Direct calculation of transport coefficients from the Kubo formulas

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A method is proposed for calculating transport coefficients directly from the Kubo formulas, without solving the kinetic equation. The method is based on expanding the scattering operator in inverse powers of the number of atoms in the crystal. In the case of elastic scattering by randomly distributed defects, this method yields the standard results of kinetic theory. In the case of inelastic scattering (e.g., a scattering of electrons by phonons), in contrast, the use of the Kubo formula leads to an explicit expression for the conductivity. In standard kinetic theory, the conductivity can be found only through approximate solution of an integral equation.

The late 1950s were years of fundamental progress in the theory of transport phenomena. Using the equations of motion for the density matrix, Kubo managed to derive exact closed expressions for the transport coefficients in terms of correlation functions of the corresponding fluxes.[1] The static conductivity tensor, for example, is given by

$$\sigma_{\mu\nu} = \mathrm{Re}\int_0^\infty dt \int_0^\beta d\lambda\, \langle j_\nu(-i\lambda)\, j_\mu(t)\rangle, \qquad (1)$$

$$j(t) = \exp(i\mathscr{H}t)\, j \exp(-i\mathscr{H}t), \quad \beta = 1/T, \quad \hbar = 1,$$

where j is the current operator, and $\mathscr{H}$ is the Hamiltonian of the system in the absence of an electric field. With such expressions available, it should have been possible to avoid having to solve the kinetic equation for the nonequilibrium distribution function. In the case of inelastic scattering, this is an extremely important matter, since even the linearized kinetic equation is an integral equation, so it cannot, in general, be solved exactly. Furthermore, the Kubo formula makes it possible in principle to find the conductivity to any order in the interaction of the electrons with the scattering subsystem. The kinetic equation offers no such flexibility.

However, Kubo's theory actually turned out to be incomplete, since no direct methods were found for calculating the current correlation function for specific systems. In particular, attempts to construct such a correlation function by extrapolating to long times the expression derived for short times proved unsuccessful. Such attempts were in fact begun by Kubo himself.[1] In addition, essentially nothing was achieved through the use of the representation in which the complete Hamiltonian $\mathscr{H}$, including the scattering Hamiltonian, was diagonal. Expression (1) thus remained more a formality than a genuine tool for solving practical problems.

Various indirect methods were developed for calculating the current correlation function in cases in which it could be found in terms of a two-particle Green's function. Special methods were proposed for calculating such Green's functions (for example, there is the elegant but rather involved graphical technique worked out by Konstantinov and Perel',[2] and there is the method of equations of motion for two-time Green's functions[3]). These methods ultimately led to a kinetic equation which had previously been derived directly from the equation of motion for the density matrix.[4] These methods also made it possible to establish a first-principles foundation for the kinetic equation. They also made it possible to derive transport coefficients to any order in the potential of the scattering subsystem, with allowance for the renormalization of the energy spectrum of the conduction electrons caused by that subsystem.

Nevertheless, these and other methods aimed in the same direction have not yet solved the problem of how to make direct use of the Kubo formula for specific calculations. In the present paper we wish to propose a method which makes it possible to calculate transport coefficients directly from the Kubo formula without solving a kinetic equation. In this method, the current correlation function is calculated by means of a representation in which the current operator is diagonal. The scattering Hamiltonian is expanded in the inverse number of atoms in the crystal, N. In the case of elastic scattering of electrons by randomly distributed defects, this method makes it possible to derive the standard results of the kinetic theory in the Born approximation. In the case of inelastic scattering of electrons by phonons, in contrast, it becomes possible to derive an expression for the conductivity which is exact within the framework of the Born approximation. This cannot be done in the kinetic theory.

1. IMPURITY SCATTERING

We will demonstrate the general procedure for calculating the current correlation functions in (1) by discussing the example of the scattering of free electrons by randomly distributed defects. The Hamiltonian of the system is

$$\begin{gathered} \mathscr{H} = \mathscr{H}_0 + V, \\ \mathscr{H}_0 = \sum_{\mathbf{k}} E_{\mathbf{k}} a_{\mathbf{k}}^* a_{\mathbf{k}}, \quad E_{\mathbf{k}} = k^2/2m, \\ V = \sum_n v_n, \quad v_n = \frac{1}{N}\sum_{\mathbf{p},\mathbf{q}} v_{\mathbf{pq}} a_{\mathbf{p}}^* a_{\mathbf{q}} \exp[i\boldsymbol{\rho}_n(\mathbf{p}-\mathbf{q})]. \end{gathered} \qquad (2)$$

We have omitted the spin indices from the electron operators $a_{\mathbf{k}}^*$, $a_{\mathbf{k}}$; $\boldsymbol{\rho}_n$ is the position of the defect n; and $v_{\mathbf{pq}}$ is the matrix element of the potential of this defect. To simplify the expressions, we assume that the electron gas is nondegenerate. Accordingly, the contribution of each electron to the conductivity is independent of the contributions of the other electrons. We use the Born approximation, in which we ignore the renormalization of the electron spectrum due to the interaction of the electrons with defects. Making use of the isotropy of this system, we can then rewrite (1) as

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$$\sigma=\frac{2e^2}{3m^2T}\sum_k f_{\mathbf{k}}\int_0^\infty L_{\mathbf{k}}(t)\,dt,$$

$$L_{\mathbf{k}}=\operatorname{Re}\sum_{k'}[\langle\mathbf{k}|\exp(i\mathscr{H}t)\,|\mathbf{k}'\rangle\,(\mathbf{kk}')\,\langle\mathbf{k}'|\exp(-i\mathscr{H}t)\,|\mathbf{k}\rangle]_{Av}, \tag{3}$$

where $f_{\mathbf{k}}$ is the equilibrium distribution function for an electron with a momentum **k**, and the subscript Av means an average over the distribution of defects.

To calculate the matrix elements of the operator exponential functions, we use the well-known relation

$$\exp[i(A+B)t]=e^{iA^tT}\exp\Big(i\int_0^t e^{-iA\tau}Be^{iA\tau}\,d\tau\Big), \tag{4}$$

where T denotes a time ordering. Thinking of a random distribution of the impurity, we put the operator exponential functions in a form which is multiplicative in the defect index in order to carry out the averaging over the positions of the defects. For example, in order to single out v_1 we should use as the operators A and B in (4) the quantities $\mathscr{H}_1=\mathscr{H}-v_1$ and v_1, respectively. In our approximation we then find

$$\exp(i\mathscr{H}t)=\exp(i\mathscr{H}_1t)\Big[1+i\int_0^t\exp(-i\mathscr{H}_1\tau)\,v_1\exp(i\mathscr{H}_1\tau)\,d\tau$$

$$-\int_0^t\int_0^\tau d\tau\,d\tau_1\,\tilde{v}_1(-\tau_1)\,\tilde{v}(-\tau)\Big],$$

$$\tilde{B}(\tau)=\exp(i\mathscr{H}_0\tau)\,B\exp(-i\mathscr{H}_0\tau). \tag{5}$$

According to (4), on the other hand, in the same approximation we have

$$\exp(-i\mathscr{H}_1\tau)\,v_1\exp(i\mathscr{H}_1\tau)$$

$$\approx\exp(-i\mathscr{H}_0\tau)\Big\{v_1-i\int_0^t d\tau[\tilde{V}_1(\tau),v_1]\Big\}$$

$$\times\exp(i\mathscr{H}_0\tau),\quad V_1=V-v_1. \tag{6}$$

When we take a configurational average of the product of two operator exponential functions from (3), including v_1, we find that the second term in (5), (6) and the corresponding term from the complex-conjugate exponential function vanish. The reason is that these are the only terms among those of order v^2 which depend in a random way on the random coordinate ρ_1.

Continuing this procedure, we can write

$$L_{\mathbf{k}}=\operatorname{Re}\sum_{\mathbf{k}'}(\mathbf{kk}')\Big\langle\mathbf{k}\Big|\prod_n X_n\Big|\mathbf{k}'\Big\rangle\Big\langle\mathbf{k}'\Big|\prod_n X_n^*\Big|\mathbf{k}\Big\rangle,$$

$$X_n=1+i\int_0^t v_n(-\tau)\,d\tau-\int_0^t d\tau\int_0^\tau d\tau_1\,\tilde{v}_n(-\tau)\,\tilde{v}_n(-\tau_2). \tag{7}$$

Writing the matrix elements of the product of the operators χ_n in (7) in terms of the matrix elements of the operators χ_n separately, taking a configurational average over the pairs $\langle\mathbf{p}|\chi_n|\mathbf{p}'\rangle\langle\mathbf{q}'|\chi_n^*|\mathbf{q}\rangle$, and using the relation

$$\tilde{a}_k(t)=\exp(i\mathscr{H}_0t)\,a_{\mathbf{k}}\exp(-i\mathscr{H}_0t)=\exp(-iE_{\mathbf{k}}t)\,a_{\mathbf{k}}, \tag{8}$$

we find

$$L_{\mathbf{k}}=\operatorname{Re}\sum_{\{l_n\}}\sum_{\{\mathbf{r}_n\}}\prod_{n=1}^{M}\Big\{\delta_{\mathbf{l}_{n-1},\mathbf{l}_n}\delta_{\mathbf{r}_n,\mathbf{r}_{n-1}}$$

$$\times\Big[1-\sum_p(|v_{\mathbf{l}_n\mathbf{p}}|^2G_{\mathbf{l}_n\mathbf{p}}+|v_{\mathbf{r}_n\mathbf{p}}|^2G_{\mathbf{r}_n\mathbf{p}}\Big]$$

$$+v_{\mathbf{l}_{n-1}\mathbf{l}_n}v_{\mathbf{r}_n\mathbf{r}_{n-1}}F_{\mathbf{l}_{n-1}\mathbf{l}_n}F_{\mathbf{r}_n\mathbf{r}_{n-1}}\delta_{\mathbf{l}_n-\mathbf{l}_{n-1},\,\mathbf{r}_n-\mathbf{r}_{n-1}}\Big\}(\mathbf{k},\mathbf{k}_M). \tag{9}$$

Here M is the number of defects, and we are using the notation

$$F_{\mathbf{pk}}\equiv F(\omega_{\mathbf{kp}})=(i\omega_{\mathbf{kp}})^{-1}[\exp(i\omega_{\mathbf{kp}}t)-1],\quad \omega_{\mathbf{kp}}=E_{\mathbf{k}}-E_{\mathbf{p}}, \tag{10}$$

$$G_{\mathbf{lp}}=G(\omega_{\mathbf{lp}})=\omega_{\mathbf{lp}}^{-2}(1-\cos\omega_{\mathbf{lp}})+i\omega_{\mathbf{lp}}^{-1}(\omega_{\mathbf{lp}}^{-1}\sin\omega_{\mathbf{lp}}-1). \tag{11}$$

Using

$$\lim_{t\to\infty}\frac{2\sin^2(\omega t/2)}{\omega^2t}=\pi\delta(\omega) \tag{12}$$

we can write (9) in the form

$$L_{\mathbf{k}}=k^2\Big\{\Big(1-t\sum_{\mathbf{q}}W_{\mathbf{kq}}\Big)^M$$

$$+\sum_{\mathbf{q}}\Big(1-t\sum_{\mathbf{p}}W_{\mathbf{kp}}\Big)^{M-1}MW_{\mathbf{kq}}t\frac{(\mathbf{kq})}{k^2}\Big\}$$

$$\approx k^2\Big\{1-t\sum_{\mathbf{q}}W_{\mathbf{kq}}\Big[1-\frac{(\mathbf{kq})}{k^2}\Big]\Big\}^M, \tag{13}$$

where we are using the following notation for the probability for scattering from the state $|\mathbf{k}\rangle$ to the state $|\mathbf{q}\rangle$:

$$W_{\mathbf{kq}}=2\pi|v_{\mathbf{kq}}|^2\delta(\omega_{\mathbf{kq}})/N^2. \tag{14}$$

In writing (11) we note that in the case of elastic scattering with $E_{\mathbf{k}}=E_{\mathbf{q}}$ the following relation holds:

$$\sum_{\mathbf{p}}W_{\mathbf{kp}}=\sum_{\mathbf{p}}W_{\mathbf{qp}}\equiv\tilde{\tau}_{\mathbf{k}}^{-1}. \tag{15}$$

Since the second term in parentheses on the right side of (11) is of order $1/N$, the response function for (11) can be rewritten as

$$L_{\mathbf{k}}=k^2\exp(-t/\tau_{\mathbf{k}}),$$

$$\tau_{\mathbf{k}}^{-1}=M\sum_{\mathbf{q}}W_{\mathbf{kq}}\Big[1-\frac{(\mathbf{qk})}{k^2}\Big]. \tag{16}$$

The decay of $L_{\mathbf{k}}$ with the time is thus a simple exponential decay, and the scale is the ordinary relaxation time for transport processes in the Born approximation (it differs from the decay time of the state by a trigonometric factor inside the integral). According to (3) and (13), the conductivity of a nondegenerate electron gas is given by precisely the same expression which we find by solving the kinetic equation:

$$\sigma=\frac{2e^2}{3m^2T}\sum_{\mathbf{k}}k^2f_{\mathbf{k}}\tau_{\mathbf{k}}. \tag{17}$$

2. SCATTERING BY PHONONS

Below we will use the Kubo formula to derive an expression for the conductivity of a nondegenerate electron gas for the case in which a scattering by phonons is predominant. A scattering by phonons differs from a scattering by an impurity in that it is generally inelastic. For this reason, the kinetic equation cannot be solved exactly, as we have already stated. Correspondingly, we would expect that the response function corresponding to the inelastic scattering would fall off by a law more complex than the simple exponential law in (16) as time elapsed.

The Hamiltonian of the electron-phonon system is

$$\mathscr{H}=\mathscr{H}_0+V, \qquad V=\sum_q V_q,$$
$$\mathscr{H}_0=\sum_{\mathbf{k}} E_{\mathbf{k}} a_{\mathbf{k}}^* a_{\mathbf{k}}+\sum_{\mathbf{q}} \nu_{\mathbf{q}} b_{\mathbf{q}}^* b_{\mathbf{q}}, \tag{18}$$
$$V_{\mathbf{q}}=\frac{1}{N^{1/2}}\sum_{\mathbf{k}} A_q\left(b_{\mathbf{q}}^* a_{\mathbf{k}}^* a_{\mathbf{k}+\mathbf{q}}+a_{\mathbf{k}+\mathbf{q}}^* a_{\mathbf{k}} b_{\mathbf{q}}\right),$$

where $b_{\mathbf{q}}^*$, $b_{\mathbf{q}}$ are the phonon creation and annihilation operators. Since the phonon modes are independent of each other, the temperature averaging over each can be carried out separately. This circumstance greatly simplifies the calculation of the response function through an expansion of the operator exponential functions in (3) in $V_{\mathbf{q}} \propto N^{-1/2}$. Using the same calculation approach as before, we find an analog of expression (9):

$$L_{\mathbf{k}}=\sum_{\{\mathbf{l}_n\}}\sum_{\{\mathbf{r}_n\}}\prod_{n=1}^{N} U_{\mathbf{l}_n,\mathbf{r}_n}(\mathbf{l}_0\mathbf{l}_N)\,\delta_{\mathbf{l}_0,\mathbf{k}}\delta_{\mathbf{r}_0,\mathbf{k}}\delta_{\mathbf{l}_N,\mathbf{r}_N},$$
$$\begin{aligned}U_{\mathbf{l}_n,\mathbf{r}_n}&=\delta_{\mathbf{l}_{n-1},\mathbf{l}_n}\delta_{\mathbf{r}_n,\mathbf{r}_{n-1}}\Big(1-\frac{A_{\mathbf{q}_n}^2}{N}\{m_{\mathbf{q}_n}[G(\omega_{\mathbf{l}_n,\mathbf{l}_n+\mathbf{q}_n}+\nu_{\mathbf{q}_n})\\&\quad+G(\omega_{\mathbf{r}_n,\mathbf{r}_n+\mathbf{q}_n}+\nu_{\mathbf{q}_n})]+(1+m_{\mathbf{q}_n})[G(\omega_{\mathbf{l}_n,\mathbf{l}_n-\mathbf{q}_n}-\nu_{\mathbf{q}_n})\\&\quad+G(\omega_{\mathbf{r}_n,\mathbf{r}_n-\mathbf{q}_n}-\nu_{\mathbf{q}_n})]\}\Big)\\&\quad+\frac{A_{\mathbf{q}_n}^2}{N}[m_{\mathbf{q}_n}F(\omega_{\mathbf{l}_n-\mathbf{q}_n,\mathbf{l}_n}+\nu_{\mathbf{q}_n})F(\omega_{\mathbf{r}_n,\mathbf{r}_n-\mathbf{q}_n}-\nu_{\mathbf{q}_n})\\&\quad\times\delta_{\mathbf{l}_{n-1},\mathbf{l}_n-\mathbf{q}_n}\delta_{\mathbf{r}_{n-1},\mathbf{r}_n-\mathbf{q}_n}+(1+m_{\mathbf{q}_n})F(\omega_{\mathbf{l}_n+\mathbf{q}_n,\mathbf{l}_n}-\nu_{\mathbf{q}_n})\\&\quad\times F(\omega_{\mathbf{r}_n,\mathbf{r}_n+\mathbf{q}_n}+\nu_{\mathbf{q}_n})\delta_{\mathbf{l}_n,\mathbf{l}_n+\mathbf{q}_n}\delta_{\mathbf{r}_n,\mathbf{r}_n+\mathbf{q}_n}].\end{aligned} \tag{19}$$

Making use of the parity with respect to **q** of the quantities $A_{\mathbf{q}}$ and $\nu_{\mathbf{q}}$ and the average phonon numbers $m_{\mathbf{q}}$, we find the following expression[1] from (19):

$$\begin{aligned}L_{\mathbf{k}}&=k^2\exp\Big\{-t\sum_n(W_{\mathbf{k},\mathbf{k}+\mathbf{q}_n}^{+}+W_{\mathbf{k},\mathbf{k}+\mathbf{q}_n}^{-})\\&\qquad\times\Big[1-\frac{\mathbf{k}(\mathbf{k}+\mathbf{q}_n)}{k^2}\exp(tR_{\mathbf{k}n})\Big]\Big\},\\R_{\mathbf{k}n}&=\sum_{m=n+1}^{N}(W_{\mathbf{k},\mathbf{k}-\mathbf{q}_m}^{+}+W_{\mathbf{k},\mathbf{k}+\mathbf{q}_m}^{-}-W_{\mathbf{k}+\mathbf{q}_n,\mathbf{k}+\mathbf{q}_n-\mathbf{q}_m}^{+}\\&\qquad-W_{\mathbf{k}+\mathbf{q}_n,\mathbf{k}+\mathbf{q}_n+\mathbf{q}_m}^{-}),\\W_{\mathbf{r},\mathbf{k}-\mathbf{q}_n}^{+}&=\frac{2\pi}{N}|A_{\mathbf{q}_n}|^2(m_{\mathbf{q}_n}+1)\,\delta(\omega_{\mathbf{k},\mathbf{k}-\mathbf{q}_n}-\nu_{\mathbf{q}_n}),\\W_{\mathbf{k},\mathbf{k}+\mathbf{q}_n}^{-}&=\frac{2\pi}{N}|A_{\mathbf{q}_n}|^2 m_{\mathbf{q}_n}\delta(\omega_{\mathbf{k},\mathbf{k}+\mathbf{q}_n}+\nu_{\mathbf{q}_n}).\end{aligned} \tag{20}$$

According to (20), the time dependence of the response function is indeed nonexponential. From the condition that the conductivity remain finite we conclude that the quantities $R_{\mathbf{k}n}$ must definitely be negative under the condition $k^2+\mathbf{k}\cdot\mathbf{q}_n>0$. If these quantities are negative, and the condition $k^2+\mathbf{k}\cdot\mathbf{q}_n<0$ holds, then as time elapses there should be a crossover from exponential dependence with a time scale τ_k,

$$\tau_{\mathbf{k}}^{-1}=\sum_{\mathbf{q}}(W_{\mathbf{k},\mathbf{k}+\mathbf{q}}^{+}+W_{\mathbf{k},\mathbf{k}+\mathbf{q}}^{-})\left[1-\frac{\mathbf{k}(\mathbf{k}+\mathbf{q})}{k^2}\right] \tag{21}$$

(this is the analog of the transport relaxation time), to the same dependence but with time scale $\tilde{\tau}_{\mathbf{k}}$,

$$\tilde{\tau}_{\mathbf{k}}^{-1}=\sum_{\mathbf{q}}(W_{\mathbf{k},\mathbf{k}+\mathbf{q}}^{+}+W_{\mathbf{k},\mathbf{k}+\mathbf{q}}^{-}). \tag{22}$$

This time scale represents the lifetime of the state $|\mathbf{k}\rangle$.

We should point out that in the case of inelastic scattering the time $\tau_{\mathbf{k}}$ (in contrast with $\tilde{\tau}_{\mathbf{k}}$) is not positive definite. Accordingly, there is the possibility in principle that the response function $L_{\mathbf{k}}$ will be a nonmonotonic function of t, increasing at small values of t and decreasing only after a sufficiently long time, when the behavior of $L_{\mathbf{k}}$ is determined by the lifetime $\tilde{\tau}_{\mathbf{k}}$.

If, on the other hand, the quantities $R_{\mathbf{k}n}$ are positive under the condition $k^2+\mathbf{k}\cdot\mathbf{q}<0$, then for $t>R_{\mathbf{k}n}^{-1}$ the (negative) argument of the exponential function in the expression for $L_{\mathbf{k}}$ would increase exponentially with time. At such times the response function would thus fall off not exponentially but essentially abruptly with increasing t.

In the high-temperature limit, where the electron energies are high in comparison with the phonon frequencies, the inelastic nature of the scattering of electrons by phonons can be ignored. We can then write $|\mathbf{k}|=|\mathbf{k}+\mathbf{q}_n|$ in (20). Making use of the circumstance that the sums of the quantities $W_{\mathbf{k},\mathbf{k}\mp qm}^{\pm}$ and $W_{\mathbf{k}+qn,\mathbf{k}+qn\mp qm}^{\pm}$ over all vectors of the star $\mathbf{q}_m$ are equal to each other, we find that the quantity $R_{\mathbf{k}n}$ vanishes. (Strictly speaking, the summation over the vectors of the star $\mathbf{q}_{n+1}$ in the expression for $R_{\mathbf{k}n}$ may be incomplete, but since their number is finite the corresponding error is asymptotically small.) The time dependence of the response function thus becomes purely exponential, as in (16), and the time $\tau_{\mathbf{k}}$ in (21), which is positive definite in this limit, becomes a genuine relaxation time.

It is a simple matter to derive an expression for the conductivity in which the extent to which the scattering is inelastic is appreciable, but still small. This expression differs from (17) in that the actual relaxation time $\tau_{\mathbf{k}}$ is replaced by an effective time $\tau_{\mathbf{k}}^{\text{eff}}$ given by

$$\tau_{\mathbf{k}}^{ef}=\tau_{\mathbf{k}}+2Q_{\mathbf{k}}\tau_{\mathbf{k}}^3,\quad Q_{\mathbf{k}}=\sum_q\frac{\mathbf{k}(\mathbf{k}+\mathbf{q})}{k^2}(W_{\mathbf{k},\mathbf{k}+\mathbf{q}}^{+}+W_{\mathbf{k},\mathbf{k}+\mathbf{q}}^{-})R_{\mathbf{k}\mathbf{q}}.$$

When the scattering is substantially inelastic, it would apparently be necessary to appeal to numerical calculations to find the time integral of (3) with (20).

[1] Note that the result (20) should be the same as the result of the exact solution of the integrodifferential kinetic equation, if such a solution were possible.

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