Projection Techniques in the Theory of Electrical Resistivity*

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A formula for the electrical resistivity expressed in terms of a projection operator is derived and discussed. It is argued that the correct evaluation of the resistivity to the lowest order in the strength of the scattering interaction on the basis of this formula requires, as do other formal expressions, the summation of an infinite number of terms. This re-establishes the standard theory of electrical conductivity, based on the integral transport equation for the distribution function.

There exist a large number of theoretical methods[1-17] for the evaluation of the electrical conductivity of solids. Although the techniques differ, they all require[18] the solution of an integral equation, which in the lowest approximation for the scattering and for a weak, homogeneous, and static electric field is equivalent to the Boltzmann-Bloch transport equation, first proposed by Bloch and Nordheim.[19]

We present below a different method for the evaluation of the electrical conductivity, based on an adaptation of the general theory of irreversible processes recently presented by Mori.[20] By the use of a particular projection operator we obtain an expression for the conductivity that is different from the earlier ones in the following important aspect: All indicated operations in it are performed in the denominator. Thus, we obtain a formal expression for the *resistivity*.

Although a similar method has been presented earlier by Kendre and Dresden,[21] our expression provides a very convenient basis for investigating higher order terms and for summing certain subsets of them. This advantage is very important, since the application of the Kenkre and Dresden[21] method by the same authors[22,23] to the problem of dc conductivity has led to unfortunate errors.[24]

We show how our thoery yields a formula for the dc resistivity that is identical to the one obtained through the solution of the integral transport equation,[19] thus re-establishing the correctness of an entire body[1-19] of theoretical investigation. This is in contradiction to some recent claims[22,23] to the contrary.

We consider a system of electrons driven by a homogeneous electric field $E(t) = Ee^{-i\omega t} + \text{c.c.}$ of frequency ω in a particular direction. The interaction Hamiltonian is $-eE(Ae^{-i\omega t} + \text{H.c.})$, where A is the appropriate position operator. The steady-state conductivity is then

$$\sigma(\omega) = (-e^2/m)\,\mathrm{tr}[p\rho(\omega)], \qquad (1)$$

where p is the operator for the component of the momentum of the system in the direction of the field, and $\rho(\omega)$ is the steady-state density operator linear in E with the factor $(-eE)$ removed and exhibited in (1). (We have set the volume of the system equal to unity.) From the equation of motion for the density operator we have,[14] for $\rho(\omega)$ (we take $\hbar = 1$ throughout),

$$(\omega^+ - L)\rho(\omega) = [A, f_0(H)] \equiv D. \qquad (2)$$

Here L is the Liouville operator corresponding to the Hamiltonian H of the system in the absence of the electric field, i.e., for any operator X

$$LX \equiv [H, X]; \qquad (3)$$

$f_0(H)$ is the thermal equilibrium density operator, and $\omega^+ = \omega + i\epsilon$, where ϵ is a positive infinitesimal. In (1) the limit $\epsilon \to 0^+$ should be taken last. An expression for the conductivity can now be obtained by the introduction of a projection operator P, analogous to those used by Mori[20] in a different context. For any operator X, we define P by the relation

$$PX = D\,\mathrm{tr}(pX)/\mathrm{tr}(pD) = Da^{-1}\,\mathrm{tr}(pX), \qquad (4)$$

where D is defined in (2). This is possible provided $a \equiv \mathrm{tr}(pD) \neq 0$. We note immediately that

$$PD = D, \quad P'D \equiv (1 - P)D = 0, \qquad (5)$$

and thus P is a projection operator. We now introduce in (2) the splitting $\rho = P\rho + P'\rho$, and then operate on it with P and P', separately, to get with the help of (5)

$$(\omega^+ - PL)P\rho - PLP'\rho = D, \qquad (6)$$

$$(\omega^+ - P'L)P'\rho - P'LP\rho = 0. \qquad (7)$$

Solving (7) for $P'\rho$ in terms of $P\rho$ and substituting it in (6), we have

$$\{\omega^+ - PL[1 + G'(\omega)P'L]\}P\rho = D, \qquad (8)$$

where we have introduced the propagator

$$G'(\omega) = (\omega^+ - P'L)^{-1}. \tag{9}$$

We note that all terms on the left-hand side of (8) are simple scalar multiples of D, and thus from (1), (4), and (8) we find

$$\sigma(\omega) = (-e^2a^2/m) \times \{a\omega^+ - \mathrm{tr}(pL[1 + G'(\omega)P'L]D)\}^{-1}. \tag{10}$$

This can also be written in the equivalent form

$$\sigma(\omega) = (-e^2a^2/m)(1/\omega^+) \times [a - \mathrm{tr}(pLG'(\omega)D)]^{-1}, \tag{11}$$

since from the definition (9) of $G'(\omega)$ we have $1 + G'P'L = \omega^+G'$.

Equations (10) and (11) are formal expressions for $\sigma(\omega)$. They have the feature that all operators are carried out in the denominator and thus provide, directly, expressions for the resistivity.

One might think that a theory of the dc resistivity in the lowest approximation for the scattering consists in evaluating the denominator in (10) for $\omega = 0$, i.e.,

$$Q(0) \equiv \mathrm{tr}\{pL[1 + G'(0)P'L]D\}, \tag{12}$$

by keeping only terms of order λ^2, where λ characterizes the strength of the scattering interaction V; i.e., we take $H = H_0 + V$, where H_0 is the unperturbed energy of the electrons such that $[H_0, p] = 0$, while V is a momentum-independent scattering potential totally responsible for the dc resistivity. If we introduce the Liouville operators $L_0X \equiv [H_0, X]$ and $L_1X \equiv [V, X]$, we note that the first term in (12) vanishes, because $L_0p = 0$ and $[A, L_1p] = 0$ for a momentum independent V. Since now $PLD \propto \mathrm{tr}(pLD) = 0$, we have

$$Q(\omega) = \mathrm{tr}[pL_1G'(\omega)LD].$$

The propagator $G'(\omega)$ can be expanded in powers of λ in the form

$$\begin{aligned} G'(\omega) &= (\omega^+ - L_0 - P'L_1)^{-1} \\ &= G_0(\omega) + G_0(\omega)P'L_1G_0(\omega) + \dots, \end{aligned} \tag{13}$$

since $PL_0X \propto \mathrm{tr}[(L_0p)X] = 0$. In (13) we have introduced the unperturbed propagator

$$G_0(\omega) = (\omega^+ - L_0)^{-1}. \tag{14}$$

The operator $D = [A, f_0(H_0 + V)] = D_0 + D_1 + \dots$ can be expanded in powers of λ in the standard way. We note that for this system $D_0 = [A, f_0(H_0)] = (i/m)f_0'(H_0)p$, where $f_0'(x) = \partial f_0(x)/\partial x$, and therefore $L_0D_0 = 0$. Thus, $Q(\omega = 0)$ is given up to order λ^2 by

$$Q(0) \cong \mathrm{tr}[pL_1G_0(0)L_1D_0], \tag{15}$$

since the term L_0D_1 does not contribute to $Q(0)$. A straightforward evaluation of the trace in (15) in the representation $|k\rangle$ that diagonalizes both H_0 and p gives

$$Q(0) \cong (2m)^{-1} \sum_{kk'} f_0(\mathcal{E}_k)W_{kk'}(p_k - p_{k'})^2, \tag{16}$$

where

$$W_{kk'} = 2\pi|V_{kk'}|^2\delta(\mathcal{E}_k - \mathcal{E}_{k'}), \tag{17}$$

$\mathcal{E}_k$ denote the eigenvalues of H_0, and $p_k = \langle k|p|k\rangle$. Finally, since $a = \mathrm{tr}(pD) = \mathrm{tr}\{[p, A]f(H)\} = -iN$, where N is the number of electrons, Eqs. (10) and (16) yield the expression

$$\sigma(0)^{-1} \cong -\sum_{kk'} \frac{f_0'(\mathcal{E}_k)W_{kk'}(p_k - p_{k'})^2}{2N^2e^2}. \tag{18}$$

This is an explicit expression in terms of the matrix elements of V and does not involve the solution of an integral equation. An identical expression is obtained in the same order of λ, if expression (11) is used for $\sigma(0)$.

We wish now to point out that formula (18) is, in fact, generally *not* the correct expression for the dc resistivity to the lowest order in the scattering. We remark that Kenkre and Dresden[22,23] have erroneously identified an expression equivalent to (18) as the correct dc resistivity.[24]

The reason that (18) is not the correct expression for the dc resistivity is the fact that in the expansion of $Q(0)$ there are in general higher order in λ terms that diverge (in the final limit $\epsilon \to 0^+$). There are two groups of such divergent terms. The first group arises from the very choice of the projection operator P. To see this note that the expansion of $Q(0)$ in powers of λ is generated by use of the expansion (13) of $G'(\omega)$ in powers of $P'L_1 = (1 - P)L_1$ and of the expansion of D in powers of λ. In any given order in λ, the operator P, which figures in such an expansion, yields terms proportional to $\mathrm{tr}[pL_1G_0(0)\cdots L_1 \times G_0(0)D_0]$. Now since $L_0D_0 = 0$, it follows that

$$G_0(0)D_0 = (i\epsilon - L_0)^{-1}D_0 = (1/i\epsilon)D_0, \tag{19}$$

where $\epsilon \to 0^+$, and thus these terms diverge. The second group of divergent terms arises whenever in the expansion of $G'(0)$ according to (13), $G_0(0)$ operates on the part X_d of an operator X that is diagonal in the k representation, since

$$[G_0(0)X_d]_{kk'} = (i\epsilon)^{-1}X_{kk}\delta_{kk'}. \tag{20}$$

It is important to note that for the off-diagonal part X_{nd} of X, for $k' \neq k$,

$$[G_0(0)X_{nd}]_{kk'} = (i\epsilon - \mathcal{E}_k + \mathcal{E}_{k'})^{-1}X_{kk'} \tag{21}$$

has no divergent terms, since in the summation over the intermediate states in the thermodynamic limit this becomes $[-i\pi\delta(\mathcal{E}_k - \mathcal{E}_{k'}) - (\mathcal{E}_k - \mathcal{E}_{k'})_p^{-1}]X_{kk'}$ as $\epsilon \to 0^+$. Thus the procedure of keeping only the lowest order in λ terms in the expansion of $Q(0)$ is invalid.

In fact, we have shown that by summing the terms of the form of any power of $(\lambda^2/i\epsilon)$ that appear in the expansion of the denominator in (11) —a procedure equivalent to the "$\lambda^2 t$ limit" technique of Van Hove[25]—we get an expression for the dc resistivity to order λ^2 that is identical to the well-known one obtained through the solution of the *integral* transport equation and different from (18). For concreteness we have considered a system of independent electrons in a periodic potential and a set of fixed impurities, within the one-band approximation. Such a system satisfies all the previous specifications and the k representation is then the set of one-band Bloch states $|\vec{k}\rangle$ (we ignore spin throughout).

In (11) we expand[26] $G'(0)$ and D in powers of λ and sum all terms that are of the form $(\lambda^2/i\epsilon)^n$. Higher order terms can also be summed, but they give rise to corrections of the dc resistivity of order λ^3 and higher.

The identification and summation of the divergent terms is facilitated considerably by the introduction of the operator Δ that projects the part of any operator X that is diagonal in the k representation, i.e.,

$$(\Delta X)_{kk'} \equiv X_{kk}\delta_{kk'}. \tag{22}$$

From (11) we thus find[26] for the dc conductivity

$$\sigma(0) \cong (e^2/m)\,\mathrm{tr}\{p[\Delta L_1 G_0(0) L_1]^{-1} D_0\}. \tag{23}$$

It is evident that (23) gives the dc resistivity $1/\sigma(0)$ to order λ^2.

More explicitly, (23) can be written in terms of the diagonal operator

$$f \equiv -[\Delta L_1 G_0(0) L_1]^{-1} D_0 \tag{24}$$

in the usual form

$$\sigma(0) \cong (-e^2/m)\textstyle\sum_k p_k f_k. \tag{25}$$

From (24) f_k is seen to be determined from the integral equation

$$\begin{aligned}\textstyle\sum_{k'} W_{kk'}(f_{k'} - f_k) &= -(i^{-1}D_0)_{kk} \\ &= -f_0'(\mathcal{E}_k)p_k/m,\end{aligned} \tag{26}$$

with $W_{kk'}$ given by (17). This is the standard result[1] of the well-known transport theory[3,4,12,14] of electrical conduction for the lowest order in the scattering.

In order to make explicit how this result differs from that proposed by Kenkre and Dresden, we consider the isotropic case of free electrons. The transport equation (26) then has a simple solution in terms of an energy-dependent relaxation time

$$\tau(\mathcal{E}_k)^{-1} = \textstyle\sum_{k'} W_{kk'}(1 - \cos\theta_{kk'}), \tag{27}$$

where $\theta_{kk'}$ is the angle between the wave vectors $\vec{k}$ and $\vec{k}'$. The dc conductivity is then $\sigma(0) = Ne^2\tau/m$, where according to the standard expression (23)

$$\tau = -\textstyle\sum_k p_k^2 f_0'(\mathcal{E}_k)\tau(\mathcal{E}_k)/Nm, \tag{28}$$

whereas according to the expression (18)

$$\tau \to \tilde{\tau} = -Nm/\textstyle\sum_k p_k^2 f_0'(\mathcal{E}_k)\tau(\mathcal{E}_k)^{-1}. \tag{29}$$

The two expressions are clearly different in general, even in this simple case. Only for completely degenerate statistics are these two expressions equal, since then $\tau = \tilde{\tau} = \tau(\mathcal{E}_F)$, where $\mathcal{E}_F$ is the Fermi energy.

A more detailed discussion should, of course, include the important role of the randomness of the impurity distribution. We plan to discuss this and other relevant questions in a different publication.[26]

To conclude, we reiterate that the formal expressions (10) and (11) for the conductivity yield, if handled correctly—which for the system under consideration implies the use of the "$\lambda^2 t$ limit" technique or something equivalent to it—, an expression for the dc conductivity identical to the one obtained through the use of the integral transport equation.

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[24] If in fact the assertion of Kenkre and Dresden (Refs. 22, 23) were correct, it would have been of paramount importance in the theory of electrical conductivity in solids, since it would have bypassed the often difficult task of solving the integral transport equation figuring in all earlier theories. They also emphasized that their formal expression for $\sigma(0)$, equivalent to our Eq. (10), can be used without invoking the technique of the "$\lambda^2 t$ limit" of van Hove, in contrast to other formal expressions (Ref. 2) for the conductivity which necessitate the use of the "$\lambda^2 t$ limit" technique. As our discussion shows, this claim is wrong.

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[26] The details of this proof will be reported in a separate publication.

Layer Method for Band Structure of Layer Compounds

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We present a method of calculating the band structure of layer compounds that combines the transmission and reflection matrices from individual atomic layers. The computing time increases linearly with the number p of layers in the repeat unit, compared with p^3 for other methods, thus rendering the method suitable for layer compounds with complicated stacking sequences. Results for MoS_2 are described.

The method presented here is based on the layer-scattering method originally developed for low-energy electron diffraction.[1-4] We believe that it is particularly well suited for the calculation of the band structure of the layer compounds such as the transition-metal dichalcogenides. The latter compounds have recently attracted much experimental interest.[5]

The usual methods of calculating band structure [augmented plane wave (APW), Korringa-Kohn-Rostoker, etc.] when applied to crystals, especially anisotropic crystals having so many atoms per unit cell, are cumbersome to the point that calculations are possible only for points of high symmetry. Calculations made so far have mainly employed semiempirical methods because of these difficulties, though recently Mattheiss[6] has made first-principles calculations using the APW method at symmetry points, with a tight-binding scheme interpolating between the points.

All the various structures of the layered transition-metal dichalcogenides can be broken down into layers containing only one type of atom. The complexity is generated by the stacking together of layers. It is the large unit-cell dimension normal to the layers that necessitates the large number of Fourier components required to describe the wave functions. Parallel to the layers only a modest number of Fourier components are required. It would seem logical to employ a two-dimensional Fourier expansion of the wave function parallel to the layers, the z variation being represented in real space.

The treatment given here follows Pendry.[3] The