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On Quantum Theory of Transport Phenomena

——*Steady Diffusion*——

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A general formulation is given to the quantum theory of steady diffusion. In seeking for a steady solution of Liouville's equation, the boundary condition is taken into account by requiring that the solution should lead to a given distribution of average density. The distribution is to be determined by macroscopic law of diffusion and macroscopic boundary condition.

The basic equation thus obtained has a form similar to Bloch's kinetic equation and reduces to the latter in the limit of a system of weakly interacting particles. This is shown by generalizing a damping theoretical expansion of Kohn and Luttinger.

It is found that the Einstein relation is valid only for the symmetric part of diffusion- and electric conductivity tensors, in agreement with Kasuya's suggestion.

§ 1. Introduction

Recently Kubo and others[1),2)] have succeeded in formulating quantum statistical expressions for transport coefficients such as electric and thermal conductivities. These formulae are just as general and rigorous as, say, the familiar expression for the partition function $Z=\mathrm{Tr}(\exp\{-H/kT\})$. In practice appropriate approximation should, of course, be made in evaluating transport coefficients. The point is, however, that the conventional Bloch equation is nothing else but the lowest order approximation in a damping theoretical treatment of dynamical motion (see § 6) and by no means the most general way of approaching the problem.

Now, in the case of mechanical disturbances such as an external electric field, derivation of these formulae has been rather simple. The mechanical disturbance is expressed as a definite perturbing Hamiltonian and the deviation from equilibrium caused by it can be obtained by perturbation theory. On the other hand, thermal disturbances such as density and temperature gradients cannot be expressed as a perturbing Hamiltonian in an unambiguous way. Accordingly in the previous paper,[2)] use had to be made of Onsager's assumption that the average regression of spontaneous fluctuation follows the macroscopic laws. As a result, certain ambiguity has been left over, concerning galvano-magnetic effects caused by thermal disturbances.

In the present paper, a general formulation free from such an assumption will be given to the theory of thermal disturbances and, in order to show the basic idea, the case of steady diffusion will be discussed in detail. In this case, the usual Bloch equation takes the form in which the drift term due to the density gradient is balanced by the collision term. Our purpose is then to generalize the equation so as to include systems of strongly interacting particles (electrons, phonons, impurities, etc.). In other words, we shall seek for a steady solution of the quantum theoretical Liouville equation

$$i[H, \rho]=0, \tag{1·1}$$

where H is the Hamiltonian of our system and ρ the density matrix, taking $\hbar=1$. The boundary condition should be such that a steady gradient of average density is established by attaching suitable sources at the boundary. But for such a boundary condition, (1·1) would lead to an equilibrium density matrix, microcanonical, canonical or grand canonical. The microscopic detail of the interaction with sources at the boundary, however, should not be essential to the law of diffusion as an intrinsic property of a large system. We need only to suppose that the solution of (1·1) should lead to a given distribution of average density. The distribution is in turn to be determined by the macroscopic law of diffusion together with a given *macroscopic* boundary condition. The law of diffusion itself is a consequence from our solution of (1·1), so that the method is self-consistent.

In this sense, the thermal disturbance is a constraint upon dynamical motion and in fact appears as an effective potential in our basic equation (§ 4). The equation takes a form similar to the Bloch equation and reduces to the latter in the limit of a system of weakly interacting particles. This will be shown by applying a damping theoretical expansion due to Kohn and Luttinger[3] (§ 6).

An important consequence of the theory is that the well-known Einstein relation is valid only for the symmetric part of diffusion- and electric conductivity tensors. In other words, as regards the Hall effect, the gradient of chemical potential is *not* equivalent to the electric field. The difference becomes appreciable at low temperatures and under strong magnetic fields. Such a difference has first been suggested by Kasuya and is confirmed far beyond doubt by the present theory (§ 5).

From technical points of view, the present theory is similar to the so-called method of pseudo-potential.[4] It may also be regarded as generalization of Enskog's classical kinetic theory.[5] Indeed, Matsubara[6] has once tried the theory of hydrodynamic properties from the latter point of view. It seems, however, that neither physical nor mathematical details has ever been examined by these previous authors.

§ 2. Local equilibrium

For definiteness, let us take a system of similar particles (say, electrons in a metal), in which there exists a steady gradient of average density. The number density of particles is represented by the operator

$$n(\boldsymbol{x})=\sum_j \delta(\boldsymbol{x}-\boldsymbol{x}_j)=\Omega^{-1}\sum_k n_k e^{i\boldsymbol{k}\cdot\boldsymbol{x}}, \tag{2·1}$$

where Ω is the volume of the system and $n_k=\sum \exp\{-i\boldsymbol{k}\cdot\boldsymbol{x}_j\}$ should not be confused with occupation numbers. The average density is then given by

$$\mathrm{Tr}(\rho n(\boldsymbol{x}))=\langle n(\boldsymbol{x})\rangle. \tag{2·2}$$

As mentioned in § 1, we suppose that the right-hand side of (2·2) is given as a solution of the macroscopic diffusion equation, hence (2·2) is the condition for the solution of (1·1) to satisfy.

Let us describe the system in equilibrium by the grand canonical distribution

$$\rho_e = \exp\{\xi N - \beta H\} / \mathrm{Tr}(\exp\{\xi N - \beta H\}), \tag{2·3}$$

where ξ is the chemical potential, β the temperature and N the operator representing the total number of particles and commutable with the Hamiltonian H. We shall assume that the system in equilibrium is homogeneous so that

$$\langle n(\boldsymbol{x}) \rangle_e \equiv \mathrm{Tr}(\rho_e n(\boldsymbol{x})) = n \tag{2·4}$$

is constant. Hence (2·3), though stationary, does not satisfy (2·2) when the density gradient does exist.

A possibility of satisfying (2·2) is given by the so-called local equilibrium distribution

$$\rho_l = \exp\{\psi + \xi N - \beta H + \sum_{k \neq 0}{}' \xi_k n_{-k}\}. \tag{2·5}$$

Here ψ is a normalization constant to make

$$\mathrm{Tr}(\rho_l) = 1 \tag{2·6}$$

and the $\xi_k (k \neq 0)$ represent the fluctuation of chemical potential in space. From (2·6) it can be easily seen that

$$\langle n_{-k} \rangle = -\partial \psi / \partial \xi_k, \quad \xi_{-k} = -\partial S / \partial \langle n_k \rangle \tag{2·7}$$

where the entropy S is defined as

$$S = -\mathrm{Tr}(\rho_l \log \rho_l). \tag{2·8}$$

Obviously, (2·2) is always satisfied by (2·5) with suitably chosen ξ_k. But (2·5) does not satisfy (1·1), $[H, \rho_l] \neq 0$.

We are thus led to assume the density matrix in the form

$$\rho = \rho_l + \rho_1. \tag{2·9}$$

Actually, however, *no* approximation is introduced in so far as writing the density matrix in this form. For any given ρ, we can always find (2·5) with parameters ψ, ξ, β and ξ_k so chosen that

$$\begin{aligned} &\mathrm{Tr}(\rho) = \mathrm{Tr}(\rho_l), \quad \mathrm{Tr}(\rho N) = \mathrm{Tr}(\rho_l N) \\ &\mathrm{Tr}(\rho H) = \mathrm{Tr}(\rho_l H), \quad \mathrm{Tr}(\rho n_k) = \mathrm{Tr}(\rho_l n_k). \end{aligned} \tag{2·10}$$

Then (2·9) can be regarded as the definition of ρ_1, which should necessarily satisfy

$$\begin{aligned} &\mathrm{Tr}(\rho_1) = 0, \quad \mathrm{Tr}(\rho_1 N) = 0, \\ &\mathrm{Tr}(\rho_1 H) = 0, \quad \mathrm{Tr}(\rho_1 n_k) = 0. \end{aligned} \tag{2·11}$$

There are an infinite number of density matrices which satisfy (2·10). Among them, (2·5) is characterized by the maximum entropy and makes it possible to introduce thermodynamical variables as shown by (2·7). This is the reason for our particular choice (2·5), because the boundary condition of our problem is most simply expressed in terms of thermodynamical variables by specifying chemical potentials of sources at the boundary.

§ 3. Linear approximation

Now let us assume that the system is not far from equilibrium so that both $\hat{\xi}_k$ and ρ_1 are small quantities of first order. Then the well-known expansion formula of ordered exponential leads to

$$\rho_l=\rho_e\Big(1+\sum{}'\hat{\xi}_k\int_0^\beta\frac{d\lambda}{\beta}n_{-k}(-i\lambda)\Big) \tag{3·1}$$

where we have made use of (2·4), i. e.,

$$\langle n_k\rangle_e=0,\quad k\neq 0 \tag{3·2}$$

and $n_k(-i\lambda)$ is obtained from Heisenberg's operator $n_k(t)=\exp(iHt)\cdot n_k\cdot\exp(-iHt)$ by replacing t with $-i\lambda$.

Under the linear approximation (3·1), the average density is given as

$$\langle n_k\rangle=\mathrm{Tr}(\rho_l n_k)=g_k\xi_k \tag{3·3}$$

where

$$g_k=\int_0^\beta\frac{d\lambda}{\beta}\langle n_{-k}(-i\lambda)n_k\rangle_e. \tag{3·4}$$

In particular, assuming g_k is continuous at $k=0$, we can show that

$$\lim_{k\to 0}g_k=\Omega(\partial n/\partial\hat{\xi}) \tag{3·5}$$

where n is defined by (2·4). From (2·7), the entropy is expressed as

$$S=S_0-\tfrac{1}{2}\sum{}'g_k^{-1}\langle n_k\rangle\langle n_{-k}\rangle \tag{3·6}$$

with the equilibrium value S_0. If the density fluctuation is gradual, i. e., only the $\hat{\xi}_k$ with small $\boldsymbol{k}$ are excited, we may replace g_k in (3·6) by (3·5), so that we obtain the well-known expansion of entropy in thermodynamics.

Let us now turn to the flow density which is defined by

$$\boldsymbol{v}(\boldsymbol{x})=\tfrac{1}{2}\sum(\dot{\boldsymbol{x}}_j\delta(\boldsymbol{x}-\boldsymbol{x}_j)+\delta(\boldsymbol{x}-\boldsymbol{x}_j)\dot{\boldsymbol{x}}_j)=\Omega^{-1}\sum\boldsymbol{v}_k e^{i\boldsymbol{k}\cdot\boldsymbol{x}}. \tag{3·7}$$

In cases of neutral particles and also of charged particles without magnetic fields, the local equilibrium (3·1) makes no contribution to the average flow. In the case of charged particles moving in a magnetic field, on the contrary, the flow does not vanish even in equilibrium, because there exists a diamagnetic current. This current, however, can be described in terms of a magnetization and, in particular, never gives rise to a net current flowing through a cross section of a conductor (except for superconductors). So we hereafter disregard this part of flow.

There still remains the flow due to the second term of (3·1)

$$\langle \boldsymbol{v}_k \rangle_l = \xi_k \int_0^\beta \frac{d\lambda}{\beta} \langle n_{-k}(-i\lambda)\, \boldsymbol{v}_k \rangle_e. \tag{3·8}$$

This vanishes if there is no magnetic field. Because then n_k is invariant and $\boldsymbol{v}_k$ changes its sign under the transformation of time reversal. In the presence of a magnetic field, however, the transformation of time reversal includes the reversal of the magnetic field, too. So we can infer only that (3·8) is reversed together with the magnetic field. In other words, the flow is antisymmetric with respect to the magnetic field. But it does vanish in the classical limit and therefore in the high temperature limit, too. In fact, in the classical limit, we can first perform the integration over particle velocities in taking the expectation value in (3·8) and this vanishes because it is linear in velocities.

A more detailed discussion of (3·8) will be given in § 5.

§ 4. Basic equation and its solution

Now inserting (2·9) together with (3·1) into (1·1), we obtain our basic equation

$$i[H,\, \rho_1] = -\sum{}' \xi_k \int_0^\beta \frac{d\lambda}{\beta} \rho_e \dot{n}_{-k}(-i\lambda) \tag{4·1}$$

where, of course,

$$\dot{n}_k \equiv i[H,\, n_k] = -i\boldsymbol{k}\cdot \boldsymbol{v}_k. \tag{4·2}$$

A particular solution of the inhomogeneous equation (4·1) is given by

$$\rho_1 = \int_0^\infty dt\, e^{-\varepsilon t}\, e^{-iHt}\, \Gamma e^{iHt} \tag{4·3}$$

where Γ stands for the right-hand side of (4·1). In fact, (4·3) is the solution which we are seeking for. This can be seen in the following way.

First, note that the macroscopic relaxation time, i. e., the relaxation time in which the system recovers equilibrium, is of the order of l^2/D. Here l is the linear dimension of the system and D the diffusion coefficient. Now suppose that the system was in equilibrium at the remote past, $t=-\infty$, and that the difference of chemical potentials at two ends of the system has been increased very slowly from zero to the present value ($t=0$). For instance, suppose that it is proportional to $\exp(\varepsilon t)$, where $0<\varepsilon \ll D/l^2$. Then we may assume that a steady diffusion is established at each instant of time from $t=-\infty$ to $t=0$. This is a sort of adiabatic change and may be represented by the solution proportional to $\exp(\mathcal{E}t)$ of the following Liouville equation

$$\dot{\rho}_1+i[H,\ \rho_1]=e^{\varepsilon t}\Gamma,$$

$$\rho_1(-\infty)=0,\ \mathcal{E}\to+0.$$

At $t=0$, we have

$$\mathcal{E}\rho_1+i[H,\ \rho_1]=\Gamma \tag{4·4}$$

whose solution is nothing but (4·3), as can be easily confirmed.

It still remains to be confirmed that (4·3) does satisfy our subsidiary conditions (2·11). For any dynamical variable α, we have

$$\mathrm{Tr}(\rho_1\,\alpha)=-\sum\nolimits'\bar{\xi}_k\int_0^\infty dt\,e^{-\varepsilon t}\int_0^\beta\frac{d\lambda}{\beta}\langle\dot{n}_{-k}(-i\lambda)\,\alpha(t)\rangle_{\mathrm{e}}. \tag{4·5}$$

If we take $\alpha=1$, the left-hand side is $\mathrm{Tr}(\rho_1)$, and the right-hand side contains $\langle\dot{n}_{-k}\rangle_{\mathrm{e}}$. This should vanish, because any flow in equilibrium is steady. The first condition in (2·11) is thus satisfied. As for the second condition, we take $\alpha=N$. Since N commutes with the Hamiltonian, the right-hand side of (4·5) contains $\langle\dot{n}_{-k}N\rangle_{\mathrm{e}}$. This should also vanish, because

$$\mathrm{Tr}\,(e^{\xi N-\beta H}\dot{n}_{-k}N)=\frac{\partial}{\partial\bar{\xi}}\mathrm{Tr}(e^{\xi N-\beta N}\dot{n}_{-k})=0.$$

Thus the second condition is satisfied. Similarly, it can be seen by taking $\alpha=H$ that the third condition is also satisfied.

As for the final condition in (2·11), we have

$$\mathrm{Tr}(\rho_1 n_k)=-i\boldsymbol{k}\bar{\xi}_k\cdot\int_0^\infty dt\,e^{-\varepsilon t}\int_0^\beta\frac{d\lambda}{\beta}\langle\boldsymbol{v}_{-k}(-i\lambda)\,n_k(t)\rangle_{\mathrm{e}} \tag{4·6}$$

where we have made use of the continuity equation (4·2). In general, (4·6) does not vanish. We should, therefore, restrict ourselves to the case where the density fluctuation is so gradual that we may replace $\langle\cdots\rangle_{\mathrm{e}}$ in (4·6) by $\langle \boldsymbol{V}N\rangle_{\mathrm{e}}$. Here $\boldsymbol{V}$ is the net flow, i. e., $\boldsymbol{v}_k$ with $\boldsymbol{k}=0$. Since there is no net flow in equilibrium as mentioned before, we have

$$\mathrm{Tr}(e^{\xi N-\beta H}\boldsymbol{V}N)=\frac{\partial}{\partial\bar{\xi}}\mathrm{Tr}(e^{\xi N-\beta H}\boldsymbol{V})=0.$$

Thus, *under our restriction*, the fourth condition in (2·11) is satisfied.

The restriction can more precisely be expressed in the following way. In terms of space coordinates, (4·6) is written as

$$\mathrm{Tr}(\rho_1 n(\boldsymbol{x}))=-\int d\boldsymbol{x}'\,\boldsymbol{R}(\boldsymbol{x}-\boldsymbol{x}')\cdot\nabla\bar{\xi}(\boldsymbol{x}') \tag{4·7}$$

with

$$R(x-x')=\int_0^\infty dt\, e^{-\varepsilon t}\int_0^\beta \frac{d\lambda}{\beta}\langle v(x',\ -i\lambda)n(x,\ t)\rangle_e.$$

Except for such singular systems as superconductors and superfluids, the relaxation function $R(x)$ will decay off within a finite distance. The gradient of chemical potential $\nabla\xi$ should be nearly constant over this distance. This is the precise formulation of our restriction. If the condition is not satisfied, the simple themodynamical notion of diffusion is not applicable in describing the phenomenon.

§ 5. Diffusion constant and Einstein's relation

Now, we take $\alpha=v_k$ in (4·5), then the flow arising from ρ_1 is given as

$$\langle v_k\rangle_1\equiv\mathrm{Tr}(\rho_1 v_k)=-\xi_k\int_0^\infty dt\, e^{-\varepsilon t}\int_0^\beta\frac{d\lambda}{\beta}\langle\dot{n}_{-k}(-i\lambda)v_k(t)\rangle_e. \tag{5·1}$$

Making use of the continuity equation (4·2), we see that in the limit of $k\to 0$ the diffusion equation takes the form

$$\langle v_{k\mu}\rangle_1=-\sum_\nu D_{\mu\nu}^{(1)}\times(ik_\nu\xi_k), \tag{5·2}$$

$$\mu,\ \nu=x,\ y,\ z.$$

In terms of space coordinates, this is written as

$$\langle v_\mu(x)\rangle_1=-\sum_\nu D_{\mu\nu}^{(1)}\frac{\partial\xi(x)}{\partial x_\nu}. \tag{5·3}$$

Here the diffusion tensor $D_{\nu\mu}$ is given by

$$D_{\mu\nu}^{(1)}=\int_0^\infty dt\, e^{-\varepsilon t}\int_0^\beta\frac{d\lambda}{\beta}\langle V_\nu(-i\lambda)V_\mu(t)\rangle_e \tag{5·4}$$

where V is the net flow.

On the other hand, it has been found[1] that the electric conductivity tensor is given, in general, by

$$\sigma_{\mu\nu}=\int_0^\infty dt\, e^{-\varepsilon t}\int_0^\beta d\lambda\langle J_\nu(-i\lambda)J_\mu(t)\rangle_e \tag{5·5}$$

where $J=eV$ is the electric current and e the charge of the particle. Comparing (5·4) with (5·5), we obtain the well-known Einstein relation

$$\sigma_{\mu\nu}=\beta e^2 D_{\mu\nu}^{(1)}. \tag{5·6}$$

It should be remembered, however, that in the presence of a magnetic field we have the flow arising from the local equilibrium distribution, (3·8), which is antisymmetric and thus makes contribution to the antisymmetric part of the diffusion tensor. Thus we obtain the important conclusion that the Einstein relation is valid only for the symmetric part of diffusion and electric conductivity tensors.

In order to see the situation in more detail, let us take a system of electrons in a metal. For simplicity we shall neglect the interaction with phonons, taking account of impurity scattering alone. The Hamiltonian then takes the form

$$H=\sum_j H'(\boldsymbol{x}_j),$$

$$H'(\boldsymbol{x})=\frac{1}{2m}\left(\boldsymbol{p}-\frac{e}{c}\boldsymbol{A}(\boldsymbol{x})\right)^2+\varphi(\boldsymbol{x}),$$

where $\boldsymbol{A}$ is the vector potential of the magnetic field and φ the scalar potential including both periodic and impurity potentials. Hereafter an operator of one electron will be primed as H'. Let us introduce the system of one electron eigenfunctions

$$H'u_r=E_r u_r.$$

Then the Hamiltonian can be written as

$$H=\sum E_r a_r^* a_r, \tag{5·7}$$

where a_r, a_r^* are destruction and creation operators of electrons in the r-state. Similarly

$$\begin{aligned} n_k&=\sum\langle r|n_k'|s\rangle a_r^* a_s, \\ \boldsymbol{v}_k&=\sum\langle r|\boldsymbol{v}_k'|s\rangle a_r^* a_s, \end{aligned} \tag{5·8}$$

where

$$\begin{gathered} n_k'=e^{ik\cdot x}, \quad \boldsymbol{v}_k'=\tfrac{1}{2}(\dot{\boldsymbol{x}}e^{ik\cdot x}+e^{ik\cdot x}\dot{\boldsymbol{x}}), \\ \dot{\boldsymbol{x}}=i[H', \boldsymbol{x}]. \end{gathered} \tag{5·9}$$

Remember that

$$e^{iHt}a_r^* a_s e^{-iHt}=a_r^* a_s e^{i(E_r-E_s)t}$$

and also that

$$\langle a_s^* a_r a_{r'}^* a_{s'}\rangle_{\mathrm{e}}=\delta_{ss'}\delta_{rr'}f(E_s)(1-f(E_r))$$

where f is the Fermi distribution function

$$f(E)=[\exp(\beta E-\hat{\xi})+1]^{-1}. \tag{5·10}$$

Then it is easily seen that (5·1) can be written as

$$\langle\boldsymbol{v}_k\rangle_1=-\xi_k\sum\frac{f(E_r)-f(E_s)}{\beta(E_r-E_s)}\langle s|\dot{n}'_{-k}|r\rangle\langle r|\boldsymbol{v}_k'|s\rangle\left\{\pi\delta(E_r-E_s)+\frac{P}{i(E_r-E_s)}\right\} \tag{5·11}$$

where P indicates taking the principal value. The flow arising from this part is anti-symmetric, whereas the flow arising from the δ-function is symmetric.

Similarly, (3·8) can be written as

$$\langle\boldsymbol{v}_k\rangle_l=\xi_k\sum\frac{f(E_r)-f(E_s)}{\beta(E_r-E_s)}\langle s|n'_{-k}|r\rangle\langle r|\boldsymbol{v}_k'|s\rangle. \tag{5·12}$$

For the sum of those terms in which $E_r \neq E_s$, we can make use of

$$\langle s|\dot{n}'_{-k}|r\rangle = i(E_s - E_r)\langle s|n'_{-k}|r\rangle \tag{5·13}$$

so that the sum exactly cancels the antisymmetric part of (5·11). On the other hand, the terms with $E_r = E_s$ in (5·12) can be transformed as

$$\tilde{\xi}_k \sum \frac{1}{\beta}\frac{\partial f(E_s)}{\partial E}\langle s|\tfrac{1}{2}(n'_{-k}\boldsymbol{v}_k{}' + \boldsymbol{v}_k{}' n'_{-k})|s\rangle - \tilde{\xi}_k \sum_{E_r \neq E_s}\sum \frac{1}{\beta}\frac{\partial f(E_s)}{\partial E}$$
$$\times \tfrac{1}{2}\{\langle s|n'_{-k}|r\rangle\langle r|\boldsymbol{v}_k{}'|s\rangle + \langle s|\boldsymbol{v}_k{}'|r\rangle\langle r|n'_{-k}|s\rangle\}. \tag{5·14}$$

From (5·9) we see

$$\tfrac{1}{2}(n'_{-k}\boldsymbol{v}_k{}' + \boldsymbol{v}_k{}' n'_{-k}) = \dot{\boldsymbol{x}}$$

so that the first term of (5·14) vanishes. For the second term, we can again make use of (5·13). Taking the limit of $k \to 0$ we find the antisymmetric part of the diffusion tensor

$$D^{(A)}_{\mu\nu} = \sum \frac{1}{\beta}\frac{\partial f(E_s)}{\partial E}\cdot\frac{P}{i(E_s - E_r)} \times \tfrac{1}{2}\{\langle s|\dot{x}_\nu|r\rangle\langle r|\dot{x}_\mu|s\rangle - \langle s|\dot{x}_\mu|r\rangle\langle r|\dot{x}_\nu|s\rangle\}. \tag{5·15}$$

On the other hand, the antisymmetric part of the electric conductivity tensor is given as

$$\frac{1}{\beta e^2}\sigma^{(A)}_{\mu\nu} = \sum \frac{f(E_r) - f(E_s)}{\beta(E_r - E_s)}\cdot\frac{P}{i(E_s - E_r)} \times \tfrac{1}{2}\{\langle s|\dot{x}_\nu|r\rangle\langle r|\dot{x}_\mu|s\rangle - \langle s|\dot{x}_\mu|r\rangle\langle r|\dot{x}_\nu|s\rangle\}. \tag{5·16}$$

Now, characteristic frequencies of the electron velocity $\langle s|\dot{x}|r\rangle \exp\{i(E_s - E_r)t\}$ are cyclotron frequency ω_c, collision frequency τ^{-1}, and also the average interval of interband transitions ΔE. If all these frequencies satisfy

$$\beta\omega_c \ll 1, \quad \beta\tau^{-1} \ll 1, \quad \beta\Delta E \ll 1 \tag{5·17}$$

then the difference quotient of f in (5·16) is practically the same as the differential quotient in (5·15), and we have the Einstein relation for the antisymmetric part, too. It is to be noted here that the second of (5·17) is the well-known criterion for applicability of Bloch's kinetic equation, although actually this is too stringent.

§ 6. Damping theoretical expansion

Finally, we shall show that our basic equation (4·1) reduces to the usual Bloch equation in the limit of a system of weakly interacting particles. In fact (4·1) has mathematically the same form as discussed by Kohn and Luttinger[3] in the case of a steady electric field. They have dealt with a simple model in which an electron is scattered by impurities. Actually their method can be applied to integration of the Liouville equation in general, provided that the Hamiltonian satisfies certain conditions.

First let us introduce a symbolic method due to Kubo. Define the linear operator $\mathcal{L}$ which operates always from the left on any dynamical variable η as

$$\mathcal{L}\cdot\eta \equiv i[H,\ \eta]. \tag{6·1}$$

Incidentally, the operator of this sort has been introduced in classical statistical mechanics to prove the ergodic theorem.[7] The Liouville equation can be written as

$$\left(\frac{\partial}{\partial t}+\mathcal{L}\right)\rho(t)=0. \tag{6·2}$$

Let us introduce the Laplace transform

$$\rho(s)=\int_0^\infty dt\, e^{-st}\rho(t) \tag{6·3}$$

which converges for $\Re s>0$. Then (6·2) is transformed into

$$(s+\mathcal{L})\rho(s)=\rho_0 \tag{6·4}$$

where ρ_0 is the initial density matrix at $t=0$. Replacing $\rho(s)$ by ρ_1, ρ_0 by Γ, and taking the limit $s\rightarrow+0$, we obtain our basic equation (4·4). But we shall be concerned with the general case (6·4) for the moment.

Now, assume that the Hamiltonian takes the form

$$H=H_0+gH_1 \tag{6·5}$$

where g is a small numerical parameter indicating the order of perturbation H_1. Correspondingly the operator $\mathcal{L}$ splits as

$$\mathcal{L}=\mathcal{L}_0+g\mathcal{L}_1. \tag{6·6}$$

Let us fix the basic state vectors $|\alpha\rangle$ as

$$H_0|\alpha\rangle=\omega_\alpha|\alpha\rangle.$$

In the case of the electron-phonon interaction, for instance, α stands for a set of occupation numbers of free electrons and phonons. We introduce linear operators $\mathcal{D}$ and $\mathcal{H}$ which also operate from the left on any dynamical variable as

$$\langle\alpha|\mathcal{D}\eta|\alpha'\rangle=\langle\alpha|\eta|\alpha\rangle\delta_{\alpha\alpha'},$$

$$\langle\alpha|\mathcal{H}\eta|\alpha'\rangle=\langle\alpha|\eta|\alpha'\rangle(1-\delta_{\alpha\alpha'}).$$

Without loss of generality we assume that $\mathcal{D}H_1=0$. Following Kohn and Luttinger, we decompose the density matrix into diagonal and non-diagonal parts

$$\begin{aligned}&\rho(s)=\rho_d(s)+\rho_n(s),\\ &\rho_d=\mathcal{D}\rho,\quad \rho_n=\mathcal{H}\rho.\end{aligned} \tag{6·7}$$

Inserting (6·7) together with (6·6) into (6·4) and taking diagonal and non-diagonal parts of the equation respectively, we obtain

$$\begin{aligned}&s\rho_d(s)+g\mathcal{D}\mathcal{L}_1\rho_n(s)=\mathcal{D}\rho_0,\\ &(s+\mathcal{L}_0+g\mathcal{H}\mathcal{L}_1)\rho_n(s)=\mathcal{H}\rho_0-g\mathcal{L}_1\rho_d(s).\end{aligned} \tag{6·8}$$

Eliminating ρ_n from these, we have a formal solution for the diagonal part

$$s\rho_d(s)-g^2\mathcal{D}\mathcal{L}_{\mathrm{I}}\frac{1}{s+\mathcal{L}_0+g\mathcal{H}\mathcal{L}_{\mathrm{I}}}\mathcal{L}_{\mathrm{I}}\rho_d(s)=\mathcal{D}\left(\rho_0-\frac{1}{s+\mathcal{L}_0+g\mathcal{H}\mathcal{L}_{\mathrm{I}}}\mathcal{H}\rho_0\right). \qquad (6\cdot 9)$$

We can derive a power series expansion from (6·9), supposing that

$$\rho_d(s)=O(g^{-2}) \qquad (6\cdot 10)$$

and making use of

$$\frac{1}{s+\mathcal{L}_0+g\mathcal{H}\mathcal{L}_{\mathrm{I}}}=\frac{1}{s+\mathcal{L}_0}+\frac{1}{s+\mathcal{L}_0}g\mathcal{H}\mathcal{L}_{\mathrm{I}}\frac{1}{s+\mathcal{L}_0}+\cdots\cdots. \qquad (6\cdot 11)$$

In particular the lowest order approximation satisfies

$$s\rho_d^{(0)}(s)-g^2\mathcal{D}\mathcal{L}_{\mathrm{I}}\frac{1}{s+\mathcal{L}_0}\mathcal{L}_{\mathrm{I}}\rho_d^{(0)}(s)=\mathcal{D}\rho_0. \qquad (6\cdot 12)$$

Remember that

$$\frac{1}{s+\mathcal{L}_0}\eta=\int_0^\infty dt\exp(-st)\cdot\exp(-iH_0t)\cdot\eta\exp(iH_0t).$$

Then, taking the explicit matrix representation of (6·12), we find

$$\begin{aligned} &sP_\alpha(s)-g^2\sum_{\alpha'}\frac{2s}{s^2+(\omega_\alpha-\omega_{\alpha'})^2}|\langle\alpha|H_{\mathrm{I}}|\alpha'\rangle|^2(P_{\alpha'}(s)-P_\alpha(s))=\langle\alpha|\rho_0|\alpha\rangle, \\ &P_\alpha(s)=\langle\alpha|\rho_d^{(0)}(s)|\alpha\rangle. \end{aligned} \qquad (6\cdot 13)$$

In the limit of $s\rightarrow+0$, we have

$$\frac{2s}{s^2+(\omega_\alpha-\omega_{\alpha'})^2}\sim 2\pi\delta(\omega_\alpha-\omega_{\alpha'}).$$

Hence (6·13) is nothing else but the Laplace transform of the so-called master equation

$$\begin{aligned} &\dot{P}_\alpha(t)=\sum 2\pi g^2|\langle\alpha|H_{\mathrm{I}}|\alpha'\rangle|^2\delta(\omega_\alpha-\omega_{\alpha'})(P_{\alpha'}(t)-P_\alpha(t)), \\ &P_\alpha(t=0)=\langle\alpha|\rho_0|\alpha\rangle. \end{aligned} \qquad (6\cdot 14)$$

which van Hove[8] has obtained by means of rather a lengthy expansion.

Now replacing ρ by ρ_1, ρ_0 by Γ, and taking the limit $s\rightarrow+0$, we have

$$2\pi g^2\sum_{\alpha'}|\langle\alpha|H_{\mathrm{I}}|\alpha'\rangle|^2\delta(\omega_\alpha-\omega_{\alpha'})(F_{\alpha'}-F_\alpha)=\langle\alpha|\Gamma|\alpha'\rangle \qquad (6\cdot 15)$$

where F_α is the diagonal element of ρ_1 in the lowest order approximation. The equation (6·15) says that the drift term due to the gradient of chemical potential is balanced by the collision term due to perturbation H_{I}. More precisely, F_α is still a many-particle distribution function and we have further to reduce (6·15) to obtain the Bloch equation of one particle distribution function.

Of course, certain conditions should be satisfied in order that the transport equation

(6·12) be already a good approximation. Smallness of the parameter g is by no means sufficient. For instance, in the case of an electron scattered by impurities, the contribution of the second term in (6·11) relative to the first would not be simply proportional to g, but to $g\Omega$, if impurities were on regular lattice points. In this case the transport equation can never be a good approximation, because $g\Omega$ can be increased indefinitely by increasing the volume Ω. In general, the size dependence of perturbation in a large system plays an essential role here. We shall not enter into this problem, as the detailed analyses have been given by van Hove.[8]

§ 7. Conclusions

Quantum statistical mechanics of steady diffusion has been formulated. The theory is the most natural generalization of the Bloch kinetic equation and in fact reduces to the latter under certain conditions. An important conclusion is that the Einstein relation is valid only for the antisymmetric part of diffusion- and electric conductivity tensors.

Obviously, the theory can be generalized so as to include heat conduction and viscosity, which will be discussed in a subsequent paper.

The expressions for transport coefficients derived in this way are general and rigorous. In statistical thermodynamics, we have the general expression for the partition function and introduce approximate methods in evaluating this; the virial expansion in the case of imperfect gases, normal vibrations in the case of crystals, and so on. In just the same way, we should introduce appropriate methods of approximation to evaluate transport coefficients, starting with our general expressions. Thus we may couclude that quantum theory of transport coefficients now stands on the same level as statistical mechanics of equilibrium properties, though admittedly we know few methods of approximation such as Bloch's kinetic equation which is nothing but the lowest order approximation in a damping theoretical expansion.

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