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Irreversible Processes and Prigogine's Theory of Subdynamics

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Abstract

Theory of subdynamics is formulated as the variational principle which has been presented by the present authors. The von Neumann equation for the system of conduction elctrons as a typical charge carriers which are scattered by the static impurity potential and exposed to an applied electric field is reduced to the Boltzmann type equation, where the collision operator is essentially identical to the block-diagonalized Liouville operator in the theory of subdynamics. This superoperator is known to be positive definite, which leads to damping of the deviation of the state from equilibrium and manifests the irreversibility. On the other hand, the collision operator on the Boltzmann type equation which is positive definite and self adjoint provides the formulation of the variational principle which represents the principle of entropy production and thus demonstrate the irreversibility. It is concluded that these two theory is intimately related to each other.

1 Introduction

We have investigated the variational principles of irreversible processes based on the von Neumann equation for the density matrix of the many-body system[1-5]. Contracting the information of the density matrix in the equation, we have derived the Umeda-Kohler-Sondheimer(UKS) variational principle[6] on the Boltzmann-Bloch equation for the conduction electrons in solids, which concerns with the entropy production and thus irreversibility. That is, the contraction of information causes irreversibility.

On the other hand, in the so-called theory of subdynamics[7-12] the Liouville superoperator is block-diagonalized by means of non-unitary transformation, where the Liouville superoperator with exclusively positive eigenvalues has been derived. This superoperator shows that any state of the system necessarily damps towards the equilibrium, manifesting irreversibility.

In this paper, we formulate an extremum variational principle on the basis of the theory of subdynamics for the system of conduction electrons in solids which are elastically scattered by static impurity potentials. In Sec.2 and 3, we obtain the von Neumann equation for the system to which an external electric field is switched on and off adiabatically is reduced to the Boltzmann type equation concerning the diagonal elements of the density matrix. Owing to the Liouville superoperator with positive definite nature, we present the extremum variational principle in Sec.4. We finally summarize the result in Sec.5

2 General formulation

We investigate the system of conduction electrons elastically scattered by impurities in solids, the Hamiltonian of which is H. Under the electric field $E(t)$, we express the density matrix $\rho(t)$ as

$$\rho(t) = \rho_C + \rho_C \int_0^\beta d\tau \exp(\tau H)\Phi(t)\exp(-\tau H), \tag{2.1}$$

where ρ_C is the grand canonical density matrix given by

$$\rho_C = K \exp[-\beta(H - \mu N)]. \tag{2.2}$$

The von Neumann equation for Φ is

$$\frac{\partial}{\partial t}\Phi(t) = -iL\Phi(t) + E(t)j, \tag{2.3}$$

where j is the current operator and the superoperator L is defined as

$$L\Phi \equiv \frac{1}{\hbar}[H, \Phi]. \tag{2.4}$$

Introducing the creation operator a_k^+ and the annihiration operator a_k of the conduction electron with wave vector k, we express the Hamiltonian, the density matrix and the current operator as

$$H = \sum_{k,k'} \langle k|h|k'\rangle a_k^+ a_{k'}, \tag{2.5}$$

$$\begin{aligned} h &= h_0 + V, && (2.6) \\ \Phi(t) &= \sum_{k,k'} \langle k|\phi(t)|k'\rangle a_k^+ a_{k'} && (2.7) \\ j &= \sum_k \langle k|ev|k\rangle a_k^+ a_k, \qquad v \equiv \frac{p}{m}, && (2.8) \end{aligned}$$

in which V is the perturbation potential due to the impurities. Then the von Neumann equation is

$$\frac{\partial}{\partial t}\phi(t) = -il\phi(t) + evE(t), \tag{2.9}$$

where the superoperator l is defined as

$$l\phi \equiv \frac{1}{\hbar}[h, \phi]. \tag{2.10}$$

According to the theory of Subdynamics,the superoperator l is block-diagonalized by the non-unitary transformation as

$$\begin{aligned} \lambda^{-1} l \lambda = \theta &\equiv \begin{pmatrix} \theta_0 & 0 \\ 0 & \theta_C \end{pmatrix}, && (2.11) \\ \lambda^{-1} &\equiv \begin{pmatrix} A & AD \\ -CA & 1 - CAD \end{pmatrix}, && (2.12) \\ \lambda &\equiv \begin{pmatrix} 1 & -D \\ C & 1 \end{pmatrix}. && (2.13) \end{aligned}$$

A, C, D and θ are defined, in terms of the projection superoperator P which projects any operator onto the diagonal one in the scheme of diagonalizing the unperturbed Hamiltonian h_0, and the complementary superoperator $Q = 1 - P$, as

$$\Psi(z) \equiv PlP + PlQ\frac{1}{z - QlQ}QlP, \tag{2.14}$$

$$
\begin{aligned}
A &\equiv \sum_{j=0} \frac{1}{j!}\frac{d^j}{dz^j}\Psi^j(z), & (2.15)\\
AD &\equiv \sum_{j=0} \frac{1}{j!}\frac{d^j}{dz^j}\Psi^j(z)PlQ\frac{1}{z-QlQ}, & (2.16)\\
CA &\equiv \sum_{j=0} \frac{1}{j!}\frac{d^j}{dz^j}\frac{d^j}{dz^j}\frac{1}{z-QlQ}QlP\Psi^j(z), & (2.17)\\
\theta_0 &\equiv PlP + PlQC, & (2.18)\\
\theta_C &\equiv QlQ - QlPD, & (2.19)
\end{aligned}
$$

where $z = i\epsilon$ and ϵ is a positive infinitesimal. $i\Psi$ is called the collision operator which appear explicitly in the Boltzmann-Bloch equation as shown in the next section. Multiplying both sides of (2.9) by λ^{-1}, and defining the privileged density matrix $\phi^{(p)}$ as

$$\phi^{(p)}(t) \equiv \lambda^{-1}\phi(t), \tag{2.20}$$

we get the von Neumann equation

$$\frac{\partial}{\partial t}\phi^{(p)}(t) = -i\theta\phi^{(p)}(t) + i\lambda^{-1}evE(t). \tag{2.21}$$

Using the equations (2.14)-(2.18), we can express θ_0 in a power series of the collision operator Ψ as

$$\theta_0 = \Psi + \frac{d\Psi}{dz}\Psi + \cdots, \tag{2.22}$$

where $i\Psi$ is a positive definite as shown in a following section. Neglecting higher order terms of Ψ in the right hand side of (2.22), $i\theta_0 = i\Psi$ is positive definite, and the diagonal part $\phi_0^{(p)}$ damps in the future in a absence of an electric field.

3 Boltzmann-Bloch equation

We consider a situation in which an electric field is adiabatically applied from the infinite past

$$E(t) = E\exp(st), \tag{3.1}$$

where s is a positive infinitesimal, and assume, corresponding to this situation

$$\phi^{(p)}(t) = \phi^{(p)}\exp(st). \tag{3.2}$$

Setting $\frac{\partial}{\partial t}\phi^{(p)}(t) = 0$, we get the von Neumann equation

$$i\theta\phi^{(p)} = \lambda^{-1}evE, \tag{3.3}$$

which is written separately, for the diagonal part $\phi_0^{(p)}$ and the off-diagonal part $\phi_C^{(p)}$ as

$$i\theta_0\phi_0^{(p)} = AevE, \tag{3.4}$$

$$i\theta_C\phi_C^{(p)} = -CAevE. \tag{3.5}$$

These equations show the relation

$$\phi_C^{(p)} = -\theta_C^{-1}C\theta_0\phi_0^{(p)}, \tag{3.6}$$

that the off-diagonal part $\phi_C^{(p)}$ is expressed in terms of the diagonal part $\phi_0^{(p)}$. We transform $\phi_0^{(p)}$ to the diagonal part ϕ_0, as

$$\phi_0^{(p)} = \left(A + AD\frac{1}{z - QlQ}QlP\right)\phi_0, \tag{3.7}$$

and $\phi_C^{(p)}$ as

$$\phi_C^{(p)} = \left(-CA + (1 - CAD)\frac{1}{z - QlQ}QlP\right)\phi_0. \tag{3.8}$$

This corresponds to express the off-diagonal density matrix ϕ_C in terms of the diagonal part ϕ_0 as

$$\phi_C = \frac{1}{z - QlQ}QlP\phi_0. \tag{3.9}$$

Using the relations

$$\theta_0\left(A + AD\frac{1}{z - QlQ}QlP\right) = A\Psi, \tag{3.10}$$

$$\theta_C\left(-CA + (1 - CAD)\frac{1}{z - QlQ}QlP\right) = -CA\Psi, \tag{3.11}$$

which can be proved from (2.14)-(2.19), we write (3.4) and (3.5) as

$$iA\Psi\phi_0 = AevE, \tag{3.12}$$

$$-iCA\Psi\phi_0 = -CAevE, \tag{3.13}$$

both of which are satisfied by Boltzmann-Bloch equation for ϕ_0

$$i\Psi\phi_0 = evE. \tag{3.14}$$

The collision operator $i\Psi$ appears instead of $i\theta_0$, by transformation (3.7) from $\phi_0^{(p)}$ to ϕ_0 .

4 Extremum principle

A complete orthonormal basis of the superspace $|k;k')$ is given in terms of dyadic operators $|k\rangle\langle k'|$ expressed in terms of the unperturbed eigenstates of

h_0 by

$$|k;k') \equiv ||k\rangle\langle k'|). \tag{4.1}$$

The matrix element of $i\Psi$ is

$$i(k;k|\Psi|k';k') = \frac{2\pi}{\hbar}\left(\delta_{kk'}\sum_q |\langle k|T(E_k)|q\rangle \delta(E_k - E_q) - |\langle k|T(E_k)|k'\rangle|^2 \delta(E_k - E_{k'})\right), \tag{4.2}$$

where T-matrix is defined in terms of the perturbed potential V as

$$T(E_k) = V + V\frac{1}{i\epsilon + E_k - h_0}T(E_k). \tag{4.3}$$

Using an abbreviation ϕ_k for the diagonal part of the density matrix as

$$\phi_k \equiv \langle k|\phi|k\rangle, \tag{4.4}$$

we express the Boltzmann-Bloch equation (3.14) as

$$\frac{2\pi}{\hbar}\sum_q |\langle k|T(E_k)|q\rangle|^2 \delta(E_k - E_q)(\phi_k - \phi_q) \;=\; ev_k E, \tag{4.5}$$

$$v_k \;\equiv\; \frac{\hbar k}{m}. \tag{4.6}$$

This equation is expressed as the extremum principle as follows. We first define the inner product $\langle \phi, \psi \rangle$ between the diagonal operators ϕ and ψ as

$$\langle \phi, \psi \rangle \;\equiv\; -\sum_k \frac{\partial f_k^0}{\partial E_k}\phi_k \psi_k, \tag{4.7}$$

$$\;=\; \int_0^\beta tr\{\phi f^0 \exp(\tau h_0)\psi(1 - f^0)\exp(-\tau h_0)\}d\tau, \tag{4.8}$$

where f^0 is the Fermi distribution function

$$f_k^0 \equiv \frac{1}{\exp(\beta E_k - \beta\mu) + 1}. \tag{4.9}$$

We then introduce the variational functional $W(\phi)$ as a function of a diagonal operator ϕ as

$$W(\phi) \equiv -\langle \phi, i\Psi\phi \rangle + 2\langle \phi, evE \rangle. \tag{4.10}$$

Due to the positive definite properties of $i\Psi$, the inner product $\langle \phi, i\Psi\phi \rangle$ is shown to be positive as

$$\langle \phi, i\Psi\phi \rangle = -\sum_k \frac{\partial f_k^0}{\partial E_k} \frac{\pi}{\hbar} |\langle k|T(E_k)|k'\rangle|^2 \delta(E_k - E_{k'})(\phi_k - \phi_{k'})^2 \geq 0. \tag{4.11}$$

Maximizing W with respect to ϕ, we get the Boltzmann-Bloch equation (4.5). This is the Umeda-Kohler-Sondheimer variational principle.

5 Conclusion

The UKS type variational principle is obtained by transforming the diagonal component of the privileged density matrix into the diagonal density matrix in the theory of subdynamics. The extremum nature of the principle is due to the positive definite collision operator which is essentially equal to the diagonal component of the block-diagonalized liouville superoperator. Irreversibility is concerned with the positive definite nature ot the relevant superoperator.

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