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Time Reversal Symmetry, Information Contraction and Irreversibility in Transport Processes

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Variation principles presented here reveals some remarkable features of the transport processes concerning the time reversal operation leading to irreversibility. For the electrical transport process in solid taken as a typical example, a quantum mechanical variation principle is formulated as a stationarity problem in the same way as for the quantum mechanical scattering pocess, in which two kinds of waves ,incoming and outgoing, are involved in the variational functional, necessarily coupling with each other.

In contrast, the Umeda-Kohler-Sondheimer variation principle for the Boltzmann-Bloch equation, on the basis of which various transport processes have been investigated for a long time, is formulated as an extremum problem, with regard to a single sort of distribution function. This extremum property is due to the positive definiteness of entropy production or more basically to the H theorem and related to thermodynamics and irreversibility .

The stationarity property of the quantum-mechanical principle for transport processes characteristic of the dynamical stage of the theory in contrast with the case of the Boltzmann-Bloch equation, is discussed from an informational point of view. By contracting the information of irrelevant part even with time reversal, the quantum mechanical variation principle with respect to the odd part which is relevant reduces to the extremum property of the same sort as the Boltzmann-Bloch case.

§1.Introduction

The conventional theory of transport process is based upon the Boltzmann-Bloch equation, which is usually confined to the linear response as to the external field, has been formulated as a variation principle, viz. the Umeda-Kohler-Sondheimer principle(referred to as UKS hereafter)[1)2)3)4)5)]. The UKS is presented as an extremum problem with respect to a functional of the distribution function of carrier particles, which is proportional to the temporal development of the entropy of the carrier system consisting of two parts. One is due to the collision process intrinsic to the system and called the entropy production. The other is due to the external disturbance or extrinsic. The UKM principle is basically related to the H-theorem or the second law of thermodynamics and furthermore corresponds to a typical case of Onsager's thermodynamical theory of reciprocity relation.[6)7)8)9)].

The quantum mechanical(classical) theory of the same sort of

transport problem is formulated on the basis of the von-Neumann (Liouville) equation. In the present paper the formulation is exclusively given quatum-mechanically, as it is readily translated into the classical case. The variation principle[10] is given in the same way as in the theory of scattering process.[11] In the latter, the interaction between the incident particle and the scattering centre is regarded as the perturbation, which is first adiabatically switched on at the infinite past and secondly switched off at the infinite future. Corresponding to these two boundary conditions, the incoming and outgoing wave functions are calculated in the so-called interaction representation, by means of a pair of unitary time evolution transformations, which are time reversal to each other. This pair appear, being coupled in the variation principle.

The von-Neumann equation linearized with the external field can be solved by assuming the density matrix of the system in the form as a generalization of the distribution function assumed in the theory of the Boltzmann-Bloch equation. As to the temporal boundary onditions, the situation is similar as in the scattering theory: in the one case is applied the incoming field and in the other the outgoing field. That is, the external field is switched on at the infinite past in the former and switched off towards the infinfite future in the latter. The solutions of these two boundary value problems are coupled in the variation principle presented for the transport proceces as a stationarity problem [10][12][13][14][15], similarly to the case of scattering process.

Such a stationarity character is proper to the basic equation concerned in the dynamical stage.

It is further noticed[10)16)] that the even component with time reversal never couple with the external disturbance but only the odd component does in the variation functional. Therefore the even part can be eliminated as irrelevant to lead to an extremum problem similar to the case of UKS, concerning the relevant odd component. So to speak, the contraction of information of the even component brings about theirreversible character into the variation principle.

The UKS principle for the Boltzmann-Bloch equation is presented in §2, by taking the case of static scattering centre against conduction electrons in solid for the sake of brevity of description. The terms of entropy production and drift effect are derived explicitly and the variation principle is found to be equivalent to the one which is proposed by Onsager[6)7)8)9)] from a general thermodynamical point of view.

The quantum transport process in the system of conduction electrons in solid is investigated in §4 as a representative case, in parallel with the discussion on the Boltzmann-Bloch equation in §3. The variation principle is applied to solve the von Neumann equation for the density matrix, in which the boundary conditions of incoming and outgoing fields enter. In the variational functional for the electrical conductivity, the component even with time reversal, which does not couple with the external field, can be eliminated to lead to the variation

principle only with respect to the odd component. The resultant principle appears as an extremum problem as same as UKS for the Boltzmann-Bloch equation. In §5, some additive remarks are given concerning the problem of time-reversal as well as as a short summary.

§2. The Boltzmann-Bloch equation and UKS variation principle

The kinetic theory of gas originally due to Boltzmann is based upon the well-known equation,

$$\frac{\partial f}{\partial t} = - \mathbf{F} \cdot \frac{\partial f}{\partial \mathbf{p}} - \frac{\mathbf{p}}{m} \cdot \frac{\partial f}{\partial \mathbf{r}} + \left(\frac{\partial f}{\partial t} \right)_c , \tag{1}$$

where m, $\mathbf{p}$ and $\mathbf{r}$ denote the mass, momentum and space coodinate of the molecule, f is the distribution function of $\mathbf{p}$, $\mathbf{r}$ and the time t, and $\mathbf{F}$ is the external force acting on the molecule. The last term on the right hand side represents the so-called collision term, which is not explicitly shown here. For brevity, we confine ourselves to the electron transport, which has also been investigated in the same scheme since Bloch. In the case of scattering due to static imperfections therein, the collision term is expressed as

$$\left(\frac{\partial f}{\partial t} \right)_c = \int d^3 p \; W(\mathbf{p}, \mathbf{p}') \delta(\varepsilon - \varepsilon')(f' - f), \tag{2}$$

where $W(\mathbf{p}, \mathbf{p}')$ including the delta-function of the difference between the electron energies ε and ε', represents the

transition probability according to the so-called golden rule. We confine ourselves to this case, for the sake of brevity. The details of the system and scaterin mechanism do not matter the essence of the theory and the generalization to other types of system can be readily made. For example, the application to the electrn-phonon system can be readily made, even with phonon drag effect being taken into account.[4)5)]

Now, the distribution function f is assumed as

$$f = f_0 - \frac{\partial f_0}{\partial \varepsilon} \phi, \tag{3}$$

where f_0 represents the equilibrium. By substituting (3) into (1) and retaining only the terms linear with the external disturbance, we obtain

$$\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t} \right)_C + \left(\frac{\partial f}{\partial t} \right)_D , \tag{4}$$

where the first term in the right-hand side, viz. the collision term, is expressed as

$$\left(\frac{\partial f}{\partial t} \right)_C = - \frac{\partial f_0}{\partial \varepsilon} L\phi \tag{5}$$

in terms of the collision operatorer L defined by

$$L\phi \equiv \int d^3 p W(p, p') \delta(\varepsilon - \varepsilon')(\phi - \phi'). \tag{6}$$

The second term in the right-hand side of eq.(4), called the

drift term, comes from the first two terms in the right-hand side of eq.(1) and is expressed as

$$\left(\frac{\partial f}{\partial t} \right)_D = - \frac{\partial f_0}{\partial \varepsilon} X \tag{7}$$

by defining the external disturbance by X. We confine ourselves hereafter to the homogeneous temperature, in order to describe as briefly as possible, in which X is obtained as

$$X = j \cdot E. \tag{8}$$

in terms of the electric current density j and the external electric field E. By substituting (5) and (7) into (4) under the condition that the system is stationary with time, we obtain

$$L\phi = X. \tag{9}$$

In general, the collision operator L satisfies the relations

$$(\phi, L\psi) = (\psi, L\phi), \tag{10}$$

$$(\phi, L\phi) \geq 0, \tag{11}$$

for any pair of distribution functions ϕ and ψ of the sort defined by (3), where the inner product has been defined as

$$(\phi, \psi) \equiv -\int \frac{\partial f_0}{\partial \varepsilon} \phi\psi d^3 p. \tag{12}$$

Equations (10) and (11), which show that the operator L is self-adjoint and positive-definite, provide the basis of the

variation principles characteristic of the transport process. From this point of view, the system of electronic system in solids was investigated by Umeda and Sondheimer.[1)3)] The case of molecular system of gas was similaly done by Kohler[2)].

It is readily proved that the linearized Boltzmann-Bloch equation (9) is equivalelnt to some variation principles with respect to an arbitrary infinitesimal variation of the function ϕ. The following is in particular pertinent to the investigation in the next section.

【 I 】 The functional $(\phi, L\phi)$ is made maximum,
under the condition that $(\phi, L\phi)=(\phi, X)$.

【 II 】 The functional $2(\phi, X)-(\phi, L\phi)$ is made maximum.

The solution of (9) gives the maximum value, which is equal to the average (ϕ, X) of X with respect to the true distribution function ϕ or the observed value of X:viz. the work done by the applied field or the Joule heat,

$$j \cdot E=\sum_{\mu}\sum_{\nu}\sigma_{\mu\nu} E_{\mu} E_{\nu} /2. \tag{13}$$

In a special case that $E_{\mu}=1$ and the other orthogonal components of the field vanish, the maximum value equals the electrical conductivity

$$\sigma=\sigma_{\mu\mu} . \tag{14}$$

The variational functionals are intimately related to the temporal change of the entropy S or of the H-function H, which is

equal to minus entropy divided by the Boltzmann constant k_B. They are given by

$$H = \int d^3p[f\ln f-(1-f)\ln(1-f)] = -\frac{S}{k_B}, \tag{15}$$

in terms of the distribution f. The rate of temporal change of (15) is due to that of the distribution function and expressed as

$$\frac{dH}{dt} = \int d^3p \frac{\partial f}{\partial t} \ln\left(\frac{f}{1-f}\right) = -\frac{S}{k_B}. \tag{16}$$

First substituting (5) and next (7) for $\partial f/\partial t$ in eq.(16) multiplied by $-k_B$ and retaining only the lowest order with the external disturbance, we obtain

$$\left(\frac{\partial S}{\partial t}\right)_C = \frac{(\phi, L\phi)}{T}, \tag{17}$$

$$\left(\frac{\partial S}{\partial t}\right)_D = -\frac{(\phi, X)}{T}, \tag{18}$$

which represent the changes of entropy with time due to the collision and to the drift caused by the external field, respectively. The former, which is intrinsic to the system, is called the entropy production. In terms of eqs. (17) and (18), the physical meaning of the variation principles 【 I 】 and 【 II 】 are quite obvious. The positive-definite or non-negative property (11) of the collision operator L provides the proof of the H-theorem, as the intrinsic change of the H-function with

the sign opposite to S is thus concluded to be monotonic and decreasing according to eq.(17).

§3.Quantum-statistical variation principles

The motion of the system exposed to the time-dependent external electric field $E(t)$ can be described in terms of the von-Neumann equation for the density matrix ρ:

$$i\hbar \frac{\partial \rho}{\partial t} = [H-P\cdot E(t),\rho], \tag{19}$$

where P represents the polarization operator of the system.

In the linear approximation with the external disturbance,

$$\rho(t)=\rho_C+\rho_1(t), \tag{20}$$

where ρ_C represents the equilibrium given by the grand canonical distribution depending on the Hmiltonian H and the total number N of carriers as

$$\rho_C=K\exp(-\beta H-\xi N), \tag{21}$$

K, $\beta=1/k_B T$ and $\xi=-\mu/k_B T$ being a normalization constant, the inverse temperature and minus the chemical potential divided by temperture, respectively. The remainder $\rho_1(t)$ is proportional to the applied field. By substituting (20) into (19) and taking account of (21), we obtain

$$i\hbar \frac{\partial \rho_1}{\partial t} =[H,\rho_1]-[P\cdot E(t),\rho_C] \tag{22a}$$

$$=[H,\rho_1]+i\hbar\int_0^\beta \rho_c \exp(\lambda H)\mathrm{j}\cdot \mathrm{E}\exp(-\lambda H)d\lambda \tag{22b}$$

to the extent of linearity with the extrnal field. In (22b) the operator j represents the electric current density, which relates to the polarization P as $j=i[H,P]/\hbar$.

From the second term of (22b), it is relevant to define an operator Φ from ρ_1 by

$$\rho_1=\rho_c\int_0^\beta \exp(\lambda H)\Phi\exp(-\lambda H)d\lambda . \tag{23}$$

Equation (20), as substituted for ρ_1 from (23), is reduced to eq. (4), if it is transformed into the one-body description in which the interaction between the conduction electrons with the static imperfection is neglected in the Hamiltonian H. Inserting (23) into (22b), we obtain

$$\frac{\partial\Phi}{\partial t} = \frac{i}{\hbar}[\Phi,H] + \mathrm{j}\cdot\mathrm{E}. \tag{24}$$

Here in analogy with the temporal boundary conditions assumed in the theory of scattering, the incoming and outgoing waves, the external electric fields are assumed as follows:

$$[A]\ \mathrm{E}(t)=\mathrm{E}\exp(st), \qquad (t<0) \tag{25a}$$

$$[B]\ \mathrm{E}(t)=\mathrm{E}\exp(-st), \qquad (t>0) \tag{25b}$$

where E is the field strength at the time $t=0$ and s is a

positive infinitesimal.

The solutions of (24) according to the boundary conditions [A] and [B] are expressed as $\Phi_+ \exp(st)$ and $\Phi_- \exp(-st)$, respectively. Te time-independent factors Φ_+, Φ_- satisfy the equations

$$L_s \Phi_+ = j \cdot E, \tag{26a}$$

$$L_{-s} \Phi_- = j \cdot E. \tag{26b}$$

Here, L_s, as applied to an operator Φ, is given by

$$L_s \Phi = s\Phi + i[H,\Phi]\Phi/\hbar, \tag{27}$$

and L_{-s} is, as a matter of course, obtained by changing the sign of s in L_s.

Let us define the inner product between a pair of operators Φ and Ψ as

$$(\Phi,\Psi)=(\Psi,\Phi)=\int_0^\beta \mathrm{Tr}\{\Phi\rho_C \exp(\lambda H)\Psi\exp(-\lambda H)d\lambda, \tag{28}$$

which is reduced to (12) for the case of the Boltzmann-Bloch equation, by rewriting in the scheme of one-body description and by neglecting the interaction Hamiltonian of the conduction electron with the static imperfections. As to the inner product (28), the operator L_s satisfies the relation

$$(\Phi, L_s \Psi)=-(\Psi, L_{-s} \Phi). \tag{29}$$

The variation principle is presented in this scheme as

follows. Find out the operators Φ_+ and Φ_- which make the functional

$$W(\Phi_+,\Phi_-)=(\Phi_+-\Phi_-,E\cdot j)+(\Phi_-,L_s\Phi_+). \tag{30}$$

stationary. The operators satisfying this condition is equal to the solutions of eqs. (26a) and (26b) and the stationary value equals the Joule heat generated,

$$W = J_s\cdot E = -J_{-s}\cdot E, \tag{31}$$

where J_s and J_{-s} denote the current density at t=0 in the cases [A] and [B], respectively.

Let E be unit vectors parallel with the ν-axis and with the μ-axis for the boundary conditions [A] and [B], respectively. Then the stationary value is equal to the $\mu\nu$-component of the conductivity tensor

$$\sigma_{\mu\nu}=\int_0^\infty dt(j_\mu(t),j_\nu)\exp(-st). \tag{32}$$

In particular, the functional

$$\sigma(\Phi_+,\Phi_-)=(\Phi_+-\Phi_-,j_\mu)+(\Phi_-,L_s\Phi_+) \tag{33}$$

should be made stationary and then it reduces to the electical conductivity

$$\sigma=\int_0^\infty dt\int_0^\beta d\lambda\ \mathrm{Tr}\{\rho_C\, j_\mu(t-i\hbar\lambda)j_\mu\}. \tag{34}$$

§3.Time reversal of operators and eigenstates

It is essential to notice the symmetry properties of operators and the wave functions as to time reversal. As time reversal being applied to, they are indicated by upper lines. The effect of time reversal is easily examined in the scheme of the orthogonal coordinates diagonalized, in which the conjugate momenta are minus i times derivatives by those coodinates: e.g. a coordinate $x \rightarrow x$, and its momentum $p \rightarrow -i\partial/\partial x$. Thus, the time reversal is manifested by taking the complex conjugate in such a way as $\bar{x}=x$, $\bar{p}=-p$. It is readily seen that the Hamiltonian $H(\mathrm{H})$ is transformed into $H(-\mathrm{H})$ in the presence of magnetic field: viz. $\bar{H}(\mathrm{H})=H(-\mathrm{H})$. Accordingly, the Hamiltonian H in the absence of magnetic field is invariant by time reversal: viz. $\bar{H}=H$, to which we confine ourselves hereafter.

In the representation by which the Hamiltonian H is diagonalized, it is evident that its eigenfunction $|n\rangle$ for the eigenstate desinated as n is necessarily accompanied with its time reversal $|\bar{n}\rangle$ with the same energy eigenvalue E_n, as seen from the Schrödinger equations

$$H|n\rangle=E_n\cdot|n\rangle, \qquad H|\bar{n}\rangle=E_n\cdot|\bar{n}\rangle. \tag{35}$$

The latter equation in (35) is readily proved by taking the complex conjugate of the former equation and noticing that $\bar{H}=H$, E_n is real and $|\bar{n}\rangle$ is complex conjugate of $|n\rangle$.

In eq. (26a), the matrix element of the left-hand side is written down as

$$\langle m|L_s\Phi_+|n\rangle=(s+i\omega_{mn})\langle m|\Phi_+|n\rangle$$

$$=-(-s+i\omega_{nm})\langle\bar{n}|\Phi_+|\bar{m}\rangle=-i\langle\bar{n}|L_{-s}\Phi_+|\bar{m}\rangle, \tag{36}$$

where $\omega_{mn}=(E_m-E_n)/\hbar$. For the right-hand side of (26a), we have

$$\langle m|j\cdot E|n\rangle=-\langle\bar{n}|j\cdot E|\bar{m}\rangle, \tag{37}$$

as the time reversal $\bar{j}$ of j equals -j. By equating (36) with (37) and comparing the result with eq. (26b), it is found that $\overline{\Phi_+}$ can be identified with Φ_-. Then, by rewriting $\overline{\Phi_+}$ simply as ϕ, Φ_- can be identified with its time reversal $\bar{\phi}$.

Now, it is advatageous to rewrite the various expressions presented so far, to make apparent the interrelationships of the operators therein with respect to time reversal operation. The inner product (28) is redefined between Φ and Ψ as

$$\langle\langle\phi,\psi\rangle\rangle=-\int_0^\beta d\lambda\,\mathrm{Tr}\{\bar{\Phi}\rho_C\exp(\lambda H)\Psi\exp(-\lambda H)\}. \tag{38}$$

The variational expressions (30) and (33) are rewritten in the scheme of this inner product, as

$$w(\phi)=\langle\langle\phi,j\cdot E\rangle\rangle+\langle\langle j\cdot E,\Phi\rangle\rangle-\langle\langle\Phi,L_s\Phi\rangle\rangle, \tag{39}$$

$$\sigma(\Phi)=\langle\langle\Phi,j_\mu\rangle\rangle+\langle\langle j_\mu,\Phi\rangle\rangle-\langle\langle\Phi,L_s\Phi\rangle\rangle, \tag{40}$$

respectively.

§4.Contraction of information in the variation principles

If the operator Φ is decomposed into Φ' and Φ'', which are odd and even, respectively, as to time reversal, so that

$$\Phi=\Phi'+\Phi'', \quad \overline{\Phi}=-\Phi'+\Phi'', \quad \overline{\Phi'}=-\Phi, \quad \overline{\Phi''}=\Phi'', \tag{41}$$

the variational expressions (39) are rewitten down as

$$W(\Phi)=2\langle\langle j\cdot E,\Phi'\rangle\rangle+s(\langle\langle\Phi',\Phi'\rangle\rangle-\langle\langle\Phi'',\Phi''\rangle\rangle)$$
$$-2i\langle\langle\Phi'',[H,\Phi']\rangle\rangle/\hbar. \tag{42}$$

It is remarkable in (42) that only the odd component Φ' couples with the external disturbace $j\cdot E$ and the even component Φ'' does not at all. There exists a coupling between these coponents intrinsic to the system, independent of the external disturbace, through which ϕ'' can be expressed in terms of ϕ' and eliminated in the variational functional (42). That is, the stationarity condition for (42) as to an infinitesimal variation of Φ'' leads to the relation

$$\Phi''=i[\Phi',H]/(\hbar s). \tag{43}$$

By substituting (43) into (42), we obtain the variation principle as to the odd component Φ', stating that

$$W(\Phi')=2\langle\langle\Phi',j\cdot E\rangle\rangle-\langle\langle\Phi',L\Phi'\rangle\rangle \tag{44}$$

should be maximum with Φ', where the operation L is defined, as applied to an operaor Φ, by

$$L\Phi=([H,[H,\Phi]+\hbar^2 s^2 \Phi)/(\hbar^2 s). \tag{45}$$

The maximum value equals the Joule heat generated in the system.

In the same way, the variation functional (40) is reduced to

$$\sigma(\Phi')=2\langle\langle \Phi',j_\mu \rangle\rangle - \langle\langle \Phi',L\Phi' \rangle\rangle , \tag{46}$$

which is required to be maximum and the maximum value is equal to the conductivity.

The variation principles with (44) and (46) are formally equivalent to the UKS principle for the Boltzmann-Bloch equation, in particular, of the type 【 I 】 . It is needless to say that any other types of the UKS variation principle are also applicable to the present case.

§5. Concluding remarks

The variation principle for the von Neumann equation for quantum transport process has been originally formulated in the form of stationarity problem, in the same way as in the case of quantum-mechanical theory of scattering, where the incoming and outgoing waves appear coupling with each other. Such a coupling between the two cases of boundary conditions which are time reversal of each other is a distinctive feature of the variation principles in the dynamical stage.

In contrast with this, the UKS variation principle for the Boltzmann-Bloch equation, which holds in the kinetic stage and

provides the basis of the investigation of irreversible transport processes, is given in the form of extremum problem.

It is further noticed that the odd component as to time reversal is relevant in quantum transport process and the even component can be eliminated as irrelevant to lead to the variation principle in which the variational functional should be made extremum with respect to the odd component. In consequence, the principle is reduced to the same type as the UKS for the Boltzmann-Bloch equation, so to speak through a contraction of information in the original variation principle in the dynamical stage. The complete information in the original variation principle is diminished to a certain amount in the final form. In consequence, the irreversibility comes about.

Finally the following is remarked. To the purpose of studying the susceptibility of the system in a previous paper,[10] the perturbed density matrix ρ_1 was expressed in terms of an operator Ψ, which stands in the relation

$$\Phi=\partial\Psi/\partial t=i[H,\Psi]/\hbar \tag{48}$$

with Φ defined by (23). As to the decomposition of Ψ, as follows,

$$\Psi=\Psi'+\Psi'', \quad \overline{\Psi'}=-\Psi, \quad \overline{\Psi''}=\Psi'', \tag{49}$$

we have

$$\Phi'=\partial\Psi''/\partial t, \quad \Phi''=\partial\Psi'/\partial t. \tag{50}$$

It is obvious from these relations that the odd and even components of Φ are interchanged with each other in those of Ψ. Therefore, if use is made of the operator Ψ in place of Φ in the present variation principle, the even component Ψ'' is turned to be relevant and the odd one Ψ' is eliminated as irrelevant, on the contrary to the case of Φ. In consequence, the variation principle appears as an extremum problem as to Ψ''.

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