Calculation of transport coefficients
in solids by generalized kinetic equations

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1. Introduction

Now as before there is a great interest in the calculation
of transport coefficients in solids in order to explain the
experimental results as well as to get information on the
microscopic structure of the solids. There exist a lot of
theoretical methods for the calculation of transport coeffi-
cients as a rule having a fairly restricted range of validity
and applicability. The most popular and succesful approach
starts from the linearized Boltzmann equation which can be
derived assuming weak scattering processes. On the other
hand transport coefficients can be calculated by means of
exact quantummechanical linear response expressions as the
Kubo formula for the electrical conductivity. These exact
correlation function expressions can be directly evaluated
only in a few special cases without using sophisticated many-
body techniques or fairly bad approximations. One of the most
suitable methods is the Mori projection operator technique
where the linear response correlation function can be trans-
formed into other correlation functions more convenient for
a practical calculation. As an example we consider the d.c.
electrical conductivity

$$\sigma = \frac{e^2}{3m^2\Omega}\,\langle \vec{P};\ \vec{P}\rangle = \frac{e^2}{3m^2\Omega}\int_{-\infty}^{0}dt\,e^{\eta t}\int_{0}^{\beta}d\lambda\,\mathrm{Tr}\{\varrho\,\vec{P}(t-i\lambda)\vec{P}\};\ \eta\to 0^+ \quad (1)$$

where $\vec{P}$ is the total momentum of the electrons. Representing
$\vec{P}$ as a sum of operators A_i (relevant observables) which can be
chosen properly to describe the system considered (see below),
the corresponding correlation functions $\langle A_i ; A_j \rangle$ can be
calculated by the set of equations

$$\sum_k \left[i\eta\,\delta_{ik} - i\sum_l (\dot{A}_l|A_l)(\chi^{-1})_{lk} + i\sum_l \pi_{il}(\chi^{-1})_{lk}\right]\langle A_k ; A_j\rangle = i\chi_{ij} \quad (2)$$

where

$$\chi_{ij} = (A_i | A_j) \qquad \sum \chi_{ik}(\chi^{-1})_{kj} = \delta_{ij} \quad (3)$$

$$(A_i | A_j) = \int_0^\beta d\lambda\,\mathrm{Tr}\{\varrho\,A_i(-i\lambda)\,A_j\} \qquad \varrho = \frac{1}{z}e^{-\beta H} \quad (4)$$

and

$$\pi_{ij} = \langle \dot{A}_i\,\tilde{Q} | Q\,\dot{A}_j\rangle^Q \qquad \dot{A}_i = i\,[H, A_i] \ . \quad (5)$$

The operator $\tilde{Q} = 1 - \tilde{P}$ is a projection operator with
$\tilde{P} = \sum_{ij} |A_i)(\chi^{-1})_{ij} (A_j|$ and $\langle ... \rangle^Q$ denotes that in the time
evolution of this correlation function $L = i\,[H, ...]$ is to be
replaced by $Q\,L\,Q$. By solving the set of equations (2) the
correlation functions $\langle A_i ; A_j\rangle$ which we started from are
replaced by the correlation functions (5), and with a proper
choice of the relevant observables these correlation functions
can be calculated in a fairly simple approximation /1/. It is,
however, difficult to go beyond this first approximation and,
in particular, to take into account the projection operators
(cf. /2/). Furthermore this method is restricted to the cal-
culation of transport coefficients where the exact linear
response expressions are known; a generalization to thermal
transport coefficients is not trivial. In this paper a general
formalism for the calculation of transport coefficients is
given which includes the approaches mentioned above and which

can be adapted to the problem investigated.

2. Quasi - equilibrium operator approach

For simplicity of notation we restrict our consideration here
on the influence of a stationary external electrical field.
In the linear response theory the density matrix of the system
becomes

$$\varrho_{LR} = \frac{e\vec{E}}{m} \int_{-\infty}^{t} dt' \, e^{\eta(t'-t)} \int_{0}^{\beta} d\lambda \, \varrho \vec{P}(t' - t - i\lambda), \quad \eta \to 0^{+} \qquad (6)$$

where the time dependence in P(t) is given by the total
Hamiltonian of the system without the interaction term with
the electrical field. From another point of view we can say
that there is a reaction of the system on the external field
which can be described by relevant observables such as shift
of the Fermi body or a redistribution of the single particle
occupation numbers etc. Hence, for small external fields the
system can be described in a fairly good approximation by the
quasi-equilibrium density matrix

$$\varrho_q = \frac{1}{Z_q} e^{-\beta(H - \sum \alpha_i A_i)} \qquad (7)$$

where the A_i are the observables relevant for the reaction
of the system and the α_i are parameters proportional to the
external field. Of course, the density matrix (7) is not a
solution of the Liouville equation, but an exact solution can be found
easily starting from (7) as an initial condition:

$$\varrho_s = \varrho_q - i \int_{-\infty}^{0} dt' \, e^{\eta(t'-t)} \, e^{iH_s(t'-t)} \, \varrho_q \, e^{-iH_s(t'-t)} \qquad (8)$$

where $H_s = H - e \vec{E} \sum_i \vec{r}_i$. In order to determine the parameters
α_i we demand that the mean values of the relevant observables
A_i are equal in the quasi-equilibrium state ϱ_q and in the real
state ϱ_s, i.e.

$$Tr\{\varrho_s A_i\} = Tr\{\varrho_q A_i\} . \qquad (9)$$

This condition is equivalent to the stationarity condition

$$\frac{d}{dt} Tr\{\varrho_s A_i\} = 0 . \qquad (10)$$

For a sufficiently complete set of operators A_i the condition
(9) ensures that ϱ_q describes the system with a sufficient
accuracy. Linearizing (9) with respect to the parameters α_i
and the external field E one obtains the set of equations

$$\sum \alpha_j \left[\frac{1}{i} Tr\{\varrho[A_j, A_i]\} + \langle \dot{A}_j ; \dot{A}_i \rangle \right] = \frac{e\vec{E}}{m} \left[(\vec{P}|A_i) + \langle \vec{P} ; \dot{A}_i \rangle \right] . \qquad (11)$$

The set of equations (11) can be shown to be equivalent to
(2), where in the higher orders of interaction the equations
(11) are more convenient to handle because the time dependences
are given here in an explicit form without any projection.
With the parameters α_i the current density is given by

$$\vec{J} = \frac{e}{m\Omega} Tr\{\varrho_q \vec{P}\} = \frac{e}{m\Omega} \sum_i \alpha_i (A_i|\vec{P}) \qquad (12)$$

Supposing that the total momentum P of the electrons can be
built up by the operators A_i ist can be shown easily, that the
equations (11) and (12) include the Kubo expression for the
conductivity. In order to solve the system of equations (11) a
generalized variational principle can be formulated, but the
reduction of the number of parameters α_i by a variational ansatz
corresponds to a new restricted choice of the relevant observable A_i .

3. Weak scattering limit

The applicability of the equations (11), (12) to for a given
problem strongly depends on the choice of the operators A .
The first condition to be fulfilled is that the mean values of
the occupation numbers of all quasiparticles in volved in the
transport process should be time independent, i.e.

$$\frac{d}{dt} \, Tr\{\varrho_s(\alpha_i) \, n_k\} = 0 \quad \text{or} \quad Tr\{\varrho_s(\alpha_i) \, n_k\} = Tr\{\varrho_q(\alpha_i) \, n_k\}.$$

(13)

Of course, this condition is fulfilled trivially for $A_i \rightarrow n_k$, but in this case the equations (11) cannot be solved in practice. In the most cases, however, there can be found a reduced set of operators sufficiently complete to describe the reaction of the system on the external field. It can be shown that under certain conditions the scattering process can be described by on one relaxation time only and then the set of relevant operators reduces to the total momentum of the electrons describing a homogenous shift of the Fermi body in the Bloch space. These conditions are fulfilled for a spherical Fermi body at temperatures small in comparison to the degeneration temperature and for an isotropic scattering mechanism where the scatterers remain in the thermal equilibrium. In this simple case (10) and (11) reduce to the so-called resistivity formula /3/. For non-spherical Fermi bodies the set of relevant observables has to be extended in order to take into account not only its shift in the k-space but also its deformation. In general the Fermi surface $E(\vec{k}) = \varepsilon_f$ transforms under the influence of the electrical field into $\tilde{E}(k) = \varepsilon_f$ where

$$\tilde{E}(\vec{k}) = E(\vec{k}) + m \, \vec{v}_1 \, \frac{\partial E}{\partial \vec{k}} + m \sum_{i=2}^{n} \vec{v}_i \, \Phi^i(\vec{k}) \, \frac{\partial E}{\partial \vec{k}} + \dots$$

(14)

The last term in (14) describes the deformation of the Fermi body where the polynomials $\Phi^i(\vec{k})$ have to be chosen in correspondence with the symmetry of the crystal /4/.
Corresponding to (14) the relevant operators are given by

$$A_i \rightarrow m \sum_{k\sigma} \Phi^i(\vec{k}) \, \frac{\partial E}{\partial k} \, a_{k\sigma}^+ \, a_{k\sigma} \quad \text{with} \quad \Phi^1 = 1 \, .$$

(15)

In the weak scattering limit the correlation functions in (11) can be calculated straightforwardly replacing in the operator $A_i(t) = \exp(iHt) \, A_i \exp(-iHt)$ the total Hamiltonian of the system by the Hamiltonian of the free quasiparticles. The results obtained in this approximation coincide with variational solutions of the linearized Boltzmann equation where, however, the choice of the relevant observables is more evident than the variational ansatz for the solution of the Boltzmann equation.

As an example we consider a tight-binding electron system and take into consideration electron-electron and electron-phonon interactions. The Hamiltonian of the system is in a standard notation

$$H = H_e + H_p + H_{ee} + H_{ep}$$

(16)

where

$$H_e = \sum_{\vec{k}} E(\vec{k}) \, a_{k\sigma}^+ \, a_{k\sigma} = \sum_{\Delta R, \vec{k}} t(\Delta \vec{R}) \, e^{i\vec{k}\Delta\vec{R}} \, a_{k\sigma}^+ a_{k\sigma}$$

(17)

$$H_{ee} = \frac{U}{N} \sum_{\vec{k}_1 \vec{k}_2} \sum_{\vec{k}_3 \vec{k}_4} \sum_{\vec{G}} a_{k_1\uparrow}^+ a_{k_2\uparrow} a_{k_3\downarrow}^+ a_{k_4\downarrow} \, \delta(\vec{k}_1 - \vec{k}_2 + \vec{k}_3 - \vec{k}_4 + \vec{G})$$

(18)

$$H_{ep} = \sum_{\vec{k}\vec{k}_1} \sum_{\vec{q}\vec{G}} \sum_{\sigma\nu} g_{kk_1}^\nu \, a_{k_1\sigma}^+ \, a_{k\sigma} \, (b_q + b_{-q}^+) \, \delta(\vec{k}_1 - \vec{k} - \vec{q} + \vec{G})$$

(19)

$$H_p = \sum_{\vec{q}\nu} \omega(\vec{q}\nu) \, (b_{q\nu}^+ b_{q\nu} + \tfrac{1}{2}) \, .$$

(20)

For tight-binding electrons the matrix element $g_{kk_1}^\nu$ of the electron-phonon coupling is given in /5/. Using the set of relevant operators (15) and restricting it to only one deformation term (i.e. $\Phi^i(\vec{k}) \rightarrow 0$ for $i \gtrless 3$) we obtain in the weak scattering limit for the temperature dependence of the resistivity

$$R = \frac{E}{J} = \frac{(a_1 T^2 + b_1 T^5)(a_2 T^2 + b_2 T^5) - (a_{12} T^2 + b_{12} T^5)^2}{c(a_1 T^2 + b_1 T^5) + d(a_2 T^2 + b_2 T^5) - \sqrt{cd}(a_{12} T^2 + b_{12} T^5)} \quad (21)$$

where the coefficients a_ν, b_ν, c, d are integrals depending on the parameters of the model.

4. Selfconsistent calculation of transport coefficients

By (11) and (12) an exact expression for the electrical resistivity of a quantummechanical system is given where in some problems the correlation functions in (11) are more convenient to be calculated than the current-current-correlation function in the Kubo expression (1) for the conductivity. However, it is not significant whether the Kubo formula or the formalism given by (11) and (12) are used as a starting point for a calculation using standard many body technique. On the other hand, we can use these two approaches being in a certain sense inverse to each other to find a calculation scheme for transport coefficients adapted to the problem considered. For this end we start from the condition

$$Tr\{\varrho_{LR} B_i\} = Tr\{\varrho_S B_i\} \quad (22)$$

where the density matrices are given by (6) and (8). For operators B_i which can be represented by linear combinations of the relevant observables A_i (9) the equation (22) is fulfilled exactly where for other operators the equations (22) seems to be plausible if the relevant observables have been chosen properly. The conditions (22) make it possible to determine a set of parameters which can be used in approximate expressions for the correlation functions. In simple cases the conditions (22) even allow to calculate the correlation functions in (11) without resorting to another technique. As

an example we consider the one-band Hubbard model

$$H = H_e + H_{ee} \quad (23)$$

in the limit $|t|/U \ll 1$. We know that in this limit the band splits into two sub-bands separated by the correlation energy U. In order to take into account the band-split we have to project the one-electron operators onto the sub-bands and for a spherical uncorrelated band the relevant operators are

$$\vec{P}^{\alpha\beta} = m \sum_{k\sigma} \frac{\partial \varepsilon}{\partial k} n_{k\sigma}^{\alpha\beta} \quad (24)$$

where

$$n_{k\sigma}^{\alpha\beta} = N^{-1} \sum_{ij} e^{ik(\vec{R}_i - \vec{R}_j)} a_{i\sigma}^+ n_{i-\sigma}^\alpha a_{j\sigma} n_{j-\sigma}^\beta \quad (25)$$

with the projection operators

$$n_{i-\sigma}^\alpha = \begin{cases} n_{i-\sigma} \\ 1 - n_{i-\sigma} \end{cases} \quad \text{for } \alpha = \pm \quad (26)$$

$\vec{P}^{\alpha\alpha}$ is the operator of the total momentum of the electrons in the sub-band α, and $\vec{P}^{\alpha\beta}$ ($\alpha \neq \beta$) describes kinematical transitions between the sub-bands. It can be shown that correlation functions $\langle \vec{P}^{\alpha\beta} ; \vec{P}^{\gamma\delta} \rangle$ and $\langle \vec{P}^{\alpha\alpha} ; \vec{P}^{\beta\beta} \rangle$ vanish for $\alpha \neq \beta$ in the limit $|t|/U \ll 1$. Decoupling higher order correlation functions in $|t|/U$ (cf. /6/) and taking into account nearest neighbour hopping terms only the correlation functions $\langle \vec{P}^{\alpha\alpha} ; \vec{P}^{\alpha\alpha} \rangle$ ($\alpha = \pm$) can be calculated directly by (22) where $B_i \rightarrow \vec{P}^{\alpha\alpha}$. The conductivity becomes

$$\sigma = A T^{-1} \sum_\sigma \sum_\alpha \langle n_\sigma^\alpha \rangle^{-1/2} \langle n_\sigma^\alpha n_{-\sigma}^\alpha \rangle (\langle n_\sigma^\alpha \rangle - \langle n_\sigma^\alpha n_{-\sigma}^\alpha \rangle) \quad (27)$$

where

$$A = \frac{e^2}{3 m^2 \Omega k} \frac{1}{\sqrt{2} z} \frac{1}{|t|} \sum_k \left(\frac{\partial \varepsilon}{\partial k}\right)^2 \quad (28)$$

and

$$\langle A \rangle = \mathrm{Tr}\{\varrho A\} \qquad \varrho = \frac{1}{Z} e^{-\beta H} . \qquad (29)$$

z is the number of nearest neighbours and t the nearest neighbour hopping element. With the well-known expressions for the mean values $\langle n_\sigma^\alpha \, n_{-\sigma}^\alpha \rangle$ we find the conductivity in dependence on the electron number:

$$0 \leq n < 1 \qquad \sigma = A\, T^{-1}\, \frac{1}{2}\, \frac{n(1-n)}{\sqrt{1-n/2}}$$

$$n = 1 \qquad \sigma = \frac{A}{\sqrt{2}}\, T^{-1}\, \exp(-U/2kT) \qquad (30)$$

$$2 \geq n > 1 \qquad \sigma = A\, T^{-1}\, \sqrt{2}\, \frac{(1-n/2)(n-1)}{\sqrt{n}}$$

Finally it should be mentioned that the method given above can be generalized straight-forwardly to the calculation of thermal and thermoelectric transport coefficients. For this end thermal and concentration gradients have to be introduced into the quasi-equilibrium density matrix.

References:

1. Forster,D., Hydrodynamic Fluctuations, Broken Symmetry and
                    Correlation Functions W.A. Benjamin, Mass.,1975
2. Церковников Ю.А., ТМФ 49 (1981) 219
3. Röpke, G and Christoph V., J. Phys. C 8 (1975) 3615
4. Каган Ю.М, Флеров Б.Н. ЖЭТФ 66 (1974) 1374
   Pinski F.J. Phys. Rev. B21 (1980) 4380
5. Barisic S., Labbe J. and Friedel J. Phys. Rev. Letters
                              25 (1970) 919
6. Christoph V., Phys. Letters, to be published