \Psi) = -(\Psi, L_{-s} \Phi). \quad (5.8)$$

The variation principle is presented as follows. Maximize

$$W(\Phi^{(+)}, \Phi^{(-)}) = 2(\Phi^{(+)} - \Phi^{(-)}, E \cdot j) - (\Phi^{(-)}, L_s \Phi^{(+)}), \quad (5.9)$$

as to $\Phi^{(+)}$ and $\Phi^{(-)}$. Then the solutions satisfy (5.5) and (5.6), respectively. The stationary value gives the Joule heat generated, which is reduced to the electrical conductivity for the field with unity strength. This corresponds to the type [II] in §4, and can also be readily rewritten in other types.

§6. Contraction of the dynamical variation principle^{4) 10)}

The time reversal is performed in the Schrödinger representation by taking the conjugate complex denoted by bar, where the Hamiltonian $H(H)$ of the system exposed to the magnetic field H is transformed as $\bar{H}(H) = H(-H)$. In the absence of magnetic field the Hamiltonian is real and invariant: $\bar{H} = H$, to which we confine ourselves. The complex conjugate $|\bar{n}\rangle$ of an eigenstate $|n\rangle$ is also an eigenstate with the same eigenvalue E_n , according to equations

$$H|n\rangle = E_n \cdot |n\rangle, \quad H|\bar{n}\rangle = E_n \cdot |\bar{n}\rangle. \quad (6.1)$$

The current density is transformed as $\bar{j} = -j$. As the time reversal of $\phi^{(+)}$ can be identified with $\phi^{(-)}$, we redefine $\phi^{(+)}$ and $\phi^{(-)}$ as ϕ and $\bar{\phi}$, respectively.

Using the decomposition with respect to time reversal symmetry

$$\phi = \phi' + \phi'', \quad \bar{\phi} = -\phi' + \phi'', \quad \bar{\phi}' = -\phi', \quad \bar{\phi}'' = \phi'', \quad (6.2)$$

we can rewrite (5.9) as

$$W(\phi) \equiv 2(\phi', j \cdot E) - s((\phi', \phi') - (\phi'', \phi'')) + (2i/\hbar)(\phi''[H, \phi']), \quad (6.3)$$

where only ϕ' couples with the external disturbance $j \cdot E$. Taking variation of (6.3) as to ϕ'' , we obtain

$$\phi'' = i[\phi', H]/(\hbar s). \quad (6.4)$$

By substituting (6.4), the expression (6.3) is rewritten as

$$W(\phi') = 2(\phi', j \cdot E) - (\phi', \mathcal{L}\phi'), \quad (6.5)$$

where $\mathcal{L}$ is defined by

$$\mathcal{L}\phi = ([H, [H, \phi] + \hbar^2 s^2 \phi]) / (\hbar^2 s). \quad (6.6)$$

The maximum of (6.5) as to ϕ' gives the Joule heat generated.

For the electric field with unity strength, (6.5) is reduced to

$$\sigma(\phi') = 2(\phi', j_u) - (\phi', \mathcal{L}\phi'), \quad (u=x, y \text{ or } z) \quad (6.7)$$

of which maximum gives the electrical conductivity (5.11).

The dynamical variation principle concerning (5.9) manifests itself as a stationarity problem in contrast to the kinetic extremum problem presented in §4 implying irreversibility. By

contracting the irrelevant component of the density matrix even with respect to time reversal, it is converted into an extremum problem as to the odd component ϕ' . By further contracting non-diagonal elements in the representation diagonalizing the unperturbed Hamiltonian for the system of sensitive to the initial condition or chaotic system such as the conduction electron system in solid, the variation principle concerning the diagonal elements can be rewritten in a form similar to the kinetic variation principle described in §4.¹⁰⁾ The latter is the result of the lowest perturbation.

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