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ELECTRONIC TRANSPORT IN METALLIC SYSTEMS AND GENERALIZED KINETIC EQUATIONS

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This paper reviews some selected approaches to the description of transport properties, mainly electroconductivity, in crystalline and disordered metallic systems. A detailed qualitative theoretical formulation of the electron transport processes in metallic systems within a model approach is given. Generalized kinetic equations which were derived by the method of the nonequilibrium statistical operator are used. Tight-binding picture and modified tight-binding approximation (MTBA) were used for describing the electron subsystem and the electron-lattice interaction correspondingly. The low- and high-temperature behavior of the resistivity was discussed in detail. The main objects of discussion are nonmagnetic (or paramagnetic) transition metals and their disordered alloys. The choice of topics and the emphasis on concepts and model approach makes it a good method for a better understanding of the electrical conductivity of the transition metals and their disordered binary substitutional alloys, but the formalism developed can be applied (with suitable modification), in principle, to other systems. The approach we used and the results obtained complements the existent theories of the electrical conductivity in metallic systems. The present study extends the standard theoretical format and calculation procedures in the theories of electron transport in solids.

Keywords: Transport phenomena in solids; electrical conductivity in metals and alloys; transition metals and their disordered alloys; tight-binding and modified tight-binding approximation; method of the nonequilibrium statistical operator; generalized kinetic equations.

1. Introduction

Transport properties of matter constitute the transport of charge, mass, spin, energy and momentum.[1–8] It has not been our aim to discuss all the aspects of the charge and thermal transport in metals. We are concerned in the present work mainly with some selected approaches to the problem of electric charge transport (mainly electroconductivity) in crystalline and disordered metallic systems. Only the fundamentals of the subject are treated. In the present work, we aim to obtain a better understanding of the electrical conductivity of the transition metals and their disordered binary substitutional alloys both by themselves and in relationship with each other within the statistical mechanical approach. Thus our consideration will concentrate on the derivation of generalized kinetic equations suited for the relevant models of metallic systems.

The problem of electronic transport in solids is an interesting and actual part of the physics of condensed matter.[9–26] It includes the transport of charge and heat in crystalline and disordered metallic conductors of various nature. Transport of charge is connected with an electric current. Transport of heat has many aspects, most important of which is the heat conduction. Other important aspects are the thermoelectric effects. The effect, termed Seebeck effect, consists of the occurrence of a potential difference in a circuit composed of two distinct metals at different temperatures. Since the earlier seminal attempts to construct the quantum theory of the electrical, thermal[27–30] and thermoelectric and thermomagnetic transport phenomena,[31] 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 materials.[32–35]

A number of physical effects enter the theory of quantum transport processes in solids at various density of carriers and temperature regions. A variety of theoretical models have been proposed to describe these effects.[1–6,9–14,16–22,24,25,36–41] Theories of the electrical and heat conductivities of crystalline and disordered metals and semiconductors have been developed by many authors during last decades.[1–6,20,36–41] There exists a number of theoretical methods for the calculation of transport coefficients,[18,20,36–38,42–46] as a rule having a fairly restricted range of validity and applicability. In the present work, the description of the electronic and some aspects of heat transport in metallic systems are briefly reviewed, and the theoretical approaches to the calculation of the resistance at low and high temperature are surveyed. As a basic tool we use the method of the nonequilibrium statistical operator[42,43] (NSO). It provides a useful and compact description of the transport processes. Calculation of transport coefficients within NSO approach[42] was presented and discussed in the author's work.[45] The present paper can be considered as the second part of the review article.[45] The close related works on the study of electronic transport in metals are briefly summarized in the present work. It should be emphasized that the choice of generalized kinetic equations among all other methods of the theory of transport in metals is related to its efficiency and compact form. They are an alternative (or complementary) tool for studying of transport processes, which complement other existing methods.

Due to the lack of space, many interesting and actual topics must be omitted. An important and extensive problem of thermoelectricity was mentioned very briefly; thus it has not been possible to do justice to all the available theoretical and experimental results of great interest. The thermoelectric and transport properties of the layered high-T_c cuprates were reviewed by us already in the extended review article.[47]

Another interesting aspect of transport in solids which we did not touch upon is the spin transport.[7,8] The spin degree of freedom of charged carriers in metals and semiconductors has attracted huge attention in the last decades and continues to play a key role in the development of many applications, establishing a field that is now known as spintronics. Spin transport and manipulation in not only ferromagnets but also nonmagnetic materials are currently being studied actively in a variety of artificial structures and newly designed materials. This enables the fabrication of spintronic properties on intention. A study on spintronic device structures was reported as early as in late 1960s. Studies of spin-polarized internal field emission using the magnetic semiconductor EuS sandwiched between two metal electrodes opened a new epoch in electronics. Since then, many discoveries have been made using spintronic structures.[7,8] Among them is giant magnetoresistance in magnetic multilayers. Giant magnetoresistance has enabled the realization of sensitive sensors for hard-disk drives, which has facilitated successful use of spintronic devices in everyday life. There is huge literature on this subject and any reasonable discussion of the spin transport deserves a separate extended review. We should mention here that some aspects of the spin transport in solids were discussed in the papers of Refs. 45 and 48.

In the present study, a qualitative theory for conductivity in metallic systems is developed and applied to systems like transition metals and their disordered alloys. The nature of transition metals is discussed in details and the tight-binding approximation and method of model Hamiltonians are described. For the interaction of the electron with the lattice vibrations we use the modified tight-binding approximation (MTBA). Thus this approach cannot be considered as the first-principle method and has the same shortcomings and limitations as describing a transition metal within the Hubbard model. In the following sections, we shall present a formulation of the theory of the electrical transport in the approach of NSO. Because several other sections in this review require a certain background in the use of statistical–mechanical methods, physics of metals, etc., it was felt that some space should be devoted to this background. Sections 2 to 8 serves as an extended introduction to the core sections 9–12 of the present paper. Thus those sections are intended as a brief summary and short survey of the most important notions and concepts of charge transport (mainly electroconductivity) for the sake of a self-contained formulation. We wish to describe those concepts which have proven to be of value, and those notions which will be of use in clarifying subtle points.

First, in order to fix the domain of study, we must briefly consider the various formulations of the subject and introduce the basic notions of the physics of metals and alloys.

2. Metals and Nonmetals: Band Structure

The problem of the fundamental nature of the metallic state is long standing.[1–3,13] It is well-known that materials are conveniently divided into two broad classes: insulators (nonconducting) and metals (conducting).[13,49–51] More specific classification divided materials into three classes: metals, insulators and semiconductors.

Table 1. Five categories of crystals.

Type of crystal	Substances
Ionic	Alkali halides, alkaline oxides, etc.
Homopolar bounded (covalent)	Diamond, silicon, etc.
Metallic	Various metals and alloys
Molecular	Ar, He, O_2, H_2, CH_4, etc.
Hydrogen bonded	Ice, KH_2PO_4, fluorides, etc.

The most characteristic property of a metal is its ability to conduct electricity. If we classify crystals in terms of the type of bonding between atoms, they may be divided into the following five categories (see Table 1).

Ultimately we are interested in studying all of the properties of metals.[1] At the outset it is natural to approach this problem through studies of the electrical conductivity and closely related problem of the energy band structure.[32–35]

The energy bands in solids[13,33,35] represent the fundamental electronic structure of a crystal just as the atomic term values represent the fundamental electronic structure of the free atom. The behavior of an electron in one-dimensional periodic lattice is described by Schrödinger equation

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0\,, \tag{2.1}$$

where V is periodic with the period of the lattice a. The variation of energy $E(k)$ as a function of quasi-momentum within the Brillouin zones, and the variation of the density of states $D(E)dE$ with energy, are of considerable importance for the understanding of real metals. The assumption that the potential V is small compared with the total kinetic energy of the electrons (approximation of nearly free electrons) is not necessarily true for all metals. The theory may also be applied to cases where the atoms are well separated, so that the interaction between them is small. This treatment is usually known as the approximation of "tight binding."[13] In this approximation, the behavior of an electron in the region of any one atom being only slightly influenced by the field of the other atoms.[33,52] Considering a simple cubic structure, it is found that the energy of an electron may be written as

$$E(k) = E_a - t_\alpha - 2t_\beta(\cos(k_x a) + \cos(k_y a) + \cos(k_z a))\,, \tag{2.2}$$

where t_α is an integral depending on the difference between the potentials in which the electron moves in the lattice and in the free atom, and t_β has a similar significance[33,52] (details will be given below). Thus, in the tight-binding limit, when electrons remain to be tightly bound to their original atoms, the valence electron moves mainly about individual ion core, with rare hopping from ion to ion. This is the case for the d-electrons of transition metals. In the typical transition metal, the radius of the outermost d-shell is less than half the separation between the atoms. As a result, in the transition metals, the d-bands are relatively narrow. In the nearly free whose electron limit, the bands are derived from the s- and p-shells whose radii are significantly larger than half the separation between the atoms. Thus, according to this simplified picture, simple metals have nearly-free-electron energy bands. Fortunately, in the case of simple metals, the combined results of the energy band calculation and experiment have indicated that the effects of the interaction between the electrons and ions which make up the metallic lattice is extremely weak. It is not the case for transition metals and their disordered alloys.[53,54]

An obvious characterization of a metal is that it is a good electrical and thermal conductor.[1,2,13,55,56] Without considering details, it is possible to see how the simple Bloch picture outlined above accounts for the existence of metallic properties, insulators and semiconductors. When an electric current is carried, electrons are accelerated, that is, promoted to higher energy levels. For this to occur, there must be vacant energy levels above that occupied by the most energetic electron in the absence of an electric field, into which the electron may be excited. At some conditions there exist many vacant levels within the first zone into which electrons may be excited. Conduction is therefore possible. This case corresponds with the noble metals. It may happen that the lowest energy in the second zone is lower than the highest energy in the first zone. It is then possible for electrons to begin occupying energy contained within the second zone, as well as to continue to fill up the vacant levels in the first zone and a certain number of levels in the second zone will be occupied. In this case, the metallic conduction is possible as well. The polyvalent metals are materials of this class.

If, however, all the available energy levels within the first Brillouin zone are full and the lowest possible electronic energy at the bottom of the second zone is higher than the highest energy in the first zone by an amount ΔE, there exist no vacant levels into which electrons may be excited. Under these conditions, no current can be carried by the material and an insulating crystal results.

For another class of crystals, the zone structure is analogous to that of insulators but with a very small value of ΔE. In such cases, at low temperatures the material behaves as an insulator with a higher specific resistance. When the temperature increases, a small number of electrons will be thermally excited across the small gap and enter the second zone, where they may produce metallic conduction. These substances are termed semiconductors,[13,55,56] and their resistance decreases with rise in temperature in marked contrast to the behavior of real metals (for a detailed review of semiconductors see Refs. 57, 58).

The differentiation between metal and insulator can be made by measurement of the low frequency electrical conductivity near $T = 0$ K. For the substance which we can refer as an ideal insulator the electrical conductivity should be zero, and for metal it remains finite or even becomes infinite. Typical values for the conductivity of metals and insulators differ by a factor of the order 10^{10}–10^{15}. So a huge difference in the electrical conductivity is related directly to a basic difference in the structural and quantum chemical organization of the electron and ion subsystems of solids. In an insulator, the position of all the electrons are highly connected with each other and with the crystal lattice and a weak direct current field cannot move them. In a metal this connection is not so effective and the electrons can be easily displaced by the applied electric field. Semiconductors occupy an intermediate position due to the presence of the gap in the electronic spectra.

An attempt to provide a comprehensive empirical classification of solids types was carried out by Zeitz[55] and Kittel.[56] Zeitz reanalyzed the generally accepted classification of materials into three broad classes: insulators, metals and semiconductors, and divided materials into five categories: metals, ionic crystals, valence or covalent crystals, molecular crystals and semiconductors. Kittel added one more category: hydrogen-bonded crystals. Zeitz also divided metals further into two major classes, namely, monoatomic metals and alloys.

Alloys constitute an important class of the metallic systems.[25,49,55,56,59–61] This class of substances is very numerous.[49,59–61] A metal alloy is a mixed material that has metal properties and is made by melting at least one pure metal along with another pure chemical or metal. Examples of metal alloys Cu–Zn, Au–Cu and an alloy of carbon and iron, or copper, antimony and lead. Brass is an alloy of copper and zinc, and bronze is an alloy of copper and tin. Alloys of titanium, vanadium, chromium and other metals are used in many applications. The titanium alloys (interstitial solid solutions) form a big variety of equilibrium phases. Alloy metals are usually formed to combine properties of metals and the exact proportion of metals in an alloy will change the characteristic properties of the alloy. We confine ourselves to those alloys which may be regarded essentially as very close to pure metal with the properties intermediate to those of the constituents.

There are different types of monoatomic metals within the Bloch model for the electronic structure of a crystal: simple metals, alkali metals, noble metals, transition metals, rare-earth metals, divalent metals, trivalent metals, tetravalent metals, pentavalent semimetals, lantanides, actinides and their alloys. The classes of metals according to crude Bloch model provide us with a simple qualitative picture of the variety of metals. This simplified classification takes into account the state of valence atomic electrons when we decrease the interatomic separation towards its bulk metallic value. Transition metals have narrow d-bands in addition to the nearly-free-electron energy bands of the simple metals.[53,54] In addition, the correlation of electrons plays an essential role.[53,54,62] The Fermi energy lies within the d-band so that the d-band is only partially occupied. Moreover the Fermi surface have much more complicated form and topology. The concrete calculations of the band structure of many transition metals (Nb, V, W, Ta, Mo, etc.) can be found in Refs. 13, 32–35, 53, 63–66 and in Landolt–Bornstein reference books.[60,67]

The noble metal atoms have one s-electron outside of a just completed d-shell. The d-bands of the noble metals lie below the Fermi energy but not too deeply. Thus they influence many of the physical properties of these metals. It is, in principle, possible to test the predictions of the single-electron band structure picture by comparison with experiment. In semiconductors it has been performed with the measurements of the optical absorption, which gives the values of various energy differences within the semiconductor bands. In metals the most direct approach is related to the experiments which studied the shape and size of the Fermi surfaces. In spite of their value, these data represent only a rather limited scope in comparison to the many properties of metals which are not so directly related to the energy band structure. Moreover, in such a picture, there are many weak points: there is no sharp boundary between insulator and semiconductor, the theoretical values of ΔE have discrepancies with experiment, the metal–insulator transition[68] cannot be described correctly, and the notion "*simple*" metal have no single meaning.[69] The crude Bloch model even met more serious difficulties when it was applied to insulators. The improved theory of insulating state was developed by Kohn[70] within a many-body approach. He proposed a new and more comprehensive characterization of the insulating state of matter. This line of reasoning was continued further in Refs. 68, 71 and 72 on a more precise and firm theoretical and experimental basis.

Anderson[50] gave a critical analysis of the Zeitz and Kittel classification schemes. He concluded that "in every real sense the distinction between semiconductors and metals or valence crystals as to type of binding, and between semiconductor and any other type of insulator as to conductivity, is entirely artificial; semiconductors do not represent in any real sense a distinct class of crystal"[50] (see, however, Refs. 13, 23, 38, 55 and 56). Anderson has pointed also the extent to which the standard classification falls. His conclusions were confirmed by further development of solid state physics. During the last decades, many new substances and materials were synthesized and tested. Their conduction properties and temperature behavior of the resistivity are differed substantially and constitute a difficult task for consistent classification[73] (see Fig. 1). Bokij[74] carried out an interesting analysis of notions "metals" and "nonmetals" for chemical elements. According to him, there are typical metals (Cu, Au, Fe) and typical nonmetals (O, S, halogens), but the boundary between them and properties determined by them are still an open question. The notion "metal" is defined by a number of specific properties of the corresponding elemental substances, e.g., by high electrical conductivity and thermal capacity, the ability to reflect light waves (luster), plasticity and ductility. Bokij emphasizes,[74] that when defining the notion of a metal, one has also to take into account the crystal structure. As a rule, the structure of metals under normal conditions is characterized by rather high symmetries and high coordination numbers of atoms equal to or higher than eight, whereas the structures of crystalline nonmetals under normal conditions are characterized by lower symmetries and coordination numbers of atoms (2–4).

It is worth noting that topics such as studies of the strongly correlated electronic systems,[62] high-T_c superconductivity,[75] colossal magnetoresistance[5] and multiferroicity[5] have led to a new development of solid state physics during the last decades. Many transition-metal oxides show very large ("colossal") magnitudes of the dielectric constant and thus have immense potential for applications in modern microelectronics and for the development of new capacitance-based energy-storage devices. These and other interesting phenomena to a large extent have first been re-

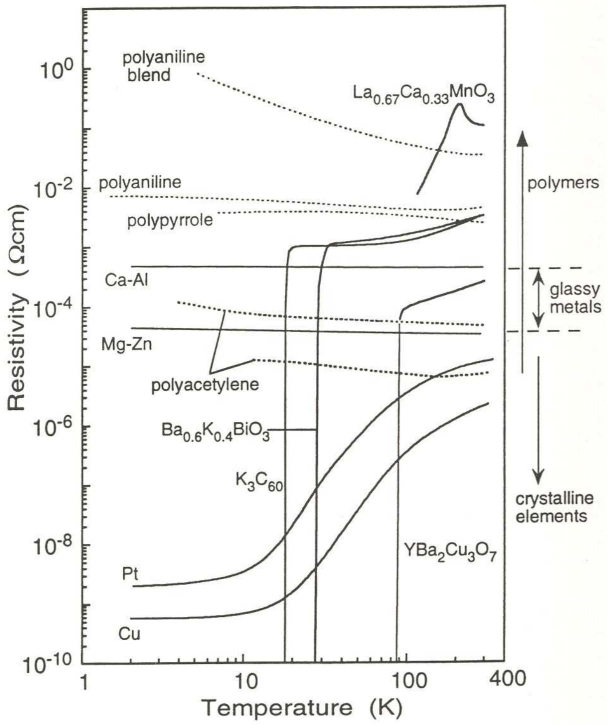

Fig. 1. Resistivity of various conducting materials (from Ref. 73).

vealed and intensely investigated in transition metal oxides. The complexity of the ground states of these materials arises from strong electronic correlations, enhanced by the interplay of spin, orbital, charge and lattice degrees of freedom.[62] These phenomena are a challenge for basic research and also bear huge potentials for future applications as the related ground states are often accompanied by so-called "colossal" effects, which are possible building blocks for tomorrow's correlated electronics. The measurement of the response of transition metal oxides to ac electric fields is one of the most powerful techniques to provide detailed insight into the underlying physics that may comprise very different phenomena, e.g., charge order, molecular or polaronic relaxations, magnetocapacitance, hopping charge transport, ferroelectricity or density-wave formation. In the recent work,[76] the authors thoroughly discussed the mechanisms that can lead to colossal values of the dielectric constant, especially emphasizing effects generated by external and internal interfaces, including electronic phase separation. The authors of the work[76] studied the materials showing so-called colossal dielectric constants, i.e., values of the real part of the permittivity ε' exceeding 1,000. For long, materials with high dielectric constants are the focus of interest, not only for purely academic reasons but also because new high-ε' materials are urgently sought after for the further development of modern electronics. In addition, authors of the work[76] provided a detailed overview and discussion of the dielectric properties of $\mathrm{CaCu_3Ti_4O_{12}}$ and related systems, which is now the most investigated material with colossal dielectric constant. Also, a variety of further transition metal oxides with large dielectric constants were treated in detail, among them the system $\mathrm{La}_{2-x}\mathrm{Sr}_x\mathrm{NiO}_4$, where electronic phase separation may play a role in the generation of a colossal dielectric constant. In general, for the miniaturization of capacitive electronic elements materials with high-ε' are a prerequisite. This is true not only for the common silicon-based integrated circuit technique but also for stand-alone capacitors.

Nevertheless, with regard to metals, the workable practical definition of Kittel can be adopted: metals are characterized by high electrical conductivity, so that a portion of electrons in metal must be free to move about. The electrons available to participate in the conductivity are called conduction electrons. Our picture of a metal, therefore, must be that it contains electrons which are free to move, and which may, when under the influence of an electric field, carry a current through the material.

In summary, the 68 naturally occurring metallic and semimetallic elements[49] can be classified as it is shown in Table 2.

3. Many-Particle Interacting Systems and Current Operator

Let us now consider a general system of N interacting electrons in a volume Ω described by the Hamiltonian

$$H = \left(\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \sum_{i=1}^{N} U(\mathbf{r}_i) \right) + \frac{1}{2} \sum_{i \neq j} v(\mathbf{r}_i - \mathbf{r}_j) = H_0 + H_1 \,. \tag{3.1}$$

Here $U(\mathbf{r})$ is a one-body potential, e.g., an externally applied potential similar to that due to the field of the ions in a solid, and $v(\mathbf{r}_i - \mathbf{r}_j)$ is a two-body potential similar to the Coulomb potential between electrons. It is essential that $U(\mathbf{r})$ and $v(\mathbf{r}_i - \mathbf{r}_j)$ do not depend on the velocities of the particles.

It is convenient to introduce a "quantization" in a continuous space[77–79] via the operators $\Psi^\dagger(\mathbf{r})$ and $\Psi(\mathbf{r})$ which create and destroy a particle at $\mathbf{r}$. In terms of $\Psi^\dagger$

Table 2. Metallic and semimetallic elements.

Item	Number	Elements
Alkali metals	5	Li, Na, K, Rb, Cs
Noble metals	3	Cu, Ag, Au
Polyvalent simple metals	11	Be, Mg, Zn, Cd, Hg, Al, Ga, In, Tl, Sn, Pb
Alkali-earth metals	4	Ca, Sr, Ba, Ra
Semimetals	4	As, Sb, Bi, graphite
Transition metals	23	Fe, Ni, Co, etc.
Rare earths	14	
Actinides	4	

and Ψ we have

$$H = \int d^3r \Psi^\dagger(\mathbf{r}) \left(\frac{-\nabla^2}{2m} + U(\mathbf{r}) \right) \Psi(\mathbf{r})$$
$$+ \frac{1}{2} \iint d^3r d^3r' \Psi^\dagger(\mathbf{r}) \Psi^\dagger(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') \Psi(\mathbf{r}') \Psi(\mathbf{r}) \,. \tag{3.2}$$

Studies of flow problems lead to the continuity equation[20,42]:

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} + \nabla \mathbf{j} = 0 \,. \tag{3.3}$$

This equation based on the concept of conservation of certain extensive variable. In nonequilibrium thermodynamics,[42] the fundamental flow equations are obtained using successively mass, momentum and energy as the relevant extensive variables. The analogous equations are known from electromagnetism. The central role is played by a global conservation law of charge, $\dot{q}(t) = 0$, for it refers to the total charge in a system. Charge is also conserved locally.[80] This is described by Eq. (3.3), where $n(\mathbf{r}, t)$ and $\mathbf{j}$ are the charge and current densities, respectively.

In quantum mechanics, there is the connection of the wavefunction $\psi(\mathbf{r}, t)$ to the particle mass-probability current distribution $\mathbf{J}$:

$$\mathbf{J}(\mathbf{r}, t) = \frac{\hbar}{2mi} (\psi^* \nabla \psi - \psi \nabla \psi^*) \,, \tag{3.4}$$

where $\psi(\mathbf{r}, t)$ satisfy the time-dependent Schrödinger equation[79,81]

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = H \psi(\mathbf{r}, t) \,. \tag{3.5}$$

Consider the motion of a particle under the action of a time-independent force determined by a real potential $V(\mathbf{r})$. Equation (3.5) becomes

$$\left(\frac{\mathbf{p}^2}{2m} + V \right) \psi = \frac{\hbar}{2m} \nabla^2 \psi + V \psi = i\hbar \frac{\partial}{\partial t} \psi \,. \tag{3.6}$$

It can be shown that for the probability density $n(\mathbf{r}, t) = \psi^* \psi$ we have

$$\frac{\partial n}{\partial t} + \nabla \mathbf{J} = 0 \,. \tag{3.7}$$

This is the equation of continuity and it is quite general for real potentials. The equation of continuity mathematically states the local conservation of particle mass probability in space.

A thorough consideration of a current carried by a quasi-particle for a uniform gas of fermions, containing N particles in a volume Ω, which was assumed to be very large, was performed within a semi-phenomenological theory of Fermi liquid.[82] This theory describes the macroscopic properties of a system at zero temperature and requires knowledge of the ground-state and the low-lying excited states. The current carried by the quasi-particle $\mathbf{k}$ is the sum of two terms: the current which is equal to the velocity v_k of the quasi-particle and the backflow of the medium.[82]

The precise definition of the current J in an arbitrary state $|\varphi\rangle$ within the Fermi liquid theory is given by

$$J = \left\langle \varphi | \sum_i \frac{p_i}{m} | \varphi \right\rangle , \tag{3.8}$$

where p_i is the momentum of the ith particle and m its bare mass. To measure J it is necessary to use a reference frame moving with respect to the system with the uniform velocity $\hbar q/m$. The Hamiltonian in the rest frame can be written

$$H = \sum_i \frac{p_i^2}{2m} + V \, . \tag{3.9}$$

It was assumed that V depends only on the positions and the relative velocities of the particles; it is not modified by a translation. In the moving system, only the kinetic energy changes; the apparent Hamiltonian becomes

$$H_q = \sum_i \frac{(p_i - \hbar q)^2}{2m} + V = H - \hbar q \sum_i \frac{p_i}{m} + N \frac{(\hbar q)^2}{2m} \, . \tag{3.10}$$

Taking the average value of H_q in the state $|\varphi\rangle$, and let E_q be the energy of the system as seen from the moving reference frame, one find in the $\lim q \to 0$

$$\frac{\partial E_q}{\partial q_\alpha} = -\hbar \left\langle \varphi | \sum_i \frac{p_{i\alpha}}{m} | \varphi \right\rangle = -\hbar J_\alpha \, , \tag{3.11}$$

where α refers to one of the three coordinates. This expression gives the definition of current in the framework of the Fermi liquid theory. For the particular case of a translationally invariant system, the total current is a constant of the motion, which commutes with the interaction V and which, as a consequence, does not change when V is switched on adiabatically. For the particular state containing one quasi-particle $\mathbf{k}$, the total current J_k is the same as for the ideal system

$$J_k = \frac{(\hbar k)}{m} \, . \tag{3.12}$$

This result is a direct consequence of Galilean invariance.

Let us consider now the many-particle Hamiltonian (3.2)

$$H = H_1 + H_2 \, . \tag{3.13}$$

It will also be convenient to consider density of the particles in the following form[20]

$$n(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \, .$$

The Fourier transform of the particle density operator becomes

$$n(\mathbf{q}) = \int d^3 r \exp(-i\mathbf{q}\mathbf{r}) \sum_i \delta(\mathbf{r} - \mathbf{r}_i) = \sum_i \exp(-i\mathbf{q}\mathbf{r}_i) \, . \tag{3.14}$$

The particle mass-probability current distribution $\mathbf{J}$ in this "lattice" representation will take the form

$$\mathbf{J}(\mathbf{r}) = n(\mathbf{r})\mathbf{v} = \frac{1}{2}\sum_i \left\{ \frac{\mathbf{p}_i}{m}\delta(\mathbf{r}-\mathbf{r}_i) + \delta(\mathbf{r}-\mathbf{r}_i)\frac{\mathbf{p}_i}{m} \right\}$$

$$= \frac{1}{2}\sum_i \left\{ \frac{\mathbf{p}_i}{m}\exp(-i\mathbf{q}\mathbf{r}_i) + \exp(-i\mathbf{q}\mathbf{r}_i)\frac{\mathbf{p}_i}{m} \right\}, \tag{3.15}$$

$$[\mathbf{r}_i, \mathbf{p}_k] = i\hbar\delta_{ik}\,.$$

Here $\mathbf{v}$ is the velocity operator. The direct calculation shows that

$$[n(\mathbf{q}), H] = \frac{1}{2}\sum_i \left\{ \frac{\mathbf{q}\mathbf{p}_i}{m}\exp(-i\mathbf{q}\mathbf{r}_i) + \exp(-i\mathbf{q}\mathbf{r}_i)\frac{\mathbf{q}\mathbf{p}_\mathbf{i}}{m} \right\} = \mathbf{q}\mathbf{J}(\mathbf{q})\,. \tag{3.16}$$

Thus the equation of motion for the particle density operator becomes

$$\frac{dn(\mathbf{q})}{dt} = \frac{i}{\hbar}[H, n(\mathbf{q})] = -\frac{i}{\hbar}\mathbf{q}\mathbf{J}(\mathbf{q})\,, \tag{3.17}$$

or in another form

$$\frac{dn(\mathbf{r})}{dt} = \mathrm{div}\mathbf{J}(\mathbf{r})\,, \tag{3.18}$$

which is the continuity equation considered above. Note that

$$[n(\mathbf{q}), H_1]_- = [n(\mathbf{q}), H_2]_- = 0\,.$$

These relations holds in general for any periodic potential and interaction potential of the electrons which depend only on the coordinates of the electrons.

It is easy to check the validity of the following relation

$$[[n(\mathbf{q}), H], n^\dagger(\mathbf{q})] = [\mathbf{q}\mathbf{J}(\mathbf{r}), n^\dagger(\mathbf{q})] = \frac{Nq^2}{m}\,. \tag{3.19}$$

This formulae is the known f-sum rule[82] which is a consequence from the continuity equation (for a more general point of view, see Ref. 83).

Now consider the second-quantized Hamiltonian (3.2). The particle density operator has the form[77,84,85]

$$n(\mathbf{r}) = e\Psi^\dagger(\mathbf{r})\Psi(\mathbf{r})\,, \quad n(\mathbf{q}) = \int d^3r\exp(-i\mathbf{q}\mathbf{r})n(\mathbf{r})\,. \tag{3.20}$$

Then we define

$$\mathbf{j}(\mathbf{r}) = \frac{e\hbar}{2mi}(\Psi^\dagger\nabla\Psi - \Psi\nabla\Psi^\dagger)\,. \tag{3.21}$$

Here $\mathbf{j}$ is the probability current density, i.e., the probability flow per unit time per unit area perpendicular to $\mathbf{j}$. The continuity equation will persist for this case too. Let us consider the equation motion

$$\frac{dn(\mathbf{r})}{dt} = -\frac{i}{\hbar}[n(\mathbf{r}), H_1] - \frac{i}{\hbar}[n(\mathbf{r}), H_2]$$

$$= \frac{e\hbar}{2mi}(\Psi^\dagger(\mathbf{r})\nabla^2\Psi(\mathbf{r}) - \nabla^2\Psi^\dagger(\mathbf{r})\Psi(\mathbf{r}))\,. \tag{3.22}$$

Note that $[n(\mathbf{r}), H_2] \equiv 0$.

We find

$$\frac{dn(\mathbf{r})}{dt} = -\nabla \mathbf{j}(\mathbf{r})\,. \tag{3.23}$$

Thus the continuity equation have the same form in both the "particle" and "field" versions.

4. Tight-Binding and MTBA

Electrons and phonons are the basic elementary excitations of a metallic solid. Their mutual interactions[2,52,86–89] manifest themselves in such observations as the temperature dependent resistivity and low-temperature superconductivity. In the quasiparticle picture, at the basis of this interaction is the individual electron-phonon scattering event, in which an electron is deflected in the dynamically distorted lattice. We consider here the scheme which is called MTBA. But first, we remind shortly the essence of the tight-binding approximation. The main purpose in using the tight-binding method is to simplify the theory sufficiently to make workable. The tight-binding approximation considers solid as a giant molecule.

4.1. *Tight-binding approximation*

The main problem of the electron theory of solids is to calculate the energy level spectrum of electrons moving in an ion lattice.[52,90] The tight-binding method[52,91–94] for energy band calculations has generally been regarded as suitable primarily for obtaining a simple first approximation to a complex band structure. It was shown that the method should also be quite powerful in quantitative calculations from first principles for a wide variety of materials. An approximate treatment requires to obtain energy levels and electron wavefunctions for some suitable chosen one-particle potential (or pseudopotential), which is usually local. The standard molecular orbital theories of band structure are founded on an independent particle model.

As atoms are brought together to form a crystal lattice the sharp atomic levels broaden into bands. Provided there is no overlap between the bands, one expects to describe the crystal state by a Bloch function of the type,

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_n e^{i\mathbf{k}\mathbf{R}_n}\phi(\mathbf{r} - \mathbf{R}_n)\,, \tag{4.1}$$

where $\phi(\mathbf{r})$ is a free atom single-electron wavefunction, for example $1s$ and $\mathbf{R}_n$ is the position of the atom in a rigid lattice. If the bands overlap or approach each other, one should use instead of $\phi(\mathbf{r})$ a combination of the wavefunctions corresponding to the levels in question, e.g., $(a\phi(1s)+b\phi(2p))$, etc. In other words, this approach, first introduced to crystal calculation by Bloch, expresses the eigenstates of an electron in a perfect crystal in a linear combination of atomic orbitals and termed LCAO method.[52,91–94]

Atomic orbitals are not the most suitable basis set due to the nonorthogonality problem. It was shown by many authors[52,95–97] that the very efficient basis set for the expansion (4.1) is the atomic-like Wannier functions $\{w(\mathbf{r}-\mathbf{R}_n)\}$.[52,95–97] These are the Fourier transforms of the extended Bloch functions and are defined as

$$w(\mathbf{r}-\mathbf{R}_n) = \mathcal{N}^{-1/2}\sum_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{R}_n}\psi_{\mathbf{k}}(\mathbf{r})\,. \tag{4.2}$$

Wannier functions $w(\mathbf{r}-\mathbf{R}_n)$ form a complete set of mutually orthogonal functions localized around each lattice site $\mathbf{R}_n$ within any band or group of bands. They permit one to formulate an effective Hamiltonian for electrons in periodic potentials and span the space of a singly energy band. However, the real computation of Wannier functions in terms of sums over Bloch states is a complicated task.[33,97]

To define the Wannier functions more precisely, let us consider the eigenfunctions $\psi_{\mathbf{k}}(\mathbf{r})$ belonging to a particular simple band in a lattice with the one type of atom at a center of inversion. Let it satisfy the following equations with one-electron Hamiltonian H

$$H\psi_{\mathbf{k}}(\mathbf{r}) = E(\mathbf{k})\psi_{\mathbf{k}}(\mathbf{r})\,, \quad \psi_{\mathbf{k}}(\mathbf{r}+\mathbf{R}_n) = e^{-i\mathbf{k}\mathbf{R}_n}\psi_{\mathbf{k}}(\mathbf{r})\,, \tag{4.3}$$

and the orthonormality relation $\langle\psi_{\mathbf{k}}|\psi_{\mathbf{k}'}\rangle = \delta_{\mathbf{k}\mathbf{k}'}$ where the integration is performed over the $\mathcal{N}$ unit cells in the crystal. The property of periodicity together with the property of the orthonormality lead to the orthonormality condition of the Wannier functions

$$\int d^3r w^*(\mathbf{r}-\mathbf{R}_n)w(\mathbf{r}-\mathbf{R}_m) = \delta_{nm}\,. \tag{4.4}$$

The set of the Wannier functions is complete, i.e.,

$$\sum_i w^*(\mathbf{r}'-\mathbf{R}_i)w(\mathbf{r}-\mathbf{R}_i) = \delta(\mathbf{r}'-\mathbf{r})\,. \tag{4.5}$$

Thus, it is possible to find the inversion of Eq. (4.2) which has the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = \mathcal{N}^{-1/2}\sum_{\mathbf{k}} e^{i\mathbf{k}\mathbf{R}_n}w(\mathbf{r}-\mathbf{R}_n)\,. \tag{4.6}$$

These conditions are not sufficient to define the functions uniquely since the Bloch states $\psi_{\mathbf{k}}(\mathbf{r})$ are determined only within a multiplicative phase factor $\varphi(\mathbf{k})$ according to

$$w(\mathbf{r}) = \mathcal{N}^{-1/2}\sum_{\mathbf{k}} e^{i\varphi(\mathbf{k})}u_{\mathbf{k}}(\mathbf{r})\,, \tag{4.7}$$

where $\varphi(\mathbf{k})$ is any real function of $\mathbf{k}$, and $u_{\mathbf{k}}(\mathbf{r})$ are Bloch functions.[98] The phases $\varphi(\mathbf{k})$ are usually chosen so as to localize $w(\mathbf{r})$ about the origin. The usual choice of phase makes $\psi_{\mathbf{k}}(\mathbf{0})$ real and positive. This lead to the maximum possible value in $w(\mathbf{0})$ and $w(\mathbf{r})$ decaying exponentially away from $\mathbf{r} = 0$. In addition, function $\psi_{\mathbf{k}}(\mathbf{r})$ with this choice will satisfy the symmetry properties

$$\psi_{-\mathbf{k}}(\mathbf{r}) = (\psi_{\mathbf{k}}(\mathbf{r}))^* = \psi_{\mathbf{k}}(-\mathbf{r})\,.$$

It follows from the above consideration that the Wannier functions are real and symmetric,

$$w(\mathbf{r}) = (w(\mathbf{r}))^* = w(-\mathbf{r})\,.$$

Analytical, three-dimensional Wannier functions have been constructed from Bloch states formed from a lattice gaussians. Thus, in the condensed matter theory, the Wannier functions play an important role in the theoretical description of transition metals, their compounds and disordered alloys, impurities and imperfections, surfaces, etc.

4.2. *Interacting electrons on a lattice and the Hubbard model*

There are huge difficulties in description of the complicated problems of electronic and magnetic properties of a metal with the d-band electrons which are really neither "local" nor "itinerant" in a complete sense. A better understanding of the electronic correlation effects in metallic systems can be achieved by formulating a suitable flexible model that could be used to analyze major aspects of both the insulating and metallic states of solids in which electronic correlations are important.

The Hamiltonian of the interacting electrons with pair interaction in the second-quantized form is given by Eq. (3.2). Consider this Hamiltonian in the Bloch representation. We have

$$\Psi_\sigma(\mathbf{r}) = \sum_k \varphi_{\mathbf{k}\sigma}(\mathbf{r})a_{k\sigma}\,, \quad \Psi^\dagger_\sigma(\mathbf{r}) = \sum_k \varphi^*_{\mathbf{k}\sigma}(\mathbf{r})a^\dagger_{k\sigma}\,. \tag{4.8}$$

Here $\varphi_\sigma(\mathbf{k})$ is the Bloch function satisfying the equation

$$\begin{gathered} H_1(r)\varphi_{\mathbf{k}\sigma}(\mathbf{r}) = E_\sigma(\mathbf{k})\varphi_{\mathbf{k}\sigma}(\mathbf{r})\,, \quad E_\sigma(\mathbf{k}) = E_\sigma(-\mathbf{k})\,, \\ \varphi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}\mathbf{r})u_k(r)\,, \quad u_k(r+l) = u_k(r)\,, \\ \varphi_{\mathbf{k}\sigma}(\mathbf{r}) = \varphi_{-\mathbf{k}\sigma}(-\mathbf{r})\,, \quad \varphi^*_{\mathbf{k}\sigma}(\mathbf{r}) = \varphi_{-\mathbf{k}\sigma}(\mathbf{r})\,. \end{gathered} \tag{4.9}$$

The functions $\{\varphi_{\mathbf{k}\sigma}(\mathbf{r})\}$ form a complete orthonormal set of functions

$$\begin{gathered} \int d^3r\varphi^*_{\mathbf{k}'}(\mathbf{r})\varphi_{\mathbf{k}}(\mathbf{r}) = \delta_{kk'}\,, \\ \sum_k \varphi^*_{\mathbf{k}}(\mathbf{r}\,')\varphi_{\mathbf{k}}(\mathbf{r}) = \delta(r-r')\,. \end{gathered} \tag{4.10}$$

We find

$$\begin{aligned} H &= \sum_{mn}\langle m|H_1|n\rangle a^\dagger_m a_n + \frac{1}{2}\sum_{klmn}\langle kl|H_2|mn\rangle a^\dagger_k a^\dagger_l a_m a_n \\ &= \sum_{\mathbf{k}\sigma}\langle\varphi^*_{\mathbf{k},\sigma}|H_1|\varphi_{\mathbf{k},\sigma}\rangle a^\dagger_{k\sigma}a_{k\sigma} \\ &\quad + \frac{1}{2}\sum_{\mathbf{k}_4\mathbf{k}_3\mathbf{k}_2\mathbf{k}_1}\sum_{\alpha\beta\mu\nu}\langle\varphi^*_{\mathbf{k}_4,\nu}\varphi^*_{\mathbf{k}_3,\mu}|H_2|\varphi_{\mathbf{k}_2,\beta}\varphi_{\mathbf{k}_1,\alpha}\rangle a^\dagger_{\mathbf{k}_4\nu}a^\dagger_{\mathbf{k}_3\mu}a_{\mathbf{k}_2\beta}a_{\mathbf{k}_1\alpha}\,. \end{aligned} \tag{4.11}$$

Since the method of second quantization is based on the choice of suitable complete set of orthogonal normalized wavefunctions, we take now the set $\{w_\lambda(\mathbf{r}-\mathbf{R}_n)\}$ of the Wannier functions. Here λ is the band index. The field operators in the Wannier function representation are given by

$$\Psi_\sigma(\mathbf{r}) = \sum_n w_\lambda(\mathbf{r}-\mathbf{R}_n) a_{n\lambda\sigma}\,, \quad \Psi^\dagger_\sigma(\mathbf{r}) = \sum_n w^*_\lambda(\mathbf{r}-\mathbf{R}_n) a^\dagger_{n\lambda\sigma}\,. \tag{4.12}$$

Thus, we have

$$a^\dagger_{n\lambda\sigma} = N^{-1/2}\sum_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{R}_n} a^\dagger_{\mathbf{k}\lambda\sigma}\,, \quad a_{n\lambda\sigma} = N^{-1/2}\sum_{\mathbf{k}} e^{i\mathbf{k}\mathbf{R}_n} a_{\mathbf{k}\lambda\sigma}\,. \tag{4.13}$$

Many treatments of the correlation effects are effectively restricted to a nondegenerate band. The Wannier functions basis set is the background of the widely used Hubbard model. The Hubbard model[99,100] is, in a certain sense, an intermediate model (the narrow-band model) and takes into account the specific features of transition metals and their compounds by assuming that the d-electrons form a band, but are subject to a strong Coulomb repulsion at one lattice site. The single-band Hubbard Hamiltonian is of the form[62,99]

$$H = \sum_{ij\sigma} t_{ij} a^\dagger_{i\sigma} a_{j\sigma} + \frac{U}{2}\sum_{i\sigma} n_{i\sigma} n_{i-\sigma}\,. \tag{4.14}$$

Here $a^\dagger_{i\sigma}$ and $a_{i\sigma}$ are the second-quantized operators of the creation and annihilation of the electrons in the lattice state $w(\mathbf{r}-\mathbf{R_i})$ with spin σ. The Hamiltonian includes the intra-atomic Coulomb repulsion U and the one-electron hopping energy t_{ij}. The corresponding parameters of the Hubbard Hamiltonian are given by

$$t_{ij} = \int d^3r w^*(\mathbf{r}-\mathbf{R}_i) H_1(r) w(\mathbf{r}-\mathbf{R}_j)\,, \tag{4.15}$$

$$U = \iint d^3r d^3r' w^*(\mathbf{r}-\mathbf{R}_i) w^*(\mathbf{r}'-\mathbf{R}_i) \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} w(\mathbf{r}'-\mathbf{R}_i) w(\mathbf{r}-\mathbf{R}_i)\,. \tag{4.16}$$

The electron correlation forces electrons to localize in the atomic-like orbitals which are modeled here by a complete and orthogonal set of the Wannier wavefunctions $\{w(\mathbf{r}-\mathbf{R_j})\}$. On the other hand, the kinetic energy is increased when electrons are delocalized. The band energy of Bloch electrons $E(k)$ is defined as follows:

$$t_{ij} = N^{-1}\sum_{\mathbf{k}} E(k)\exp[i\mathbf{k}(\mathbf{R}_i-\mathbf{R}_j]\,, \tag{4.17}$$

where N is the number of lattice sites. The Pauli exclusion principle which does not allow two electrons of common spin to be at the same site, $n^2_{i\sigma} = n_{i\sigma}$, plays a crucial role. Note that the standard derivation of the Hubbard model presumes the rigid ion lattice with the rigidly fixed ion positions. We note that s-electrons are not explicitly taken into account in our model Hamiltonian. They can be, however, implicitly taken into account by screening effects and effective d-band occupation.

4.3. *Current operator for the tight-binding electrons*

Let us consider again a many-particle interacting systems on a lattice with the Hamiltonian (4.11). At this point, it is important to realize the fundamental difference between many-particle system which is uniform in space and many-particle system on a lattice. For the many-particle system on a lattice, the proper definition of current operator is a subtle problem. It was shown above that a physically satisfactory definition of the current operator in the quantum many-body theory is given based upon the continuity equation. However, this point should be reconsidered carefully for the lattice fermions which are described by the Wannier functions.

Let us remind once again that the Bloch and Wannier wavefunctions are related to each other by the unitary transformation of the form

$$\begin{aligned} \varphi_k(\mathbf{r}) &= N^{-1/2}\sum_{\mathbf{R}_n} w(\mathbf{r}-\mathbf{R}_n)\exp[i\mathbf{k}\mathbf{R}_n]\,, \\ w(\mathbf{r}-\mathbf{R}_n) &= N^{-1/2}\sum_{\mathbf{k}} \varphi_k(\mathbf{r})\exp[-i\mathbf{k}\mathbf{R}_n]\,. \end{aligned} \tag{4.18}$$

The number occupation representation for a single-band case lead to

$$\Psi_\sigma(\mathbf{r}) = \sum_n w(\mathbf{r}-\mathbf{R}_n)a_{n\sigma}\,, \quad \Psi^\dagger_\sigma(\mathbf{r}) = \sum_n w^*(\mathbf{r}-\mathbf{R}_n)a^\dagger_{n\sigma}\,. \tag{4.19}$$

In this representation, the particle density operator and current density take the form

$$\begin{aligned} n(\mathbf{r}) &= \sum_{ij}\sum_\sigma w^*(\mathbf{r}-\mathbf{R}_i)w(\mathbf{r}-\mathbf{R}_j)a^\dagger_{i\sigma}a_{j\sigma}\,, \\ \mathbf{j}(\mathbf{r}) &= \frac{e\hbar}{2mi}\sum_{ij}\sum_\sigma [w^*(\mathbf{r}-\mathbf{R}_i)\nabla w(\mathbf{r}-\mathbf{R}_j) \\ &\quad - \nabla w^*(\mathbf{r}-\mathbf{R}_i)w(\mathbf{r}-\mathbf{R}_j)]a^\dagger_{i\sigma}a_{j\sigma}\,. \end{aligned} \tag{4.20}$$

The equation of the motion for the particle density operator will consist of two contributions

$$\frac{dn(\mathbf{r})}{dt} = -\frac{i}{\hbar}[n(\mathbf{r}),H_1] - \frac{i}{\hbar}[n(\mathbf{r}),H_2]\,. \tag{4.21}$$

The first contribution is

$$[n(\mathbf{r}),H_1] = \sum_{mni}\sum_\sigma F_{nm}(\mathbf{r})(t_{mi}a^\dagger_{n\sigma}a_{i\sigma} - t_{in}a^\dagger_{i\sigma}a_{m\sigma})\,. \tag{4.22}$$

Here, the notation was introduced

$$F_{nm}(\mathbf{r}) = w^*(\mathbf{r}-\mathbf{R}_n)w(\mathbf{r}-\mathbf{R}_m)\,. \tag{4.23}$$

In the Bloch representation for the particle density operator, one finds

$$[n(\mathbf{k}),H_1] = \sum_{mni}\sum_\sigma F_{nm}(\mathbf{k})(t_{mi}a^\dagger_{n\sigma}a_{i\sigma} - t_{in}a^\dagger_{i\sigma}a_{m\sigma})\,, \tag{4.24}$$

where

$$F_{nm}(\mathbf{k}) = \int d^3r \exp[-i\mathbf{k}\mathbf{r}] F_{nm}(\mathbf{r})$$
$$= \int d^3r \exp[-i\mathbf{k}\mathbf{r}] w^*(\mathbf{r} - \mathbf{R}_n) w(\mathbf{r} - \mathbf{R}_m)\,. \tag{4.25}$$

For the second contribution $[n(\mathbf{r}), H_2]$, we find

$$[n(\mathbf{r}), H_2] = \frac{1}{2} \sum_{mn} \sum_{fst} \sum_{\sigma\sigma'} F_{nm}(\mathbf{r})$$
$$\times \left(\langle mf|H_2|st\rangle a^\dagger_{m\sigma} a^\dagger_{f\sigma'} a_{t\sigma'} a_{s\sigma} - \langle fm|H_2|st\rangle a^\dagger_{m\sigma'} a^\dagger_{f\sigma} a_{t\sigma'} a_{s\sigma} \right.$$
$$\left. + \langle fs|H_2|tn\rangle a^\dagger_{f\sigma} a^\dagger_{s\sigma'} a_{t\sigma} a_{n\sigma'} - \langle fs|H_2|nt\rangle a^\dagger_{f\sigma} a^\dagger_{s\sigma'} a_{t\sigma'} a_{n\sigma} \right). \tag{4.26}$$

For the single-band Hubbard Hamiltonian, the last equation will take the form

$$[n(\mathbf{r}), H_2] = U \sum_{mn} \sum_{\sigma} F_{nm}(\mathbf{r}) a^\dagger_{n\sigma} a_{m\sigma} (n_{m-\sigma} - n_{n-\sigma})\,. \tag{4.27}$$

The direct calculations give for the case of electrons on a lattice (e is a charge of an electron)

$$\frac{dn(\mathbf{r})}{dt} = \frac{e\hbar}{2mi} \sum_{ij} \sum_{\sigma} [w^*(\mathbf{r} - \mathbf{R}_i) \nabla^2 w(\mathbf{r} - \mathbf{R}_j)$$
$$- \nabla^2 w^*(\mathbf{r} - \mathbf{R}_i) w(\mathbf{r} - \mathbf{R}_j)] a^\dagger_{i\sigma} a_{j\sigma}$$
$$- ieU \sum_{ij} \sum_{\sigma} F_{ij}(\mathbf{r}) a^\dagger_{i\sigma} a_{j\sigma} (n_{j-\sigma} - n_{i-\sigma})\,. \tag{4.28}$$

Taking into account that

$$\mathrm{div}\mathbf{j}(\mathbf{r}) = \frac{e\hbar}{2mi} \sum_{ij} \sum_{\sigma} [w^*(\mathbf{r} - \mathbf{R}_i) \nabla^2 w(\mathbf{r} - \mathbf{R}_j)$$
$$- \nabla^2 w^*(\mathbf{r} - \mathbf{R}_i) w(\mathbf{r} - \mathbf{R}_j)] a^\dagger_{i\sigma} a_{j\sigma}\,, \tag{4.29}$$

we find

$$\frac{dn(\mathbf{r})}{dt} = -\mathrm{div}\mathbf{j}(\mathbf{r}) - ieU \sum_{ij} \sum_{\sigma} F_{ij}(\mathbf{r}) a^\dagger_{i\sigma} a_{j\sigma} (n_{j-\sigma} - n_{i-\sigma})\,. \tag{4.30}$$

This unusual result was analyzed critically by many authors. The proper definition of the current operator for the Hubbard model has been the subject of intensive discussions.[101–111] To clarify the situation, let us consider the "total position operator" for our system of the electrons on a lattice

$$\mathbf{R} = \sum_{j=1}^{N} \mathbf{R}_j\,. \tag{4.31}$$

In the "quantized" picture it has the form

$$\begin{aligned}\mathbf{R} &= \sum_j \int d^3r \Psi^\dagger(\mathbf{r})\mathbf{R}_j \Psi(\mathbf{r}) \\ &= \sum_j \sum_{mn} \sum_\mu \int d^3r \mathbf{R}_j w^*(\mathbf{r}-\mathbf{R}_m) w(\mathbf{r}-\mathbf{R}_n) a^\dagger_{m\mu} a_{n\mu} \\ &= \sum_j \sum_m \sum_\mu \mathbf{R}_j a^\dagger_{m\mu} a_{m\mu}\,, \qquad (4.32)\end{aligned}$$

where we took into account the relation

$$\int d^3r w^*(\mathbf{r}-\mathbf{R}_m) w(\mathbf{r}-\mathbf{R}_n) = \delta_{mn}\,. \qquad (4.33)$$

We find that

$$\begin{aligned}[\mathbf{R}, a^\dagger_{i\sigma}]_- &= \sum_m \mathbf{R}_m a^\dagger_{i\sigma}\,, \\ [\mathbf{R}, a_{i\sigma}]_- &= -\sum_m \mathbf{R}_m a_{i\sigma}\,, \qquad (4.34) \\ [\mathbf{R}, a^\dagger_{i\sigma} a_{i\sigma}]_- &= 0\,.\end{aligned}$$

Let us consider the local particle density operator $n_{i\sigma} = a^\dagger_{i\sigma} a_{i\sigma}$.

$$\frac{dn_{i\sigma}}{dt} = -\frac{i}{\hbar}[n_{i\sigma}, H]_- = \sum_j t_{ij}(a^\dagger_{i\sigma} a_{j\sigma} - a^\dagger_{j\sigma} a_{i\sigma})\,. \qquad (4.35)$$

It is clear that the current operator should be defined on the basis of the equation

$$\mathbf{j} = e\left(\frac{-i}{\hbar}\right)[\mathbf{R}, H]_-\,. \qquad (4.36)$$

Defining the so-called polarization operator[101,103,106,107]

$$\mathcal{P} = e \sum_m \sum_\sigma \mathbf{R}_m n_{m\sigma}\,, \qquad (4.37)$$

we find the current operator in the form

$$\mathbf{j} = \dot{\mathcal{P}} = e\left(\frac{-i}{\hbar}\right) \sum_{mn} \sum_\sigma (\mathbf{R}_m - \mathbf{R}_n) t_{mn} a^\dagger_{m\sigma} a_{n\sigma}\,. \qquad (4.38)$$

This expression of the current operator is a suitable formula for studying the transport properties of the systems of correlated electron on a lattice.[112–114] The consideration carried out in this section demonstrate explicitly the specific features of the many-particle interacting systems on a lattice.

4.4. *Electron–lattice interaction in metals*

In order to understand quantitatively the electrical, thermal and superconducting properties of metals and their alloys, one needs a proper description of an electron–lattice interaction.[86] In the physics of molecules,[115] the concept of an intermolecular force requires that an effective separation of the nuclear and electronic motion can be made. This separation is achieved in the Born–Oppenheimer approximation.[115,116] Closely related to the validity of the Born–Oppenheimer approximation is the notion of adiabaticity. The adiabatic approximation is applicable if the nuclei is much slower than the electrons. The Born–Oppenheimer approximation consists of separating the nuclear motion and computing only the electronic wavefunctions and energies for fixed position of the nuclei. In the mathematical formulation of this approximation, the total wavefunction is assumed in the form of a product both of whose factors can be computed as solutions of two separate Schrödinger equations. In most applications, the separation is valid with sufficient accuracy, and the adiabatic approach is reasonable, especially if the electronic properties of molecules are concerned.

The conventional physical picture of a metal adopts these ideas[86,87] and assumes that the electrons and ions are essentially decoupled from one another with an error which involves the small parameter m/M, the ratio between the masses of the electron and the ion. The qualitative arguments for this statement are the following estimations. The maximum lattice frequency is of the order 10^{13} s^{-1} and is quite small compared with a typical atomic frequency. This latter frequency is of order of 10^{15} s^{-1}. If the electrons are able to respond in times of the order of atomic times then they will effectively be following the motion of the lattice instantaneously at all frequencies of vibration. In other words, the electron motion will be essentially adiabatic. This means that the wavefunctions of the electrons adjust instantaneously to the motion of the ions. It is intuitively clear that the electrons would try to follow the motion of the ions in such a way as to keep the system locally electrically neutral. In other words, it is expected that the electrons will try to respond to the motion of the ions in such a way as to screen out the local charge fluctuations.

The construction of an electron–phonon interaction requires the separation of the Hamiltonian describing mutually interacting electrons and ions into terms representing electronic quasiparticles, phonons and a residual interaction.[2,33,52,86–88] For the simple metals, the interaction between the electrons and the ions can be described within the pseudopotential method or the muffin-tin approximation. These methods could not handle well the *d*-bands in the transition metals. They are too narrow to be approximated as free-electron–like bands but too broad to be described as core ion states. The electron–phonon interaction in solid is usually described by the Fröhlich Hamiltonian.[86,117] We consider below the main ideas and approximations concerning to the derivation of the explicit form of the electron–phonon interaction operator.

Consider the total Hamiltonian for the electrons with coordinates $\mathbf{r}_i$ and the ions with coordinates $\mathbf{R}_m$, with the electron cores which can be regarded as tightly bound to the nuclei. The Hamiltonian of the N ions is

$$H = -\frac{\hbar^2}{2M}\sum_{m=1}^{N}\nabla^2_{\mathbf{R}_m} - \frac{\hbar^2}{2m}\sum_{i=1}^{ZN}\nabla^2_{\mathbf{r}_i} + \frac{1}{2}\sum_{i,j=1}^{ZN}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{n>m} V_i(\mathbf{R}_m - \mathbf{R}_n) + \sum_{m=1}^{N} U_{ie}(\mathbf{r}_i; \mathbf{R}_m)\,. \tag{4.39}$$

Each ion is assumed to contribute Z conduction electrons with coordinates $\mathbf{r}_i$ $(i = 1, \ldots, ZN)$. The first two terms in Eq. (4.39) are the kinetic energies of the electrons and the ions. The third term is the direct electron–electron Coulomb interaction between the conduction electrons. The next two terms are short for the potential energy for direct ion–ion interaction and the potential energy of the ZN conduction electrons moving in the field from the nuclei and the ion core electrons, when the ions take instantaneous position $\mathbf{R}_m$ $(m = 1, \ldots, N)$. The term $V_i(\mathbf{R}_m - \mathbf{R}_n)$ is the interaction potential of the ions with each other, while $U_{ie}(\mathbf{r}_i; \mathbf{R}_m)$ represents the interaction between an electron at $\mathbf{r}_i$ and an ion at $\mathbf{R}_m$. Thus, the total Hamiltonian of the system can be represented as the sum of an electronic and ionic part.

$$H = H_e + H_i\,, \tag{4.40}$$

where

$$H_e = -\frac{\hbar^2}{2m}\sum_{i=1}^{ZN}\nabla^2_{\mathbf{r}_i} + \frac{1}{2}\sum_{i,j=1}^{ZN}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{m=1}^{N} U_{ie}(\mathbf{r}_i; \mathbf{R}_m)\,, \tag{4.41}$$

and

$$H_i = -\frac{\hbar^2}{2M}\sum_{m=1}^{N}\nabla^2_{\mathbf{R}_m} + \sum_{n>m} V_i(\mathbf{R}_m - \mathbf{R}_n)\,. \tag{4.42}$$

The Schrödinger equation for the electrons in the presence of fixed ions is

$$H_e\Psi(\mathbf{K}, \mathbf{R}, \mathbf{r}) = E(\mathbf{K}, \mathbf{R})\Psi(\mathbf{K}, \mathbf{R}, \mathbf{r})\,, \tag{4.43}$$

in which $\mathbf{K}$ is the total wave vector of the system; $\mathbf{R}$ and $\mathbf{r}$ denote the set of all electronic and ionic coordinates, respectively. It is seen that the energy of the electronic system and the wavefunction of the electronic state depend on the ionic positions. The total wavefunction for the entire system of electrons plus ions $\Phi(\mathbf{Q}, \mathbf{R}, \mathbf{r})$ can be expanded, in principle, with respect to the Ψ as basis functions

$$\Phi(\mathbf{Q}, \mathbf{R}, \mathbf{r}) = \sum_{\mathbf{K}} L(\mathbf{Q}, \mathbf{K}, \mathbf{R})\Psi(\mathbf{K}, \mathbf{R}, \mathbf{r})\,. \tag{4.44}$$

We start with the approach which uses a fixed set of basis states. Let us suppose that the ions of the crystal lattice vibrate around their equilibrium positions $\mathbf{R}^0_m$ with a small amplitude, namely $\mathbf{R}_m = \mathbf{R}^0_m + \mathbf{u}_m$, where $\mathbf{u}_m$ is the deviation from the equilibrium position $\mathbf{R}_m^0$. Let us consider an idealized system in which the ions are fixed in these positions. Suppose that the energy bands $E_n(\mathbf{k})$ and wavefunctions $\psi_n(\mathbf{k},\mathbf{r})$ are known. As a result of the oscillations of the ions, the actual crystal potential differs from that of the rigid lattice. This difference can be possibly treated as a perturbation. This is the Bloch formulation of the electron–phonon interaction.

To proceed, we must expand the potential energy $V(\mathbf{r}-\mathbf{R})$ of an electron at $\mathbf{r}$ in the field of an ion at $\mathbf{R}_m$ in the atomic displacement $\mathbf{u}_m$

$$V(\mathbf{r}-\mathbf{R}_m) \simeq V(\mathbf{r}-\mathbf{R}_m^0) - \mathbf{u}_m \nabla V(\mathbf{r}-\mathbf{R}_m^0) + \cdots \tag{4.45}$$

The perturbation potential, including all atoms in the crystal is

$$\widetilde{V} = -\sum_m \mathbf{u}_m \nabla V(\mathbf{r}-\mathbf{R}_m^0)\,. \tag{4.46}$$

This perturbation will produce transitions between one-electron states with the corresponding matrix element of the form

$$M_{mk,nq} = \int \psi_m^*(\mathbf{k},\mathbf{r})\tilde{V}\psi_n(\mathbf{q},\mathbf{r})d^3r\,. \tag{4.47}$$

To describe properly the lattice subsystem, let us remind that the normal coordinate $Q_{\mathbf{q},\lambda}$ is defined by the relation[52,86]

$$(\mathbf{R}_m - \mathbf{R}_\mathbf{m}^\mathbf{0}) = \mathbf{u}_m = (\hbar/2\mathcal{N}M)^{1/2}\sum_{\mathbf{q},\nu} Q_{\mathbf{q},\nu}\mathbf{e}_\nu(\mathbf{q})\exp(i\mathbf{q}\mathbf{R}_\mathbf{m}^\mathbf{0})\,, \tag{4.48}$$

where $\mathcal{N}$ is the number of unit cells per unit volume and $\mathbf{e}_\nu(\mathbf{q})$ is the polarization vector of the phonon. The Hamiltonian of the phonon subsystem in terms of normal coordinates is written as[52,86]

$$H_i = \sum_{\mu,\mathbf{q}}^{BZ}\left(\frac{1}{2}P^\dagger_{\mathbf{q},\mu}P_{\mathbf{q},\mu} + \frac{1}{2}\Omega^2_{\mathbf{q},\mu}Q^\dagger_{\mathbf{q},\mu}Q_{\mathbf{q},\mu}\right), \tag{4.49}$$

where μ denote polarization direction and the $\mathbf{q}$ summation is restricted to the Brillouin zone denoted as BZ. It is convenient to express u_m in terms of the second-quantized phonon operators

$$\begin{aligned}\mathbf{u}_m = (\hbar/2\mathcal{N}M)^{1/2}&\sum_{\mathbf{q},\nu}[(\omega_\nu^{1/2}(\mathbf{q})]^{-1}\mathbf{e}_\nu(\mathbf{q})[\exp(i\mathbf{q}\mathbf{R}_\mathbf{m}^\mathbf{0})b_{\mathbf{q},\nu}\\ &+\exp(-i\mathbf{q}\mathbf{R}_\mathbf{m}^\mathbf{0})b^\dagger_{\mathbf{q},\nu}]\,,\end{aligned} \tag{4.50}$$

in which ν denotes a branch of the phonon spectrum, $\mathbf{e}_\nu(\mathbf{q})$ is the eigenvector for a vibrational state of wave vector $\mathbf{q}$ and branch ν, and $b^\dagger_{\mathbf{q},\nu}(b_{\mathbf{q},\nu})$ is a phonon creation (annihilation) operator. The matrix element $M_{mk,nq}$ becomes

$$M_{mk,nq} = -(\hbar/2\mathcal{N}M)^{1/2}\sum_{\mathbf{q},\nu}(\mathbf{e}_\nu(\mathbf{k}-\mathbf{q})A_{mn}(\mathbf{k},\mathbf{q})[\omega_\nu(\mathbf{k}-\mathbf{q})]^{-1/2}(b_{\mathbf{k}-\mathbf{q},\nu}+b^\dagger_{\mathbf{q}-\mathbf{k},\nu}))\,. \tag{4.51}$$

Here, the quantity A_{mn} is given by

$$A_{mn}(\mathbf{k},\mathbf{q}) = \mathcal{N} \int \psi^*_m(\mathbf{k},\mathbf{r}) \nabla V(\mathbf{r}) \psi_n(\mathbf{q},\mathbf{r}) d^3 r \,. \tag{4.52}$$

It is well-known[52,86] that there is a distinction between normal processes in which vector $(\mathbf{k}-\mathbf{q})$ is inside the Brillouin zone and *Umklapp* processes in which vector $(\mathbf{k}-\mathbf{q})$ must be brought back into the zone by addition of a reciprocal lattice vector $\mathbf{G}$.

The standard simplification in the theory of metals consists of replacement of the Bloch functions $\psi_n(\mathbf{q},\mathbf{r})$ by the plane waves

$$\psi_n(\mathbf{q},\mathbf{r}) = \mathcal{V}^{-1/2} \exp(i\mathbf{q}\mathbf{r}) \,,$$

in which $\mathcal{V}$ is the volume of the system. With this simplification we get

$$A_{mn}(\mathbf{k},\mathbf{q}) = i(\mathbf{k}-\mathbf{q}) V((\mathbf{k}-\mathbf{q})) \,. \tag{4.53}$$

Introducing the field operators $\psi(\mathbf{r})$, $\psi^\dagger(\mathbf{r})$ and the fermion second-quantized creation and annihilation operators $a^\dagger_{n\mathbf{k}}$, $a_{n\mathbf{k}}$ for an electron of wave vector $\mathbf{k}$ in band n in the plane wave basis

$$\psi(\mathbf{r}) = \sum_{\mathbf{q}n} \psi_n(\mathbf{q},\mathbf{r}) a_{n\mathbf{k}}$$

and the set of quantities

$$\Gamma_{mn,\nu}(\mathbf{k},\mathbf{q}) = -(\hbar/2M\omega_\nu(\mathbf{k}-\mathbf{q}))^{1/2} \mathbf{e}_\nu(\mathbf{k}-\mathbf{q}) A_{mn}(\mathbf{k},\mathbf{q}) \,,$$

we can write an interaction Hamiltonian for the electron–phonon system in the form

$$H_{ei} = \mathcal{N}^{1/2} \sum_{nl\nu} \sum_{\mathbf{kq}} \Gamma_{mn,\nu}(\mathbf{k},\mathbf{q}) (a^\dagger_{n\mathbf{k}} a_{l\mathbf{q}} b_{\mathbf{k}-\mathbf{q},\nu} + a^\dagger_{n\mathbf{k}} a_{l\mathbf{q}} b^\dagger_{\mathbf{q}-\mathbf{k},\nu}) \,. \tag{4.54}$$

This Hamiltonian describes the processes of phonon absorption or emission by an electron in the lattice, which were first considered by Bloch. Thus, the electron–phonon interaction is essentially dynamic and affects the physical properties of metals in a characteristic way.

It is possible to show[86] that in the Bloch momentum representation the Hamiltonian of a system of conduction electrons in metal interacting with phonons will have the form

$$H = H_e + H_i + H_{ei} \,, \tag{4.55}$$

where

$$H_e = \sum_{\mathbf{p}} E(\mathbf{p}) a^\dagger_{\mathbf{p}} a_{\mathbf{p}} \,, \tag{4.56}$$

$$H_i = \frac{1}{2} \sum_{\mathbf{q},\nu}^{|\mathbf{q}|<q_m} \omega_\nu(\mathbf{q}) (b^\dagger_{\mathbf{q}} b_{\mathbf{q}} + b^\dagger_{-\mathbf{q}} b_{-\mathbf{q}}) \,, \tag{4.57}$$

$$H_{ei} = \sum_{\nu} \sum_{\mathbf{p}'=\mathbf{p}+\mathbf{q}+\mathbf{G}} \Gamma_{\mathbf{q}\nu}(\mathbf{p}-\mathbf{p}') a^{\dagger}_{\mathbf{p}'} a_{\mathbf{p}} (b_{\mathbf{q}\nu} + b^{\dagger}_{-\mathbf{q}\nu}) \,. \tag{4.58}$$

The Fröhlich model ignores the *Umklapp* processes ($\mathbf{G} \neq 0$) and transverse phonons and takes the unperturbed electron and phonon energies as

$$E(\mathbf{p}) = \frac{\hbar^2 p^2}{2m} - E_F \,, \quad \omega(\mathbf{q}) = v_s^0 q \,, \quad (q < q_m) \,.$$

Here v_s is the sound velocity of the free phonon. The other notation are:

$$|\mathbf{q}| = q \,, \quad |\mathbf{p}| = p \,, \quad q_m = (6\pi^2 n_i)^{1/3} \,.$$

Thus we obtain

$$H_{ei} = \sum_{p,q} v(q) a^{\dagger}_{p+q} a_p (b_q + b^{\dagger}_{-q}) \,, \tag{4.59}$$

where $v(q)$ is the Fourier component of the interaction potential

$$v(q) = g(\omega(q)/2)^{1/2} \,, \quad g = [2E_F/3Mn_i v_s^2]^{1/2} \,.$$

Here n_i is the ionic density. The point we should like to emphasize in the present context is that the derivation of this Hamiltonian is based essentially on the plane wave representation for the electron wavefunction.

4.5. *Modified tight-binding approximation*

Particular properties of the transition metals, their alloys and compounds follow to a great extent, from the dominant role of d-electrons. The natural approach to description of electron–lattice effects in such type of materials is the MTBA. The electron–phonon matrix element in the Bloch picture is taken between electronic states of the undeformed lattice. For transition metals it is not easy task to estimate the electron–lattice interaction matrix element due to the anisotropy and other factors.[118–121] There is an alternative description, introduced by Fröhlich and Mitra[122–124] and which was termed the MTBA. In this approach, the electrons are moving adiabatically with the ions. Moreover, the coupling of the electron to the displacement of the ion nearest to it, is already included in zero-order of approximation. This is the basis of modified tight-binding calculations of the electron–phonon interaction which purports to remove certain difficulties of the conventional Bloch tight-binding approximation for electrons in narrow-band. The standard Hubbard Hamiltonian should be rederived in this approach in terms of the new basis wavefunctions for the vibrating lattice. This was carried out by Barisic, Labbe and Friedel.[125] They derived a model Hamiltonian which is a generalization of the single-band Hubbard model[100] including the lattice vibrations. The hopping integral t_{ij} of the single-band Hubbard model (4.14) is given by

$$t_{ij} = \int d^3 r w^*(\mathbf{r}-\mathbf{R_j}) \left(\frac{\hbar^2 p^2}{2m} + \sum_l V_{sf}(\mathbf{r}-\mathbf{R}_l) \right) w(\mathbf{r}-\mathbf{R}_i) \,. \tag{4.60}$$

Here we assumed that V_{sf} is a short-range, self-consistent potential of the lattice suitable screened by outer electrons. Considering small vibrations of ions, we replace Eq. (4.60) the ion position $\mathbf{R}_i$ by $(\mathbf{R}_i^0 + \mathbf{u}_i)$, i.e., its equilibrium position plus displacement. The unperturbed electronic wavefunctions must be written as a Bloch sum of displaced and suitable (approximately) orthonormalized atomic-like functions

$$\int d^3 r w^*(\mathbf{r} - \mathbf{R_j^0} - \mathbf{u}_j) w(\mathbf{r} - \mathbf{R_i^0} - \mathbf{u}_i) \approx \delta_{ij} \,. \tag{4.61}$$

As it follows from Eq. (4.61), the creation and annihilation operators $a_{k\sigma}^{+}, a_{k\sigma}$ may be introduced in the deformed lattice so as to take partly into account the adiabatic follow up of the electron upon the vibration of the lattice. The Hubbard–Hamiltonian equation (4.14) can be rewritten in the form[126,127]

$$H = t_0 \sum_{i\sigma} h_{i\sigma} + \sum_{i \neq j\sigma} t(\mathbf{R_j^0} + \mathbf{u}_j - \mathbf{R}_i^0 - \mathbf{u}_i) a_{i\sigma}^{\dagger} a_{j\sigma} + U/2 \sum_{i\sigma} n_{i\sigma} n_{i-\sigma} \,. \tag{4.62}$$

For small displacements $\mathbf{u}_i$, we may expand $t(\mathbf{R})$ as

$$t(\mathbf{R}_j^0 + \mathbf{u}_j - \mathbf{R}_i^0 - \mathbf{u}_i) \approx t(\mathbf{R}_j^0 - \mathbf{R}_i^0) + \frac{\partial t(\mathbf{R})}{\partial \mathbf{R}} |_{\mathbf{R} = \mathbf{R}_j^0 - \mathbf{R}_i^0} (\mathbf{u}_j - \mathbf{u}_i) + \cdots \tag{4.63}$$

Using the character of the exponential decrease of the Slater and Wannier functions, the following approximation may be used[125–127]

$$\frac{\partial t(\mathbf{R})}{\partial \mathbf{R}} \simeq -q_0 \frac{\mathbf{R}}{|\mathbf{R}|} t(\mathbf{R}) \,. \tag{4.64}$$

Here q_0 is the Slater coefficient[128] originated in the exponential decrease of the wavefunctions of d-electrons; q_0^{-1} related to the range of the d-function and is of the order of the interatomic distance. The Slater coefficients for various metals are tabulated.[125] The typical values are given in Table 3.

It is of use to rewrite the total model Hamiltonian of transition metal $H = H_e + H_i + H_{ei}$ in the quasi-momentum representation. We have

$$\begin{aligned} H_e = & \sum_{k\sigma} E(k) a_{k\sigma}^{\dagger} a_{k\sigma} \\ & + U/2N \sum_{k_1 k_2 k_3 k_4 G} a_{k_1\uparrow}^{\dagger} a_{k_2\uparrow} a_{k_3\downarrow}^{\dagger} a_{k_4\downarrow} \delta(\mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3 - \mathbf{k}_4 + \mathbf{G}) \,. \end{aligned} \tag{4.65}$$

For the tight-binding electrons in crystals we use $E(\mathbf{k}) = 2 \sum_\alpha t(a_\alpha) \cos(k_\alpha a_\alpha)$, where $t(\mathbf{a})$ is the hopping integral between nearest neighbors, and $a_\alpha (\alpha = x, y.z)$ denotes the lattice vectors in a simple lattice with an inversion center.

Table 3. Slater coefficients.

q_0 (A^{-1})	Element	Element	Element	Element	Element	Element
$q_0 = 0.93$	Ti	*V*	Cr	Mn	Fe	Co
$q_0 = 0.91$	Zr	Nb	Mo	Tc	Ru	Rh
$q_0 = 0.87$	Hf	Ta	*W*	Re	Os	Ir

The electron–phonon interaction is rewritten as

$$H_{ei} = \sum_{kk_1} \sum_{qG} \sum_{\nu\sigma} g^{\nu}_{kk_1} a^{\dagger}_{k_1\sigma} a_{k\sigma} (b^{\dagger}_{q\nu} + b_{-q\nu}) \delta(\mathbf{k}_1 - \mathbf{k} + \mathbf{q} + \mathbf{G}) \,, \tag{4.66}$$

where

$$g^{\nu}_{kk_1} = \left(\frac{1}{(\mathcal{N} M \omega_{\nu}(k))} \right)^{1/2} I^{\nu}_{kk_1} \,, \tag{4.67}$$

$$I^{\nu}_{kk_1} = 2iq_0 \sum_{\alpha} t(\mathbf{a}_{\alpha}) \frac{\mathbf{a}_{\alpha} \mathbf{e}_{\nu}(\mathbf{k}_1)}{|\mathbf{a}_{\alpha}|} (\sin(\mathbf{a}_{\alpha}\mathbf{k}) - \sin(\mathbf{a}_{\alpha}\mathbf{k}_1)) \,. \tag{4.68}$$

where $\mathcal{N}$ is the number of unit cells in the crystal and M is the ion mass. The $\mathbf{e}_{\nu}(\mathbf{q})$ are the polarization vectors of the phonon modes. Operators $b^{\dagger}_{q\nu}$ and $b_{q\nu}$ are the creation and annihilation phonon operators and $\omega_{\nu}(k)$ are the acoustical phonon frequencies. Thus we can describe[126,127,129,130] the transition metal by the one-band model which takes into consideration the electron–electron and electron–lattice interaction in the framework of the MTBA. It is possible to rewrite (4.66) in the following form[126,127]

$$H_{ei} = \sum_{\nu\sigma} \sum_{kq} V^{\nu}(\mathbf{k}, \mathbf{k} + \mathbf{q}) Q_{\mathbf{q}\nu} a^{+}_{k+q\sigma} a_{k\sigma} \,, \tag{4.69}$$

where

$$V^{\nu}(\mathbf{k}, \mathbf{k} + \mathbf{q}) = \frac{2iq_0}{(\mathcal{N} M)^{1/2}} \sum_{\alpha} t(\mathbf{a}_{\alpha}) e^{\alpha}_{\nu}(\mathbf{q}) (\sin \mathbf{a}_{\alpha}\mathbf{k} - \sin \mathbf{a}_{\alpha}(\mathbf{k} - \mathbf{q})) \,. \tag{4.70}$$

The one-electron hopping $t(\mathbf{a}_{\alpha})$ is the overlap integral between a given site $\mathbf{R}_m$ and one of the two nearby sites lying on the lattice axis $\mathbf{a}_{\alpha}$. For the ion subsystem we have

$$H_i = \frac{1}{2} \sum_{q\nu} (P^{+}_{q\nu} P_{q\nu} + \omega^2_{\nu}(q)) Q^{+}_{q\nu} Q_{q\nu} = \sum_{q\nu} \omega_{\nu}(q) (b^{\dagger}_{q\nu} b_{q\nu} + 1/2) \,, \tag{4.71}$$

where $P_{q\nu}$ and $Q_{q\nu}$ are the normal coordinates. Thus, as in the Hubbard model,[100] the d- and $s(p)$-bands are replaced by one effective band in our model. However, the s-electrons give rise to screening effects and are taken into effects by choosing proper value of U and the acoustical phonon frequencies. It was shown by Ashkenasi, Dacorogna and Peter[131,132] that the MTBA approach for calculating electron–phonon coupling constant based on wavefunctions moving with the vibrating atoms lead to same physical results as the Bloch approach within the harmonic approximation. For transition metals and narrow-band compounds, the MTBA approach seems to be yielding more accurate results, especially in predicting anisotropic properties.

5. Charge and Heat Transport

We now tackle the transport problem in a qualitative fashion. This crude picture has many obvious shortcomings. Nevertheless, the qualitative description of conductivity is instructive. Guided by this instruction the results of the more advanced and careful calculations of the transport coefficients will be reviewed in the next sections.

5.1. *Electrical resistivity and Ohm law*

Ohm law is one of the equations used in the analysis of electrical circuits. When a steady current flow through a metallic wire, Ohm law tell us that an electric field exists in the circuit, that like the current this field is directed along the uniform wire and that its magnitude is J/σ, where J is the current density and σ the conductivity of the conducting material. Ohm law states that in an electrical circuit, the current passing through most materials is directly proportional to the potential difference applied across them. A voltage source, V, drives an electric current, I, through resistor, R, the three quantities obeying Ohm law: $V = IR$.

In other terms, this is written often as: $I = V/R$, where I is the current, V is the potential difference, and R is a proportionality constant called the *resistance*. The potential difference is also known as the voltage drop and is sometimes denoted by E or U instead of V. The SI unit of current is the ampere; that of potential difference is the volt; and that of resistance is the ohm, equal to one volt per ampere. The law is named after the physicist Georg Ohm, who formulated it in 1826 . The continuum form of Ohm's law is often of use:

$$\mathbf{J} = \sigma \cdot \mathbf{E}\,, \tag{5.1}$$

where $\mathbf{J}$ is the current density (current per unit area), σ is the conductivity (which can be a tensor in anisotropic materials) and $\mathbf{E}$ is the electric field . The common form $V = I \cdot R$ used in circuit design is the macroscopic, averaged-out version. The continuum form of the equation is only valid in the reference frame of the conducting material.

A conductor may be defined as a material within which there are free charges, that is, charges that are free to move when a force is exerted on them by an electric field. Many conducting materials, mainly metals, show a linear dependence of I on V. The essence of Ohm law is this linear relationship. The important problem is the applicability of Ohm law. The relation $R{\cdot}I = W$ is the generalized form of Ohm law for the current flowing through the system from terminal A to B. Here I is a steady dc current, which is zero if the work W done per unit charge is zero, while $I \neq 0$ or $W \neq 0$. If the current in not too large, the current I must be simply proportional to W. Hence one can write $R \cdot I = W$, where the proportionality constant is called the *resistance* of the two-terminal system. The basic equations are:

$$\boldsymbol{\nabla} \times \mathbf{E} = 4\pi n\,, \tag{5.2}$$

Gauss law, and

$$\frac{\partial n}{\partial t} + \boldsymbol{\nabla} \times \mathbf{J} = 0\,, \tag{5.3}$$

charge conservation law. Here n is the number density of charge carriers in the system. Equations (5.2) and (5.3) are fundamental whereas the Ohm law is not.

However, in the absence of nonlocal effects, Eq. (5.1) is still valid. In an electric conductor with finite cross-section, it must be possible a surface conditions on the current density **J**. Ohm law does not permit this and cannot, therefore, be quite correct. It has to be supplemented by terms describing a viscous flow. Ohm law is a statement of the behavior of many, but not all conducting bodies, and in this sense should be looked upon as describing a special property of certain materials and not a general property of all matter.

5.2. *Drude-Lorentz model*

The phenomenological picture described above requires microscopic justification. We are concerned in this paper with the transport of electric charge and heat by the electrons in a solid. When our sample is in uniform thermal equilibrium, the distribution of electrons over the eigenstates available to them in each region of the sample is described by the Fermi–Dirac distribution function and the electric and heat current densities both vanish everywhere. Nonvanishing macroscopic current densities arise whenever the equilibrium is made nonuniform by varying either the electrochemical potential or the temperature from point to point in the sample. The electron distribution in each region of the crystal is then perturbed because electrons move from filled states to adjacent empty states.

The electrical conductivity of a material is determined by the mobile carriers and is proportional to the number density of charge carriers in the system, denoted by n, and their mobility, μ, according to

$$\sigma \simeq ne\mu\,. \tag{5.4}$$

Only in metallic systems the number density of charge carriers is large enough to make the electrical conductivity sufficiently large. The precise conditions under which one substance has a large conductivity and another substance has low conductivity are determined by the microscopic physical properties of the system such as energy band structure, carrier effective mass, carrier mobility, lattice properties and the presence of impurities and imperfections.

Theoretical considerations of the electric conductivity were started by Drude within the classical picture about 100 years ago.[13,133] He put forward a free-electron model that assumes a relaxation of the independent charge carriers due to driving forces (frictional force and the electric field). The current density was written as

$$J = \frac{ne^2}{m} E\tau\,. \tag{5.5}$$

Here τ is the average time between collisions, E is the electric field and m and e are the mass and the charge of the electron, respectively. The electric conductivity in the Drude model[13] is given by

$$\sigma = \frac{ne^2\tau}{m}\,. \tag{5.6}$$

The time τ is called the mean lifetime or electron relaxation time. Then the Ohm law can be expressed as the linear relation between current density **J** and electric field **E**

$$\mathbf{J} = \sigma \mathbf{E} \,. \tag{5.7}$$

The electrical resistivity R of the material is equal to

$$R = \frac{E}{J} \,. \tag{5.8}$$

The free-electron model of Drude is the limiting case of the total delocalization of the outer atomic electrons in a metal. The former valence electrons became conduction electrons. They move independently through the entire body of the metal; the ion cores are totaly ignored. The theory of Drude was refined by Lorentz. Drude–Lorentz theory assumed that the free conduction electrons formed an electron gas and were impeded in their motion through crystal by collisions with the ions of the lattice. In this approach, the number of free electrons n and the collision time τ, related to the mean free path $r_l = 2\tau v$ and the mean velocity v, are still adjustable parameters.

Contrary to this, in the Bloch model for the electronic structure of a crystal, though each valence electron is treated as an independent particle, it is recognized that the presence of the ion cores and the other valence electrons modifies the motion of that valence electron.

In spite of its simplicity, Drude model contains some delicate points. Each electron changes its direction of propagation with an average period of 2τ. This change of propagation direction is mainly due to a collision of an electron with an impurity or defect and the interaction of electron with a lattice vibration. In an essence, τ is the average time of the electron motion to the first collision. Moreover, it is assumed that the electron forgets its history on each collision, etc. To clarify these points let us consider the notion of the electron drift velocity. The electrons which contribute to the conductivity have large velocities, that is large compared to the drift velocity which is due to the electric field, because they are at the top of the Fermi surface and very energetic. The drift velocity of the carriers v_d is intimately connected with the collision time τ

$$v_d = \alpha\tau \,,$$

where $\boldsymbol{\alpha}$ is a constant acceleration between collision of the charge carriers. In general, the mean drift velocity of a particle over N free path is

$$v_d \sim \frac{1}{2}\alpha[\tau + (\Delta t)^2/\tau] \,.$$

This expression shows that the drift velocity depends not only on the average value τ but also on the standard deviation (Δt) of the distribution of times between collisions. An analysis shows that the times between collisions have an exponential probability distribution. For such a distribution, $\Delta t = \tau$ and one obtains $v_d = \alpha\tau$

and $J = ne^2/mE\tau$. Assuming that the time between collisions always has the same value τ, we find that $(\Delta t) = 0$ and $v_d = (1/2)\alpha\tau$ and $J = ne^2/2mE\tau$.

Equations (5.7) and (5.8) are the most fundamental formulas in the physics of electron conduction. Note that resistivity is not zero even at absolute zero, but is equal to the so-called "residual resistivity". For most typical cases it is reasonable to assume that scattering by impurities or defects and scattering by lattice vibrations are independent events. As a result, the relation (5.6) will take place. There is a huge variety (and irregularity) of the resistivity values for the elements, not mentioning the huge variety of substances and materials.[134–137]

In a metal with spherical Fermi surface in the presence of an electric field $\mathbf{E}$, the Fermi surface would affect a $\Delta\mathbf{k}$ displacement, $\Delta\mathbf{k} = \mathbf{k} - \mathbf{k}_0$. The simplest approximation is to suppose a rigid displacement of the Fermi sphere with a single relaxation time τ,

$$\hbar\frac{d\mathbf{k}}{dt} + \hbar\frac{(\mathbf{k} - \mathbf{k}_0)}{\tau} = e\mathbf{E}\,. \tag{5.9}$$

Thus we will have at equilibrium

$$\Delta\mathbf{k} = \frac{e\tau}{\hbar}\mathbf{E}\,. \tag{5.10}$$

The corresponding current density will take the form

$$\mathbf{J} = \frac{2}{(2\pi)^3}\int_{\Omega_k} e\mathbf{v}d\Omega_k = \frac{2}{(2\pi)^3}\int_{S_k} e\mathbf{v}\Delta\mathbf{k}\delta\mathbf{S}_{k_0}\,. \tag{5.11}$$

We get from Eq. (5.7)

$$\sigma = \frac{2}{(2\pi)^3}\frac{e^2\tau}{\hbar}\int_{S_k}\mathbf{v}d\mathbf{S}_{k_0}\,. \tag{5.12}$$

Let us consider briefly the frequency dependence of σ. Consider a gas of noninteracting electrons of number density n and collision time τ. At low frequencies, collisions occur so frequently that the charge carriers are moving as if within a viscous medium, whereas at high frequencies the charge carriers behave as if they were free. These two frequency regimes are well-known in the transverse electromagnetic response of metals.[1,2,9,11,13,18,21] The electromagnetic energy given to the electrons is lost in collisions with the lattice, which is the "viscous medium". The relevant frequencies in this case satisfy the condition $\omega\tau \ll 1$. Thus, in a phenomenological description,[138] one should introduce a conductivity σ and viscosity η by

$$\sigma = \frac{e^2\bar{\tau}_c n}{m}\,, \quad \eta = \frac{1}{2}m\overline{v^2}n\bar{\tau}_c\,. \tag{5.13}$$

On the other hand, for $\omega\tau \gg 1$ viscous effects are negligible, and the electrons behave as the nearly free particles. For optical frequencies they can move quickly enough to screen out the applied field. Thus, two different physical mechanisms are suitable in the different regimes defined by $\omega\tau \ll 1$ and $\omega\tau \gg 1$.

In a metal impurity atoms and phonons determine the scattering processes of the conduction electrons. The electrical force on the electrons is eE. The "viscous" drag force is given by $-m\mathbf{v}/\tau$. Then one can write the equation

$$m\dot{\mathbf{v}} = eE - \frac{m\mathbf{v}}{\tau}\,. \tag{5.14}$$

For $E \sim \exp(-i\omega t)$, the oscillating component of the current is given by

$$J(\omega) = ne\mathbf{v}(\omega) = \sigma(\omega)E(\omega)\,, \tag{5.15}$$

where

$$\sigma(\omega) = \frac{\sigma_0}{1 - i\omega\tau}\,, \quad \sigma_0 = \frac{e^2 n\tau}{m}\,. \tag{5.16}$$

For low frequencies we may approximate Eq. (5.14) as $\mathbf{v} \sim (e\tau/m)E$. For high frequencies we may neglect the collision term, so $\mathbf{v} \sim (e/m)E$. Thus the behavior of the conductivity as a function of frequency can be described on the basis of the formula Eq. (5.16).

Let us remark on a residual resistivity, i.e., the resistivity at absolute zero. Since real crystals always contain impurities and defects the resistivity is not equal zero even at absolute zero. If one assume that the scattering of a wave caused by impurities (or defects) and by lattice vibrations are independent events, then the total probability for scattering will be the sum of the two individual probabilities. The scattering probability is proportional to $1/\tau$, where τ is the mean lifetime or relaxation time of the electron motion. Denoting by $1/\tau_1$, the scattering probability due to impurities and defects and by $1/\tau_2$ the scattering probability due to lattice vibrations, we obtain for total probability the equality

$$1/\tau = 1/\tau_1 + 1/\tau_2\,; \quad 1/\sigma = 1/\sigma_1 + 1/\sigma_2\,. \tag{5.17}$$

This relation is called Matthiessen rule. In practice, this relation is not fulfilled well (see Refs. 139 and 140). The main reason for the violation of the Matthiessen rule are the interference effects between phonon and impurity contributions to the resistivity. References 139 and 140 give a comprehensive review of the subject of deviation from Matthiessen rule and detailed critical evaluation of both theory and experimental data.

5.3. *The low- and high-temperature dependence of conductivity*

One of the most informative and fundamental properties of a metal is the behavior of its electrical resistivity as a function of temperature. The temperature dependence of the resistivity is a good indicator of important scattering mechanisms for the conduction electrons. It can also suggest in a general way what the solid state electronic structure is like. There are two limiting cases, namely, the low-temperature dependence of the resistivity for the case when $T \leq \theta_D$, where θ_D is effective Debye temperature, and the high-temperature dependence of the resistivity, when $T \geq \theta_D$.

The electrical resistivity of metals is due to two mechanisms, namely, (i) scattering of electrons on impurities (static imperfections in the lattice), and (ii) scattering of electrons by phonons. Simplified treatment assumes that one scattering process is not influenced by the other (Matthiessen rule). The first process is usually temperature independent. For a typical metal, the electrical resistivity $R(T)$, as a function of the absolute temperature T, can be written as

$$R(T) = R_0 + R_i(T)\,, \tag{5.18}$$

where R_0 is the residual electrical resistivity independent of T, and $R_i(T)$ is the temperature-dependent intrinsic resistivity. The quantity R_0 is due to the scattering of electrons from chemical and structural imperfections. The term $R_i(T)$ is assumed to result from the interaction of electrons with other degrees of freedom of a crystal. In general, for the temperature dependence of the resistivity, three scattering mechanisms are essential: (i) electron–phonon scattering, (ii) electron-magnon scattering and (iii) electron–electron scattering. The first one gives T^5 or T^3 dependence at low temperatures.[2] The second one, the magnon scattering, is essential for the transition metals because some of them show ferromagnetic and antiferromagnetic properties.[11] This mechanism can give different temperature dependence values due to the complicated (anisotropic) dispersion of the magnons in various structures. The third mechanism, the electron–electron scattering is responsible for the $R \sim T^2$ dependence of resistivity.

Usually, the temperature-dependent electrical resistivity is tried to fit to an expression of the form

$$R(T) = R_0 + R_i(T) = R_0 + AT^5 + BT^2 + (CT^3) + \cdots \tag{5.19}$$

This dependence corresponds to Matthiessen rule, where the different terms are produced by different scattering mechanisms. The early approach for studying of the temperature variation of the conductivity[1,2,27] was carried out by Sommerfeld, Bloch and Houston. Houston explained the temperature variation of conductivity applying the wave mechanics and assuming that the wavelengths of the electrons were in most cases long compared with the interatomic distance. He then solved the Boltzmann equation, using for the collision term an expression taken from the work of Debye and Waller on the thermal scattering of X-rays. He obtained an expression for the conductivity as a function of a mean free path, which can be determined in terms of the scattering of the electrons by the thermal vibrations of the lattice. Houston found a resistance proportional to the temperature at high temperatures and to the square of temperature at low temperatures. The model used by Houston for the electrons in a metal was that of Sommerfeld — an ideal gas in a structureless potential well. Bloch improved this approach by taking the periodic structure of the lattice into account. For the resistance law at low temperatures both Houston and Bloch results were incorrect. Houston realized that the various treatments of the mean free path would give different variations of resistance with temperature. In his later work,[141] he also realized that the Debye theory of scattering was inadequate at low temperatures. He applied the Brillouin theory of scattering and arrived at T^5 law for the resistivity at low temperatures and T at high temperatures. Later on, it was shown by many authors[2] that the distribution function obtained in the steady-state under the action of an electric field and the phonon collisions does indeed lead to $R \sim T^5$. The calculations of the electron–phonon scattering contribution to the resistivity by Bloch[142] and Gruneisen[143] lead to the following expression

$$R(T) \sim \frac{T^5}{\theta^6} \int_0^{\theta/T} dz \frac{z^5}{(e^z - 1)(1 - e^{-z})} \,, \tag{5.20}$$

which is known as the Bloch–Gruneisen law.

Huge effort has been devoted to the theory of transport processes in simple metals,[11,144,145] such as the alkali metals. The Fermi surface of these metals is nearly spherical, so band structure effects can be either neglected or treated in some simple approximation. The effect of the electron–electron interaction in these systems is not very substantial. Most of the scattering is due to impurities and phonons. It is expected that the characteristic T^2 dependence of electron–electron interaction effects can only be seen at very low temperatures T, where phonon scattering contributes a negligible T^5 term. In the nonsimple metallic conductors, and in transition metals, the Fermi surfaces are usually far from being isotropic. Moreover, it can be viewed as the two-component systems[146] where one carrier is an electron and the other is an inequivalent electron (as in s–d scattering) or a hole. It was shown that anisotropy such as that arising from a nonspherical Fermi surface or from anisotropic scattering can yield a T^2 term in the resistivity at low temperatures, due to the deviations from Matthiessen rule. This term disappears at sufficiently high T. The electron–electron *Umklapp* scattering contributes a T^2 term even at high T. It was conjectured (see Ref. 147) that the effective electron–electron interaction due to the exchange of phonons should contribute to the electrical resistivity in exactly the same way as the direct Coulomb interaction, namely, giving rise to a T^2 term in the resistivity at low temperatures. The estimations of this contribution show[148] that it can alter substantially the coefficient of the T^2 term in the resistivity of simple and polyvalent metals. The role of electron–electron scattering in transition metals was discussed in Refs. 149–151. A calculation of the electrical and thermal resistivity of Nb and Pd due to electron–phonon scattering was discussed in Ref. 152. A detailed investigation[153] of the temperature dependence of the resistivity of Nb and Pd showed that a simple power law fit cannot reconcile the experimentally observed behavior of the transition metals. Matthiessen rule breaks down and simple Bloch–Gruneisen theory is inadequate to account for the experimental data. In particular, in Ref. 153 it has been shown that the resistivity of Pd can be expressed by a T^2 function where, on the other hand, the temperature dependence of the resistivity of Nb should be represented by a function of T more complicated than the T^3. It seems to be plausible that the low-temperature behavior of the resistivity of transition metals may be described by a rational function of $(AT^5 + BT^2)$. This conjecture will be justified in Sec. 11.

For real metallic systems, the precise measurements show a quite complicated picture in which the term $R_i(T)$ will not necessarily be proportional to T^5 for every metal (for detailed review see Refs. 11, 144 and 145). The purity of the samples and size-effect contributions and other experimental limitations can lead to the deviations from the T^5 law. There are many other reasons for such a deviation. First, the electronic structures of various pure metals differ very considerably. For example, the Fermi surface of sodium is nearly close to the spherical one, but those of transition and rare-earth metals are much more complicated, having groups of electrons of very different velocities. The phonon spectra are also different for different metals. It is possible to formulate that the T^5 law can be justified for a metal of a spherical Fermi surface and for a Debye phonon spectrum. Moreover, the additional assumptions are an assumption that the electron and phonon systems are separately in equilibrium so that only one phonon is annihilated or created in an electron–phonon collision, that the *Umklapp* processes can be neglected, and an assumption of a constant volume at any temperature. Whenever these conditions are not satisfied in principle, deviations from T^5 law can be expected. This takes place, for example, in transition metals as a result of the s–d transitions[1,53] due to the scattering of s-electrons by phonons. This process can be approximately described as being proportional to T^γ with γ somewhere between 5 and 3. The s–d model of electronic transport in transition metals was developed by Mott.[1,53,154] In this model, the motion of the electrons is assumed to take place in the nearly free-electron like s-band conduction states. These electrons are then assumed to be scattered into the localized d states. Owing to the large differences in the effective masses of the s- and d-bands, large resistivity result.

In Ref. 155, the temperature of the normal-state electrical resistivity of very pure niobium was reported. The measurements were carried out in the temperature range from the superconducting transition ($T_c = 9.25$ K) to 300 K in zero magnetic field. The resistance-versus-temperature data were analyzed in terms of the possible scattering mechanisms likely to occur in niobium. To fit the data, a single-band model was assumed. The best fit can be expressed as

$$\begin{aligned} R(T) = {} & (4.98 \pm 0.7)10^{-5} + (0.077 \pm 3.0)10^{-7}T^2 \\ & + (3.10 \pm 0.23)10^{-7}[T^3 J_3(\theta_D/T)/7.212] \\ & + (1.84 \pm 0.26)10^{-10}[T^5 J_5(\theta_D/T)/124.4] \,, \end{aligned} \tag{5.21}$$

where J_3 and J_5 are integrals occurring in the Wilson and Bloch theories[2] and the best value for θ_D, the effective Debye temperature, is (270 ± 10) K. Over most of the temperature range below 300 K, the T^3 Wilson term dominates. Thus it was concluded that interband scattering is quite important in niobium. Because of the large magnitude of interband scattering, it was difficult to determine the precise amount of T^2 dependence in the resistivity. Measurements of the electrical resistivity of the high purity specimens of niobium were carried out in Refs. 156–159. It was shown that Mott theory is obeyed at high-temperature in niobium. In particular, the resistivity curve reflects the variation of the density of states at the Fermi surface when the temperature is raised, thus demonstrating the predominance of s–d transitions. In addition, it was found impossible to fit a Bloch–Gruneisen or Wilson relation to the experimental curve. Several arguments were presented to indicate that even a rough approximation of the Debye temperature has no physical significance and that it is necessary to take the *Umklapp* processes into account. Measurements of low-temperature electrical and thermal resistivity of tungsten[160,161] and vanadium[162] showed the effects of the electron–electron scattering between different branches of the Fermi surface in tungsten and vanadium, thus concluding that electron–electron scattering does contribute measurable to electrical resistivity of these substances at low temperature.

In transition metal compounds, e.g., MnP, the electron–electron scattering is attributed[163] to be dominant at low temperatures, and furthermore the $3d$ electrons are thought to carry electric current. It is remarkable that the coefficient of the T^2 resistivity is very large, about 100 times those of Ni and Pd in which s-electrons coexist with d-electrons and electric current is mostly carried by the s-electrons. This fact suggests strongly that in MnP s-electrons do not exist at the Fermi level and current is carried by the $3d$ electrons. This is consistent with the picture[164] that in transition metal compounds the s-electrons are shifted up by the effect of antibonding with the valence electrons due to a larger mixing matrix, compared with the $3d$ electrons, caused by their larger orbital extension.

It should be noted that the temperature coefficients of resistance can be positive and negative in different materials. A semiconductor material exhibits the temperature dependence of the resistivity quite different than in metal. A qualitative explanation of this different behavior follows from considering the number of free charge carriers per unit volume, n, and their mobility, μ. In metals, n is essentially constant, but μ decreases with increasing temperature, owing to increased lattice vibrations which lead to a reduction in the mean free path of the charge carriers. This decrease in mobility also occurs in semiconductors, but the effect is usually masked by a rapid increase in n as more charge carriers are set free and made available for conduction. Thus, intrinsic semiconductors exhibit a negative temperature coefficient of resistivity. The situation is different in the case of extrinsic semiconductors in which ionization of impurities in the crystal lattice is responsible for the increase in n. In these, there may exist a range of temperatures over which essentially all the impurities are ionized, that is, a range over which n remains approximately constant. The change in resistivity is than almost entirely due to the change in μ, leading to a positive temperature coefficient.

It is believed that the electrical resistivity of a solid at high temperatures is primarily due to the scattering of electrons by phonons and by impurities.[2] It is usually assumed, in accordance with Matthiessen rule, that the effect of these two contributions to the resistance are simply additive. At high temperature (not lower than Debye temperature) lattice vibrations can be well represented by the Einstein model. In this case, $1/\tau_2 \sim T$, so that $1/\sigma_2 \sim T$. If the properties and concentration of the lattice defects are independent of temperature, then $1/\sigma_1$ is also independent of temperature and we obtain

$$1/\sigma \simeq a + bT \,, \tag{5.22}$$

where a and b are constants. However, this additivity is true only if the effect of both impurity and phonon scattering can be represented by means of single relaxation times whose ratio is independent of velocity.[165] It was shown[165] that the addition of impurities will always decrease the conductivity. Investigations of the deviations from Matthiessen rule at high temperatures in relation to the electron–phonon interaction were carried out in Refs. 156–159. It was shown,[159] in particular, that changes in the electron–phonon interaction parameter λ, due to dilute impurities were caused predominantly by interference between electron–phonon and electron impurity scattering.

The electron band structures of transition metals are extremely complicated and make calculations of the electrical resistivity due to structural disorder and phonon scattering very difficult. In addition the nature of the electron–phonon matrix elements is not well understood.[166] The analysis of the matrix elements for scattering between states was performed in Ref. 166. It was concluded that even in those metals where a fairly spherical Fermi surface exists, it is more appropriate to think of the electrons as tightly bound in character rather than behaving like free electrons. In addition, the "single site" approximations are not likely to be appropriate for the calculation of the transport properties of structurally disordered transition metals.

5.4. *Conductivity of alloys*

The theory of metallic conduction can be applied for explaining the conductivity of alloys.[167–172] According to the Bloch–Gruneisen theory, the contribution of the electron–phonon interaction to the dc electrical resistivity of a metal at high temperatures is essentially governed by two factors: the absolute square of the electron–phonon coupling constant and the thermally excited mean square lattice displacement. Since the thermally excited mean lattice displacement is proportional to the number of phonons, the high-temperature resistivity R is linearly proportional to the absolute temperature T, and the slope dR/dT reflects the magnitude of the electron–phonon coupling constant. However, in many high resistivity metallic alloys, the resistivity variation dR/dT is found to be far smaller than that of the constituent materials. In some cases, dR/dT is not even always positive. There are two types of alloys, one of which the atoms of the different metals are distributed at random over the lattice points, another in which the atoms of the components are regularly arranged. Anomalous behavior in electrical resistivity was observed in many amorphous and disordered substances.[168,173] At low temperatures, the resistivity increases in T^2 instead of the usual T^5 dependence. Since T^2 dependence is usually observed in alloys which include a large fraction of transition metals, it has been considered to be due to spins. In some metals, T^2 dependence might be caused by spins. However, it can be caused by disorder itself. The calculation of transport coefficients in disordered transition metal alloys becomes a complicated task if the random fluctuations of the potential are too large. It can be shown that strong potential fluctuations force the electrons into localized states. Another anomalous behavior occurs in highly resistive metallic systems[168,173] which is characterized by small temperature coefficient of the electrical resistivity, or by even negative temperature coefficient.

According to Matthiessen rule,[139,140] the electrical resistance of a dilute alloy is separable into a temperature-dependent part, which is characteristic of the pure metal, and a residual part due to impurities. The variation with temperature of the impurity resistance was calculated by Taylor.[174] The total resistance is composed of two parts, one due to elastic scattering processes, the other to inelastic ones. At the zero temperature, the resistance is entirely due to elastic scattering and is smaller by an amount γ_0 than the resistance that would be found if the impurity atom were infinitely massive. The factor γ_0 is typically of the order of 10^{-2}. As the temperature is raised, the amount of inelastic scattering increases, while the amount of elastic scattering decreases. However, as this happens the ordinary lattice resistance, which varies as T^5, starts to become appreciable. For a highly impure specimen for which the lattice resistance at room temperature, R_θ, is equal to the residual resistance, R_0, the total resistance at low temperatures will have the form

$$R(T) \approx 10^{-2}\left(\frac{T}{\theta}\right)^2 + 500\left(\frac{T}{\theta}\right)^5 + R_0\,. \tag{5.23}$$

The first term arises from incoherent scattering and the second from coherent scattering, according to the usual Bloch–Gruneisen theory. It is possible to see from this expression that T^2 term would be hidden by the lattice resistance except at temperatures below $\theta/40$. This represents a resistance change of less than $10^{-5}R_0$, and is not generally really observable.

In disordered metals, the Debye–Waller factor in electron scattering by phonons may be an origin for negative temperature coefficient of the resistivity. The residual resistivity may decreases as T^2 with increasing temperature because of the influence of the Debye–Waller factor. But resulting resistivity increases as T^2 with increasing temperature at low temperatures even if the Debye–Waller factor is taken into account. It is worthy to note that the deviation from Matthiessen rule in electrical resistivity is large in the transition metal alloys[175,176] and dilute alloys.[177,178] In certain cases the temperature dependence of the electrical resistivity of transition metal alloys at high temperatures can be connected with change electronic density of states.[179] The electronic density of states for V–Cr, Nb–Mo and Ta–W alloys have been calculated in the coherent potential approximation. From these calculated results, the temperature dependence of the electrical resistivity R at high temperature have been estimated. It was shown that the concentration variation of the temperature dependence in R/T is strongly dependent on the shape of the density of states near the Fermi level.

Many amorphous metals and disordered alloys exhibit a constant or negative temperature coefficient of the electrical resistivity[168,173] in contrast to the positive temperature coefficient of the electrical resistivity of normal metals. Any theoretical models of this phenomenon must include both the scattering (or collision) caused by the topological or compositional disorder and the modifications to this collision induced by the temperature or by electron–phonon scattering. If one assumes that the contributions to the resistivity from scattering mechanisms other than the electron–phonon interaction are either independent of T, like impurity scattering, or are saturated at high T, like magnetic scattering, the correlation between the quenched temperature dependence and high resistivity leads one to ask whether the electron–phonon coupling constant is affected by the collisions of the electrons.

The effect of collisions on charge redistributions is the principal contributor to the electron–phonon interaction in metals. It is studied as a mechanism which could explain the observed lack of temperature dependence of the electrical resistivity of many concentrated alloys. The collision time-dependent free electron deformation potential can be derived from a self-consistent linearized Boltzmann equation. The results indicates that the collision effects are not very important for real systems. It can be understood assuming that the charge redistribution produces only a negligible correction to the transverse phonon–electron interaction. In addition, although the charge shift is the dominant contribution to the longitudinal phonon–electron interaction, this deformation potential is not affected by collisions until the root mean square electron diffusion distance in a phonon period is less than the Thomas–Fermi screening length. This longitudinal phonon–electron interaction reduction requires collision times of the order of 10^{-19} s in typical metals before it is effective. Thus, it is highly probable that it is never important in real metals. Hence, this collision effect does not account for the observed, quenched temperature dependence of the resistivity of these alloys. However, these circumstances suggest that the validity of the adiabatic approximation, i.e., the Born–Oppenheimer approximation, should be relaxed far beyond the previously suggested criteria. All these factors make the proper microscopic formulation of the theory of the electron–phonon interaction in strongly disordered alloys a very complicated problem. A consistent microscopic theory of the electron–phonon interaction in substitutionally disordered crystalline transition metal alloys was formulated by Wysokinski and Kuzemsky[180] within the MTBA. This approach combines the Barisic, Labbe and Friedel model[125] with the more complex details of the CPA (coherent potential approximation).

The low-temperature resistivity of many disordered paramagnetic materials often shows a $T^{3/2}$ rather than a T^2 dependence due to spin-fluctuation-scattering resistivity. The coefficient of the $T^{3/2}$ term often correlates with the magnitude of the residual resistivity as the amount of disorder is varied. A model calculation that exhibits such behavior were carried out in Ref. 181 In the absence of disorder, the spin-fluctuations drag suppresses the spin-fluctuation T^2 term in the resistivity. Disorder produces a finite residual resistivity and also produces a finite spin-fluctuation-scattering rate.

5.5. *Magnetoresistance and the Hall effect*

The Hall effect and the magnetoresistance[182–188] are the manifestations of the Lorentz force on a subsystem of charge carries in a conductor constrained to move in a given direction and subjected to a transverse magnetic field. Let us consider a confined stream of a carriers, each having a charge e and a steady-state velocity v_x due to the applied electric field E_x. A magnetic field H in the z-direction produces a force F_y which has the following form

$$\mathbf{F} = e\left(\mathbf{E} + \frac{1}{c}\mathbf{v} \times \mathbf{H}\right) . \tag{5.24}$$

The boundary conditions lead to the equalities

$$F_y = 0 = E_y - \frac{1}{c} v_x H_z \,. \tag{5.25}$$

The transverse field E_y is termed the Hall field $E_y \equiv E^H$ and is given by

$$E^H = \frac{1}{c} v_x H_z = \frac{J_x H_z}{nec} \,; \quad J_x = nev_x \,, \tag{5.26}$$

where J_x is the current density and n is the charge carrier concentration. The Hall field can be related to the current density by means of the Hall coefficient R_H

$$E^H = R_H J_x H_z \,; \quad R_H = \frac{1}{nec} \,. \tag{5.27}$$

The essence of the Hall effect is that Hall constant is inversely proportional to the charge carrier density n, and that is negative for electron conduction and positive for hole conduction. A useful notion is the so-called Hall angle which is defined by the relation

$$\theta = \tan^{-1} \frac{E_y}{E_x} \,. \tag{5.28}$$

Thus, the Hall effect may be regarded as the rotation of the electric field vector in the sample as a result of the applied magnetic field. The Hall effect is an effective practical tool for studying the electronic characteristics of solids. The above consideration helps to understand how thermomagnetic effects[2,6,31] can arise in the framework of simple free-electron model. The Lorentz force acts as a velocity selector. In other words, due to this force, the slow electrons will be deflected less than the more energetic ones. This effect will lead to a temperature gradient in the transverse direction. This temperature difference will result in a transverse potential difference due to the Seebeck coefficient of the material. This phenomenon is called the Nernst–Ettingshausen effect.[2,6]

It should be noted that the simple expression for the Hall coefficient R_H is the starting point only for the studies of the Hall effect in metals and alloys.[182,183] It implies R_H is temperature independent and that E^H varies linearly with applied field strength. Experimentally, the dependence $R_H = 1/nec$ does not fit well the situation in any solid metal. Thus, there is a necessity to explain these discrepancies. One way is to consider an effective carrier density $n^*(n)$ which depends on n, where n is now the mean density of electrons calculated from the valency. This interrelation is much more complicated for the alloys where $n^*(n)$ is the function of the concentration of solute too. It was shown that the high-field Hall effect reflects global properties of the Fermi surface such as its connectivity, the volume of occupied phase space, etc. The low-field Hall effect depends instead on microscopic details of the dominant scattering process. A quantum-mechanical theory of transport of charge for an electron gas in a magnetic field which takes account of the quantization of the electron orbits has been given by Argyres.[185]

Magnetoresistance[10,187,189–191] is an important galvanomagnetic effect which is observed in a wide range of substances and under a variety of experimental conditions.[192–194] The transverse magnetoresistance is defined by

$$\varrho_{MR}(H) = \frac{R(H) - R}{R} \equiv \frac{\Delta R}{R}\,, \tag{5.29}$$

where $R(H)$ is the electrical resistivity measured in the direction perpendicular to the magnetic field H, and R is the resistivity corresponding to the zero magnetic field. The zero-field resistivity R is the inverse of the zero-field conductivity and is given approximately by

$$R \sim \frac{m^* \langle v \rangle}{nel}\,, \tag{5.30}$$

according to the simple kinetic theory applied to a single carrier system. Here e, m^*, n, $\langle v \rangle$ and l are, respectively, charge, effective mass, density, average speed, and mean free path of the carrier. In this simplified picture, the four characteristics, e, m^*, n, and $\langle v \rangle$, are unlikely to change substantially when a weak magnetic field is applied. The change in the mean free path l should then approximately determine the behavior of the magnetoresistance $\Delta R/R$ at low fields.

The magnetoresistance practically of all conducting pure single crystals has been experimentally found to be positive and a strong argument for this were given on the basis of nonequilibrium statistical mechanics.[10] In some substances, e.g., carbon, CdSe, Eu_2CuSi_3, etc., magnetoresistance is negative while in CdMnSe is positive and much stronger than in CdSe.[195–197] A qualitative interpretation of the magnetoresistance suggests that those physical processes which make the mean free path larger for greater values of H should contribute to the negative magnetoresistance. Magnetic scattering leads to negative magnetoresistance[198] characteristic for ferro- or paramagnetic case, which comes from the suppression of fluctuation of the localized spins by the magnetic field. A comprehensive derivation of the quantum transport equation for electric and magnetic fields was carried out by Mahan.[199]

More detailed discussion of the various aspects of theoretical calculation of the magnetoresistance in concrete substances are given in Refs. 188, 198, 200–202

5.6. *Thermal conduction in solids*

Electric and thermal conductivities are intimately connected since the thermal energy also is mainly transported by the conduction electrons. The thermal conductivity[4,203] of a variety of substances, metals and nonmetals, depends on temperature region and varies with temperature substantially.[204] Despite a rough similarity in the form of the curves for metallic and nonmetallic materials, there is a fundamental difference in the mechanism whereby heat is transported in these two types of materials. In metals,[4,205] heat is conducted by electrons; in nonmetals,[4,206] it is conducted through coupled vibrations of the atoms. The empirical data[204] show that the better the electrical conduction of a metal, the better its thermal conduction. Let us consider a sample with a temperature gradient dT/dx along the x-direction. Suppose that the electron located at each point x has thermal energy $E(T)$ corresponding to the temperature T at the point x. It is possible to estimate the net thermal energy carried by each electron as

$$E(T) - E\left(T + \frac{dT}{dx}\tau v \cos\theta\right) = -\frac{dE(T)}{dT}\frac{dT}{dx}\tau v \cos\theta\,. \tag{5.31}$$

Here we denote by θ the angle between the propagation direction of an electron and the x-direction and by v the average speed of the electron. Then the average distance travelled in the x-direction by an electron until it scatters is $\tau v \cos\theta$. The thermal current density J_q can be estimated as

$$J_q = -n\frac{dE(T)}{dT}\frac{dT}{dx}\tau v^2 \langle\cos^2\theta\rangle\,, \tag{5.32}$$

where n is the number of electrons per unit volume. If the propagation direction of the electron is random, then $\langle\cos^2\theta\rangle = 1/3$ and the thermal current density is given by

$$J_q = -\frac{1}{3}n\frac{dE(T)}{dT}\tau v^2\frac{dT}{dx}\,. \tag{5.33}$$

Here $ndE(T)/dT$ is the electronic heat capacity C_e per unit volume. We obtain for the thermal conductivity κ the following expression

$$\kappa = \frac{1}{3}C_e\tau v^2\,; \quad Q = -\kappa\frac{dT}{dx}\,. \tag{5.34}$$

The estimation of κ for a degenerate Fermi distribution can be given by

$$\kappa = \frac{1}{3}\frac{\pi^2 k_B^2 T}{2\zeta_0}n\frac{6\zeta_0}{5m}\tau = \frac{\pi^2 k_B^2 T}{5m}n\,, \tag{5.35}$$

where $1/2mv^2 = 3/5\zeta_0$ and k_B is the Boltzmann constant. It is possible to eliminate $n\tau$ with the aid of equality $\tau = m\sigma/ne^2$. Thus we obtain[17]

$$\frac{\kappa}{\sigma} \cong \frac{\pi^2}{5}\frac{k_B^2}{e^2}T\,. \tag{5.36}$$

This relation is called as the Wiedemann–Franz law. The more precise calculation gives a more accurate factor value for the quantity $\pi^2/5$ as $\pi^2/3$. The most essential conclusion to be drawn from the Wiedemann–Franz law is that κ/σ is proportional to T and the proportionality constant is independent of the type of metal. In other words, a metal having high electrical conductivity has a high thermal conductivity at a given temperature. The coefficient $\kappa/\sigma T$ is called the Lorentz number. At sufficiently high temperatures, where σ is proportional to $1/T$, κ is independent of temperature. Qualitatively, the Wiedemann–Franz law is based upon the fact that the heat and electrical transport both involve the free-electrons in the metal. The thermal conductivity increases with the average particle velocity since that increases the forward transport of energy. However, the electrical conductivity decreases with particle velocity increases because the collisions divert the electrons from forward transport of charge. This means that the ratio of thermal to electrical conductivity depends upon the average velocity squared, which is proportional to the kinetic temperature.

Thus, there are relationships between the transport coefficients of a metal in a strong magnetic field and a very low temperatures. Examples of such relations are the Wiedemann–Franz law for the heat conductivity κ, which we rewrite in a more general form

$$\kappa = LT\sigma \,, \tag{5.37}$$

and the Mott rule[207] for the thermopower S

$$S = eLT\sigma^{-1}\frac{d\sigma}{d\mu} \,. \tag{5.38}$$

Here T is the temperature, μ denotes the chemical potential. The Lorentz number $L = 1/3(\pi k_B/e)^2$, where k_B is the Boltzmann constant, is universal for all metals. Useful analysis of the Wiedemann–Franz law and the Mott rule was carried out by Nagaev.[208]

6. Linear Macroscopic Transport Equations

We give here a brief refresher of the standard formulation of the macroscopic transport equations from the most general point of view.[209] One of the main problems of electron transport theory is the finding of the perturbed electron distribution which determines the magnitudes of the macroscopic current densities. Under the standard conditions, it is reasonable to assume that the gradients of the electrochemical potential and the temperature are both very small. The macroscopic current densities are then linearly related to those gradients and the ultimate objective of the theory of transport processes in solids (see Table 4). Let η and T denote, respectively, the electrochemical potential and temperature of the electrons. We suppose that both the quantities vary from point to point with small gradients $\nabla\eta$ and ∇T. Then, at each point in the crystal, electric and heat current densities $\mathbf{J}_e$ and $\mathbf{J}_q$

Table 4. Fluxes and generalized forces.

Process	Flux	Generalized force	Tensor character
Electrical conduction	$\mathbf{J}_e$	$\nabla\phi$	Vector
Heat conduction	$\mathbf{J}_q$	$\nabla(1/T)$	Vector
Diffusion	Diffusion flux $\mathbf{J}_p$	$-(1/T)[\nabla n]$	Vector
Viscous flow	Pressure tensor $\mathbf{P}$	$-(1/T)\nabla\mathbf{u}$	Second-rank tensor
Chemical reaction	Reaction rate W_r	Affinity a_r/T	Scalar

will exist which are linearly related to the electromotive force $\boldsymbol{\mathcal{E}} = 1/e\nabla\eta$ and ∇T by the basic transport equations

$$\mathbf{J}_e = L_{11}\boldsymbol{\mathcal{E}} + L_{12}\nabla T\,, \tag{6.1}$$

$$\mathbf{J}_q = L_{21}\boldsymbol{\mathcal{E}} + L_{22}\nabla T\,. \tag{6.2}$$

The coefficients L_{11}, L_{12}, L_{21} and L_{22} in these equations are the transport coefficients which describe irreversible processes in linear approximation. We note that in a homogeneous isothermal crystal, $\boldsymbol{\mathcal{E}}$ is equal to the applied electric field $\mathbf{E}$. The basic transport equations in the form of Eqs. (6.1) and (6.2) describe responses $\mathbf{J}_e$ and $\mathbf{J}_q$ under the influence of $\boldsymbol{\mathcal{E}}$ and ∇T. The coefficient $L_{11} = \sigma$ is the electrical conductivity. The other three coefficients, L_{12}, L_{21} and L_{22} have no generally accepted nomenclature because these quantities are hardly ever measured directly. From the experimental point of view, it is usually more convenient to fix $\mathbf{J}_e$ and ∇T and then measure $\boldsymbol{\mathcal{E}}$ and $\mathbf{J}_q$. To fit the experimental situation, Eqs. (6.1) and (6.2) must be rewritten in the form

$$\boldsymbol{\mathcal{E}} = R\mathbf{J}_e + S\nabla T\,, \tag{6.3}$$

$$\mathbf{J}_q = \Pi\mathbf{J}_e - \kappa\nabla T\,, \tag{6.4}$$

where

$$R = \sigma^{-1}\,, \tag{6.5}$$

$$S = -\sigma^{-1}L_{12}\,, \tag{6.6}$$

$$\Pi = L_{21}\sigma^{-1}\,, \tag{6.7}$$

$$\kappa = L_{21}\sigma^{-1}L_{12} = L_{22}\,, \tag{6.8}$$

which are known, respectively, as the resistivity, thermoelectric power, Peltier coefficient and thermal conductivity. These are the quantities which are measured directly in experiments.

All the coefficients in the above equations are tensors of rank 2 and they depend on the magnetic induction field $\mathbf{B}$ applied to the crystal. By considering crystals with full cubic symmetry, when $\mathbf{B} = 0$, one reduces to a minimum the geometrical complications associated with the tensor character of the coefficients. In this case, all the transport coefficients must be invariant under all the operations in the point group $m3m$.[210] This high degree of symmetry implies that the coefficients must reduce to scalar multiples of the unit tensor and must therefore be replaced by scalars. When $\mathbf{B} \neq 0$ the general form of transport tensors is complicated even in cubic crystals.[31,210] In the case, when an expansion to second-order in $\mathbf{B}$ is sufficient, the conductivity tensor takes the form

$$\sigma_{\alpha\beta}(\mathbf{B}) = \sigma_{\alpha\beta}(0) + \sum_{\mu} \frac{\partial \sigma_{\alpha\beta}(0)}{\partial B_\mu} B_\mu + \frac{1}{2} \sum_{\mu\nu} \frac{\partial^2 \sigma_{\alpha\beta}(0)}{\partial B_\mu B_\nu} B_\mu B_\nu + \cdots \tag{6.9}$$

Here the $(\alpha\beta)$-th element of σ referred to the cubic axes $(0xyz)$. For the case when it is possible to confine ourselves by the proper rotations in $m3m$ only, we obtain that

$$\sigma_{\alpha\beta}(0) = \sigma_0 \delta_{\alpha\beta} \,, \tag{6.10}$$

where σ_0 is the scalar conductivity when $\mathbf{B} = 0$. We also find that

$$\frac{\partial \sigma_{\alpha\beta}(0)}{\partial B_\mu} = \varsigma \epsilon_{\alpha\beta\gamma} \,,$$

$$\frac{\partial^2 \sigma_{\alpha\beta}(0)}{\partial B_\mu B_\nu} = 2\xi \delta_{\alpha\beta} \delta_{\mu\nu} + \eta [\delta_{\alpha\mu} \delta_{\beta\nu} + \delta_{\alpha\nu} \delta_{\beta\mu}] + 2\zeta \delta_{\alpha\beta} \delta_{\alpha\mu} \delta_{\alpha\nu} \,,$$

where ς, ξ, η, ζ are all scalar and $\epsilon_{\alpha\beta\gamma}$ is the three-dimensional alternating symbol.[210] Thus, we obtain a relation between $\mathbf{j}$ and $\boldsymbol{\mathcal{E}}$ (with $\nabla T = 0$)

$$\mathbf{j} = \sigma_0 \boldsymbol{\mathcal{E}} + \varsigma \boldsymbol{\mathcal{E}} \times \mathbf{B} + \xi \mathbf{B}^2 \boldsymbol{\mathcal{E}} + \eta \mathbf{B}(\mathbf{B}\boldsymbol{\mathcal{E}}) + \zeta \Phi \boldsymbol{\mathcal{E}} \,, \tag{6.11}$$

where Φ is a diagonal tensor with $\Phi_{\alpha\alpha} = B_\alpha^2$ (see Refs. 12 and 14). The most interesting transport phenomena is the electrical conductivity under homogeneous isothermal conditions. In general, the calculation of the scalar transport coefficients σ_0, ς, ξ, η, ζ is complicated task. As was mentioned above, these coefficients are not usually measured directly. In practice, one measures the corresponding terms in the expression for $\boldsymbol{\mathcal{E}}$ in terms of $\mathbf{j}$ up to terms of second-order in $\mathbf{B}$. To show this clearly, let us iterate Eq. (6.11). We then find that

$$\boldsymbol{\mathcal{E}} = R_0 \mathbf{j} - R_H \mathbf{j} \times \mathbf{B} + R_0 (b \mathbf{B}^2 \mathbf{j} + c \mathbf{B}(\mathbf{B}\mathbf{j}) + d \boldsymbol{\Phi} \mathbf{j}) \,, \tag{6.12}$$

where

$$R_0 = \sigma_0^{-1} \,, \quad R_H = \sigma_0^{-2} \varsigma \,, \tag{6.13}$$

are, respectively, the low-field resistivity and Hall constant[10,183,184,187] and

$$b = -R_0 (\xi + R_0 \varsigma^2) \,; \quad c = -R_0 (\eta - R_0 \varsigma^2) \,; \quad d = -\varrho\zeta \tag{6.14}$$

are the magnetoresistance coefficients.[10] These are the quantities which are directly measured.

7. Statistical Mechanics and Transport Coefficients

The central problem of nonequilibrium statistical mechanics is to derive a set of equations which describes irreversible processes from the reversible equations of motion.[42–46,77,211–219] The consistent calculation of transport coefficients is of particular interest because one can get information on the microscopic structure of the condensed matter. There exist many theoretical methods for calculation of transport coefficients as a rule having a fairly restricted range of validity and applicability.[45,217–224] The most extensively developed theory of transport processes that is based on the Boltzmann equation.[44–46,222,225,226] However, this approach has strong restrictions and can reasonably be applied to a strongly rarefied gas of point particles. For systems in the state of statistical equilibrium, there is the Gibbs distribution by means of which it is possible to calculate an average value of any dynamical quantity. No such universal distribution has been formulated for irreversible processes. Thus, to proceed to the solution of problems of statistical mechanics of nonequilibrium systems, it is necessary to resort to various approximate methods. During the last decades, a number of schemes have been concerned with a more general and consistent approach to transport theory.[42,43,45,211–215,217] This field is very active and there are many aspects to the problem.[45,220,221,223,224]

7.1. *Variational principles for transport coefficients*

The variational principles for transport coefficients are the special techniques for bounding transport coefficients, originally developed by researchers in Refs. 2 and 216). This approach is equally applicable for both the electronic and thermal transport. It starts from a Boltzmann-like transport equation for the space-and-time-dependent distribution function $f_{\mathbf{q}}$ or the occupation number $n_q(\mathbf{r},t)$ of a single quasiparticle state specified by indices q (e.g., wave vector for electrons or wave vector and polarization, for phonons). Then it is necessary to find or fit a functional $F[f_{\mathbf{q}}, n_q(\mathbf{r},t)]$ which has a stationary point at the distribution $f_{\mathbf{q}}$, $n_q(\mathbf{r},t)$ satisfying the transport equation, and whose stationary value is the suitable transport coefficient. By evaluating F for a distribution only approximately satisfying the transport equation, one then obtains an upper or lower bound on the transport coefficients. Let us mention briefly the phonon-limited electrical resistivity in metals.[2,86] With the neglect of phonon drag, the electrical resistivity can be written

$$R \leq \frac{1}{2k_BT} \frac{\displaystyle\iint (\Phi_{\mathbf{k}} - \Phi_{\mathbf{k}'})^2 W(\mathbf{k},\mathbf{k}') d\mathbf{k} d\mathbf{k}'}{\left| \displaystyle\int e\mathbf{v}_{\mathbf{k}} \Phi_{\mathbf{k}} \left(\frac{\partial f^0_{\mathbf{k}}}{\partial \epsilon(\mathbf{k})} \right) d\mathbf{k} \right|^2} . \tag{7.1}$$

Here $W(\mathbf{k},\mathbf{k}')$ is the transition probability from an electron state $\mathbf{k}$ to a state $\mathbf{k}'$, $\mathbf{v}_{\mathbf{k}}$ is the electron velocity and f^0 is the equilibrium Fermi–Dirac statistical factor. The variational principle[2] states that the smallest possible value of the right-hand side obtained for any function $\Phi_{\mathbf{k}}$ is also the actual resistivity. In general, we do not know the form of the function $\Phi_{\mathbf{k}}$ that will give the right-hand side its minimal value. For an isotropic system, the correct choice is $\Phi_{\mathbf{k}} = \mathbf{u}\mathbf{k}$, where $\mathbf{u}$ is a unit vector along the direction of the applied field. Because of its simple form, this function is in general used also in calculations for real systems. The resistivity will be overestimated but it can still be a reasonable approximation. This line of reasoning leads to the Ziman formula for the electrical resistivity

$$R \leq \frac{3\pi}{e^2 k_B T S^2 \bar{k}_F^2} \sum_\nu \iint \frac{d^2\mathbf{k}}{v} \frac{d^2\mathbf{k}'}{v'} \times \frac{(\mathbf{k}-\mathbf{k}')^2 \omega_\nu(\mathbf{q}) A_\nu^2(\mathbf{k},\mathbf{k}')}{(\exp(\hbar\omega_\nu(\mathbf{q})/k_B T - 1)(1 - \exp(-\hbar\omega_\nu(\mathbf{q})/k_B T)}\,. \tag{7.2}$$

Here $\bar{k}_F$ is the average magnitude of the Fermi wave vector and S is the free area of the Fermi surface. It was shown in Ref. 227 that the formula for the electrical resistivity should not contains any electron–phonon enhancements in the electron density of states. The electron velocities in Eq. (7.2) are therefore the same as those in Eq. (7.1).

7.2. *Transport theory and electrical conductivity*

Let us summarize the results of the preceding sections. It was shown above that in zero magnetic field, the quantities of main interest are the conductivity σ (or the electrical resistivity, $R = 1/\sigma$) and the thermopower S. When a magnetic field $\mathbf{B}$ is applied, the quantity of interest is a magnetoresistance

$$\varrho_{MR} = \frac{R(\mathbf{B}) - R(B=0)}{R(B=0)} \tag{7.3}$$

and the Hall coefficient R_H. The third of the (generally) independent transport coefficients is the thermal conductivity κ. The important relation which relates κ to R at low and high temperatures is the Wiedemann–Franz law.[2,228] In simple metals and similar metallic systems, which have well-defined Fermi surface, it is possible to interpret all the transport coefficients mentioned above, the conductivity (or resistivity), thermopower, magnetoresistance and Hall coefficient in terms of the rate of scattering of conduction electrons from initial to final states on the Fermi surface. Useful tool to describe this in an approximate way is the Boltzmann transport equation, which, moreover is usually simplified further by introducing a concept of a relaxation time. In the approach of this kind, we are interested in low-rank velocity moments of the distribution function such as the current

$$\mathbf{j} = e \int \mathbf{v} f(\mathbf{v}) d^3 v\,. \tag{7.4}$$

In the limit of weak fields, one expects to find Ohm law $\mathbf{j} = \sigma\mathbf{E}$. The validity of such a formulation of the Ohm law was analyzed by Bakshi and Gross.[229] This approach was generalized and developed by many authors. The most popular kind of consideration starts from the linearized Boltzmann equation which can be derived assuming weak scattering processes. For example, for the scattering of electrons by "defect" (substituted atom or vacancy) with the scattering potential $V^d(\mathbf{r})$ the perturbation theory gives

$$R \sim \frac{3\pi^2 m^2 \Omega_0 N}{4\hbar^3 e^2 k_F^2} \int_0^{2k_F} |\langle k+q|V^d(\mathbf{r})|k\rangle|^2 q^3 dq \,, \tag{7.5}$$

where N and Ω_0 are the number and volume of unit cells, k_F the magnitude of the Fermi wave vector, the integrand $\langle k+q|V^d(\mathbf{r})|k\rangle$ represents the matrix elements of the total scattering potential $V^d(\mathbf{r})$, and the integration is over the magnitude of the scattering wave vector $\mathbf{q}$ defined by $\mathbf{q} = \mathbf{k} - \mathbf{k}'$.

Lax have analyzed in detail the general theory of carriers mobility in solids.[230] Luttinger and Kohn,[231,232] Greenwood,[233] Chester and Thellung[234] and Fujiita[222] developed approaches to the calculation of the electrical conductivity on the basis of the generalized quantum kinetic equations. The basic theory of transport for the case of scattering by static impurities has been given in the works of Kohn and Luttinger[231,232] and Greenwood[233] (see also Ref. 235). In these works, the usual Boltzmann transport equation and its generalizations were used to write down the equations for the occupation probability in the case of a weak, uniform and static electric field. It was shown that in the case of static impurities, the exclusion principle for the electrons has no effect at all on the scattering term of the transport equation. In the case of scattering by phonons, where the electrons scatter inelastically, the exclusion principle plays a very important role and the transport problem is more involved. On the other hand, transport coefficients can be calculated by means of theory of the linear response such as the Kubo formulae for the electrical conductivity. New consideration of the transport processes in solids which involve weak assumptions and easily generalizable methods are of interest because they increase our understanding of the validity of the equations and approximations used.[45,46,235] Moreover, it permits one to consider more general situations and apply the equations derived to a variety of physical systems.

8. The Method of Time Correlation Functions

The method of time correlation functions[42,43,45,62,221,223,224,236] is an attempt to base a linear macroscopic transport equation theory directly on the Liouville equation. In this approach, one starts with complete N-particle distribution function which contains all the information about the system. In the method of time correlation functions, it is assumed that the N-particle distribution function can be written as a local equilibrium N-particle distribution function plus correction terms. The local equilibrium function depends upon the local macroscopic variables, temperature, density and mean velocity and upon the position and momenta of the N particles in the system. The corrections to this distribution functions are determined on the basis of the Liouville equation. The main assumption is that at some initial time the system was in local equilibrium (quasi-equilibrium) but at later time is tending towards complete equilibrium. It was shown by many authors (for comprehensive review, see Refs. 42, 43 and 45) that the suitable solutions to the Liouville equation can be constructed and an expression for the corrections to local equilibrium in powers of the gradients of the local variables can be found as well. The generalized linear macroscopic transport equations can be derived by retaining the first term in the gradient expansion only. In principle, the expressions obtained in this way should depend upon the dynamics of all N particles in the system and apply to any system, regardless of its density.

8.1. *Linear response theory*

The linear response theory was anticipated in many works (see Refs. 42, 43, 45, 237 and 238 for details) on the theory of transport phenomena and nonequilibrium statistical mechanics. The important contributions have been made by many authors. By solving the Liouville equation to the first-order in the external electric field, Kubo[239–243] formulated an expression for the electric conductivity in microscopic terms.

He used linear response theory to give exact expressions for transport coefficients in terms of correlation functions for the equilibrium system. To evaluate such correlation functions for any particular system, approximations have to be made.

In this section, we shall formulate briefly some general expressions for the conductivity tensor within the linear response theory. Consider a many-particle system with the Hamiltonian of a system denoted by H. This includes everything in the absence of the field; the interaction of the system with the applied electric field is denoted by H_{ext}. The total Hamiltonian is

$$\mathcal{H} = H + H_{\mathrm{ext}} \,. \tag{8.1}$$

The conductivity tensor for an oscillating electric field will be expressed in the form[239]

$$\sigma_{\mu\nu} = \int_0^\beta \int_0^\infty \mathrm{Tr}\rho_0 j_\nu(0) j_\mu(t + i\hbar\lambda) e^{-i\omega t} dt d\lambda \,, \tag{8.2}$$

where ρ_0 is the density matrix representing the equilibrium distribution of the system in absence of the electric field

$$\rho_0 = \frac{e^{-\beta H}}{[\mathrm{Tr} e^{-\beta H}]} \,, \tag{8.3}$$

β being equal to $1/k_B T$. Here j_μ, j_ν are the current operators of the whole system in the μ, ν directions respectively, and j_μ represents the evolution of the current as determined by the Hamiltonian H

$$j_\mu(t) = e^{iHt/\hbar} j_\mu e^{-iHt/\hbar} \,. \tag{8.4}$$

Kubo derived his expression Eq. (8.2) by a simple perturbation calculation. He assumed that at $t = -\infty$ the system was in the equilibrium represented by ρ_0. A sinusoidal electric field was switched on at $t = -\infty$, which, however, was assumed to be sufficiently weak. Then he considered the equation of motion of the form

$$i\hbar\frac{\partial}{\partial t}\rho = [H + H_{\text{ext}}(t), \rho]\,. \tag{8.5}$$

The change of ρ to the first-order of H_{ext} is given by

$$\rho - \rho_0 = \frac{1}{i\hbar}\int_{-\infty}^{t} e^{(-Ht'/i\hbar)}[H_{\text{ext}}(t'), \rho_0]e^{(Ht'/i\hbar)} + O(H_{\text{ext}})\,. \tag{8.6}$$

Therefore, the averaged current will be written as

$$\langle j_\mu(t)\rangle = \frac{1}{i\hbar}\int_{-\infty}^{t} \text{Tr}[H_{\text{ext}}(t'), \rho_0]j_\mu(-t')dt'\,, \tag{8.7}$$

where $H_{\text{ext}}(t')$ will be replaced by $-e_dE(t')$, e_d being the total dipole moment of the system. Using the relation

$$[A, e^{-\beta H}] = \frac{\hbar}{i}e^{-\beta H}\int_{0}^{\beta} e^{\lambda H}[A, \rho]e^{-\lambda H}d\lambda\,, \tag{8.8}$$

the expression for the current can be transformed into Eq. (8.7). The conductivity can be also written in terms of the correlation function $\langle j_\nu(0)j_\mu(t)\rangle_0$. The average sign $\langle\cdots\rangle_0$ means the average over the density matrix ρ_0.

The correlation of the spontaneous currents may be described by the correlation function[239]

$$\Xi_{\mu\nu}(t) = \langle j_\nu(0)j_\mu(t)\rangle_0 = \langle j_\nu(\tau)j_\mu(t+\tau)\rangle_0\,. \tag{8.9}$$

The conductivity can be also written in terms of these correlation functions. For the symmetric ("s") part of the conductivity tensor, Kubo[239] derived a relation of the form

$$\text{Re}\,\sigma^s_{\mu\nu}(\omega) = \frac{1}{\varepsilon_\beta(\omega)}\int_0^\infty \Xi_{\mu\nu}(t)\cos\omega t dt\,, \tag{8.10}$$

where $\varepsilon_\beta(\omega)$ is the average energy of an oscillator with the frequency ω at the temperature $T = 1/k_B\beta$. This equation represents the so-called fluctuation–dissipation theorem, a particular case of which is the Nyquist theorem for the thermal noise in a resistive circuit. The fluctuation–dissipation theorems were established[244,245] for systems in thermal equilibrium. It relates the conventionally defined noise power spectrum of the dynamical variables of a system to the corresponding admittances which describe the linear response of the system to external perturbations.

The linear response theory is very general and effective tool for the calculation of transport coefficients of the systems which are rather close to a thermal equilibrium. Therefore, the two approaches, the linear response theory and the traditional kinetic equation theory share a domain in which they give identical results. A general formulation of the linear response theory was given by Kubo[240–243] for the case of mechanical disturbances of the system with an external source in terms of an additional Hamiltonian.

A mechanical disturbance is represented by a force $F(t)$ acting on the system which may be given function of time. The interaction energy of the system may then be written as

$$H_{\text{ext}}(t) = -AF(t)\,, \tag{8.11}$$

where A is the quantity conjugate to the force F. The deviation of the system from equilibrium is observed through measurements of certain physical quantities. If $\Delta\bar{B}(t)$ is the observed deviation of a physical quantity B at the time t, we may assume, if only the force F is weak enough, a linear relationship between $\Delta\bar{B}(t)$ and the force $F(t)$, namely

$$\Delta\bar{B}(t) = \int_{-\infty}^{t} \phi_{BA}(t,t')F(t')dt'\,, \tag{8.12}$$

where the assumption that the system was in equilibrium at $t = -\infty$, when the force had been switched on, was introduced. This assumption was formulated mathematically by the asymptotic condition,

$$F(t) \sim e^{\varepsilon t} \quad \text{as} \quad t \to -\infty(\varepsilon > 0)\,. \tag{8.13}$$

Equation (8.12) assumes the causality and linearity. Within this limitation, it is quite general. Kubo called the function ϕ_{BA} of response function of B to F, because it represents the effect of a delta-type disturbance of F at the time t' shown in the quantity B at a later time t. Moreover, as it was claimed by Kubo, the linear relationship (8.12) itself not in fact restricted by the assumption of small deviations from equilibrium. In principle, it should be true even if the system is far from equilibrium as far as only differentials of the forces and responses are considered. For instance, a system may be driven by some time-dependent force and superposed on it a small disturbance may be exerted; the response function then will depend both on t and t' separately. If, however, we confine ourselves only to small deviations from equilibrium, the system is basically stationary and so the response functions depend only on the difference of the time of pulse and measurement, t and t', namely

$$\phi_{BA}(t,t') = \phi_{BA}(t-t')\,. \tag{8.14}$$

In particular, when the force is periodic in time

$$F(t) = \operatorname{Re} Fe^{i\omega t}\,, \tag{8.15}$$

the response of B will have the form

$$\Delta\bar{B}(t) = \operatorname{Re}\chi_{BA}(\omega)Fe^{i\omega t}\,, \tag{8.16}$$

where $\chi_{BA}(\omega)$ is the admittance

$$\chi_{BA}(\omega) = \int_{-\infty}^{t} \phi_{BA}(t)e^{-i\omega t}dt\,. \tag{8.17}$$

More precisely,[246] the response $\Delta\bar{B}(t)$ to an external periodic force $F(t) = F\cos(\omega t)$ conjugate to a physical quantity A is given by Eq. (8.16), where the admittance $\chi_{BA}(\omega)$ is defined as

$$\chi_{BA}(\omega) = \lim_{\varepsilon\to+0}\int_0^\infty \phi_{BA}(t)e^{-(i\omega+\varepsilon)t}dt\,. \tag{8.18}$$

The response function $\phi_{BA}(\omega)$ is expressed as

$$\begin{aligned}\phi_{BA}(t) &= i\,\mathrm{Tr}[A,\rho]B(t) = -i\,\mathrm{Tr}\rho[A,B(t)]\\ &= \int_0^\beta \mathrm{Tr}\rho\dot{A}(-i\lambda)B(t)dt = -\int_0^\beta \mathrm{Tr}\rho A(-i\lambda)\dot{B}d\lambda\,,\end{aligned} \tag{8.19}$$

where ρ is the canonical density matrix

$$\rho = \exp(-\beta(H-\Omega))\,,\quad \exp(-\beta\Omega) = \mathrm{Tr}\exp(-\beta H)\,. \tag{8.20}$$

In certain problems, it is convenient to use the relaxation function defined by

$$\begin{aligned}\Phi_{BA}(t) &= \lim_{\varepsilon\to+0}\int_t^\infty \phi_{BA}(t')e^{-\varepsilon t'}dt'\\ &= i\int_t^\infty \langle[B(t'),A]\rangle dt'\\ &= -\int_t^\infty dt'\int_0^\beta d\lambda\langle A(i\lambda)\dot{B}(t')\rangle\\ &= \int_0^\beta d\lambda(\langle A(-i\lambda)B(t)\rangle - \lim_{t\to\infty}\langle A(-i\lambda)B(t)\rangle)\\ &= \int_0^\beta d\lambda\langle A(-i\lambda)B(t)\rangle - \beta\lim_{t\to\infty}\langle AB(t)\rangle\\ &= \int_0^\beta d\lambda\langle A(-i\lambda)B(t)\rangle - \beta\langle A^0B^0\rangle\,.\end{aligned} \tag{8.21}$$

It is of use to represent the last term in terms of the matrix elements

$$\begin{aligned}&\int_0^\beta d\lambda\langle A(-i\lambda)B(t)\rangle - \beta\langle A^0B^0\rangle\\ &\quad= \left(1/\sum_i\exp(-\beta E_i)\right)\sum_{n,m}\langle n|A|m\rangle\langle m|B|n\rangle e^{-it(E_n-E_m)}\\ &\qquad\times\frac{e^{-\beta E_n}-e^{-\beta E_m}}{E_m-E_n}\,.\end{aligned} \tag{8.22}$$

Here $|m\rangle$ denotes an eigenstate of the Hamiltonian with an eigenvalue E_m and A^0 and B^0 are the diagonal parts of A and B with respect to H. The response function

$\chi_{BA}(\omega)$ can be rewritten in terms of the relaxation function. We have

$$\begin{aligned}
\chi_{BA}(\omega) &= -\lim_{\varepsilon\to+0}\int_0^\infty \dot{\phi}_{BA}(t)e^{-(i\omega+\varepsilon)t}dt \\
&= \phi_{BA}(0) - i\omega \lim_{\varepsilon\to+0}\int_0^\infty \phi_{BA}(t)e^{-(i\omega+\varepsilon)t}dt \\
&= -\lim_{\varepsilon\to+0}\int_0^\infty dt\int_0^\beta d\lambda e^{-(i\omega+\varepsilon)t}\frac{d}{dt}\langle AB(t+i\lambda)\rangle \\
&= i\lim_{\varepsilon\to+0}\int_0^\infty dte^{-(i\omega+\varepsilon)t}(\langle AB(t+i\beta)\rangle - \langle AB(t)\rangle) \\
&= i\lim_{\varepsilon\to+0}\int_0^\infty dte^{-(i\omega+\varepsilon)t}\langle [B(t),A]\rangle \\
&= \sum_{n,m}\frac{A_{mn}B_{nm}}{\omega+\omega_{mn}+i\varepsilon}(e^{-\beta E_n}-e^{-\beta E_m})\,,
\end{aligned} \tag{8.23}$$

where

$$A_{mn} = \frac{\langle m|A|n\rangle}{\left(\sum_n e^{-\beta E_n}\right)^{1/2}}\,.$$

In particular, the static response $\chi_{BA}(0)$ is given by

$$\begin{aligned}
\chi_{BA}(0) &= \phi_{BA}(0) \\
&= \int_0^\beta d\lambda(\langle AB(i\lambda)\rangle - \lim_{t\to\infty}\langle AB(t+i\lambda)\rangle) \\
&= i\lim_{\varepsilon\to+0}\int_0^\infty e^{-\varepsilon t}dt(\langle AB(t+i\beta)\rangle - \langle AB(t)\rangle) \\
&= i\lim_{\varepsilon\to+0}\int_0^\infty e^{-\varepsilon t}dt\langle [B(t),A]\rangle\,.
\end{aligned} \tag{8.24}$$

This expression can be compared with the isothermal response defined by

$$\chi_{BA}^T = \int_0^\beta (\langle AB(i\lambda)\rangle - \langle A\rangle\langle B\rangle)d\lambda\,. \tag{8.25}$$

The difference of the two response functions is given by

$$\begin{aligned}
\chi_{BA}^T - \chi_{BA}(0) &= \lim_{t\to\infty}\int_0^\beta d\lambda\langle AB(t+i\lambda)\rangle - \beta\langle A\rangle\langle B\rangle \\
&= \beta\left(\lim_{t\to\infty}\langle AB(t)\rangle - \langle A\rangle\langle B\rangle\right)\,.
\end{aligned} \tag{8.26}$$

The last expression suggests that it is possible to think that the two response functions are equivalent for the systems which satisfy the condition

$$\lim_{t\to\infty}\langle AB(t)\rangle = \langle A\rangle\langle B\rangle\,. \tag{8.27}$$

It is possible to speak about these systems in terms of ergodic (or quasi-ergodic) behavior, however, with a certain reservation (for a recent analysis of the ergodic behavior of many-body systems see Refs. 247–256).

It may be of use to remind a few useful properties of the relaxation function. If A and B are both Hermitian, then

$$\Phi_{BA}(t) = \text{real}, \int_0^\infty \Phi_{AA}(t) \geq 0\,. \tag{8.28}$$

The matrix-element representation of the relaxation function have the form

$$\begin{aligned}\Phi_{BA}(t) &= \sum_{m,n}(R^1_{mn}\cos(\omega_{mn}) - R^2_{mn}\sin(\omega_{mn}))\\ &\quad + i\sum_{m,n}(R^1_{mn}\sin(\omega_{mn}) - R^2_{mn}\cos(\omega_{mn}))\,,\end{aligned} \tag{8.29}$$

where

$$\begin{aligned}R^1_{mn} &= \frac{1}{2}(A_{nm}B_{mn} + A_{mn}B_{nm})R^3_{mn}\,,\\ R^2_{mn} &= \frac{1}{2i}(A_{nm}B_{mn} - A_{mn}B_{nm})R^3_{mn}\,,\\ A_{mn} &= \frac{\langle m|A|n\rangle}{\left(\sum_n e^{-\beta E_n}\right)^{1/2}}\,,\\ R^3_{mn} &= \frac{e^{-\beta E_n} - e^{-\beta E_m}}{\omega_{mn}}\,, \quad \omega_{mn} = E_m - E_n\,.\end{aligned}$$

This matrix-element representation is very useful and informative. It can be shown that the relaxation function has the property

$$\operatorname{Im}\Phi_{BA}(t) = 0\,, \tag{8.30}$$

which follows from the odd symmetry of the matrix-element representation. The time integral of the relaxation function is given by

$$\int_0^\infty \Phi_{BA}(t)dt = \frac{\pi\beta}{2}\sum_{m,n}(A_{nm}B_{mn} + B_{nm}A_{mn})e^{-\beta E_n}\delta(\omega_{mn})\,. \tag{8.31}$$

In particular, for $A = B$, we obtain

$$\int_0^\infty \Phi_{AA}(t)dt = \pi\beta\sum_{m,n}|A_{nm}|^2 e^{-\beta E_n}\delta(\omega_{mn}) \geq 0\,. \tag{8.32}$$

It can also be shown[246] that if A and B are both bounded, then we obtain

$$\begin{aligned}\int_0^\infty \Phi_{\dot{B}\dot{A}}(t)dt &= i\int_0^\infty dt\int_t^\infty \langle[\dot{B}(t'),\dot{A}]\rangle dt' \\ &= -i\int_0^\infty dt\langle[B(t),\dot{A}]\rangle = i\langle[A,B]\rangle\,. \end{aligned} \tag{8.33}$$

For $A = B$, we have

$$\int_0^\infty \Phi_{\dot{A}\dot{A}}(t)dt = 0\,, \quad \int_0^\infty dt\int_0^\beta d\lambda\langle\dot{A}(-i\lambda),\dot{A}(t)\rangle = 0 \tag{8.34}$$

and

$$\lim_{t\to\infty}\langle\dot{A}\dot{B}(t)\rangle = 0\,, \tag{8.35}$$

if A and B are both bounded.

Application of this analysis may not be limited to admittance functions.[257] For example, if one write a frequency-dependent mobility function $\mu(\omega)$ as

$$\mu(\omega) = [i\omega + \gamma(\omega)]^{-1}\,, \tag{8.36}$$

the frequency-dependent friction $\gamma(\omega)$ is also related to a function $\phi(t)$, which is in fact the correlation function of a random force.[257] An advanced analysis and generalization of the Kubo linear response theory was carried out in series of papers by Van Vliet *et al.*[46] Fluctuations and response in nonequilibrium steady-state were considered within the nonlinear Langevin equation approach by Ohta and Ohkuma.[258] It was shown that the steady probability current plays an important role for the response and time-correlation relation and violation of the time reversal symmetry.

8.2. *Green functions in the theory of irreversible processes*

Green functions are not only applied to the case of statistical equilibrium.[42,77,99,221,259–261] They are a convenient means of studying processes where the deviation from the state of statistical equilibrium is small. The use of the Green functions permits one to evaluate the transport coefficients of these processes. Moreover, the transport coefficients are written in terms of Green functions evaluated for the unperturbed equilibrium state without explicitly having recourse to setting up a transport equation. The linear response theory can be reformulated in terms of double-time temperature-dependent (retarded and advanced) Green functions.[259–261] We shall give a brief account of this reformulation[42,260] and its simplest applications to the theory of irreversible processes.

The retarded two-time thermal Green functions arise naturally within the linear response formalism, as it was shown by Zubarev.[42,260] To show this, we consider the reaction of a quantum-mechanical system with a time-independent Hamiltonian H when an external perturbation

$$H_{\text{ext}}(t) = -AF(t)\,, \tag{8.37}$$

is switched on. The total Hamiltonian is equal to

$$\mathcal{H} = H + H_{\text{ext}}\,, \tag{8.38}$$

where we assume that there is no external perturbation at $\lim t \to -\infty$

$$H_{\text{ext}}(t)|_{\lim t\to-\infty} = 0\,. \tag{8.39}$$

The last condition means that

$$\lim_{t\to-\infty} \rho(t) = \rho_0 = \frac{e^{-\beta H}}{[\operatorname{Tr} e^{-\beta H}]}\,, \tag{8.40}$$

where $\rho(t)$ is a statistical operator which satisfies the equation of motion

$$i\hbar\frac{\partial}{\partial t}\rho(t) = [H + H_{\text{ext}}(t), \rho]\,. \tag{8.41}$$

This equation of motion together with the initial condition (8.40) suggests to look for a solution of Eq. (8.41) of the form

$$\rho(t) = \rho + \Delta\rho(t)\,. \tag{8.42}$$

Let us rewrite Eq. (8.42), taking into account that $[H, \rho] = 0$, in the following form

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}(\rho + \Delta\rho(t)) &= i\hbar\frac{\partial}{\partial t}\Delta\rho(t) \\ &= [H + H_{\text{ext}}(t), \rho + \Delta\rho(t)] \\ &= [H, \Delta\rho(t)] + [H_{\text{ext}}(t), \rho] + [H_{\text{ext}}(t), \Delta\rho(t)]\,. \end{aligned} \tag{8.43}$$

Neglecting terms $H_{\text{ext}}(t)\Delta\rho$, since we have assumed that the system is only little removed from a state of statistical equilibrium, we get then

$$i\hbar\frac{\partial}{\partial t}\Delta\rho(t) = [H, \Delta\rho(t)] + [H_{\text{ext}}(t), \rho]\,, \tag{8.44}$$

where

$$\Delta\rho(t)|_{\lim t\to-\infty} = 0\,. \tag{8.45}$$

Processes for which we can restrict ourselves in Eq. (8.44) to terms linear in the perturbation are called linear dissipative processes. For a discussion of higher-order terms, it is convenient to introduce a transformation

$$\Delta\rho(t) = e^{-iHt/\hbar}\varrho(t)e^{iHt/\hbar}\,. \tag{8.46}$$

Then we have

$$i\hbar\frac{\partial}{\partial t}\Delta\rho(t) = [H, \Delta\rho(t)] + e^{-iHt/\hbar}\left(i\hbar\frac{\partial}{\partial t}\varrho(t)\right)e^{iHt/\hbar}\,. \tag{8.47}$$

This equation can be transformed to the following form

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\varrho(t) &= [e^{iHt/\hbar}H_{\text{ext}}(t)e^{-iHt/\hbar}, \rho] \\ &\quad + [e^{iHt/\hbar}H_{\text{ext}}(t)e^{-iHt/\hbar}, \varrho(t)]\,, \end{aligned} \tag{8.48}$$

where

$$\varrho(t)|_{\lim t\to-\infty} = 0\,. \tag{8.49}$$

In the equivalent integral form, the the above equation reads

$$\begin{aligned}\varrho(t) &= \frac{1}{i\hbar}\int_{-\infty}^{t} d\lambda[e^{iH\lambda/\hbar}H_{\rm ext}(\lambda)e^{-iH\lambda/\hbar},\rho] \\ &\quad + \frac{1}{i\hbar}\int_{-\infty}^{t} d\lambda[e^{iH\lambda/\hbar}H_{\rm ext}(\lambda)e^{-iH\lambda/\hbar},\varrho(\lambda)]\,.\end{aligned} \tag{8.50}$$

This integral form is convenient for the iteration procedure which can be written as

$$\begin{aligned}\varrho(t) = {}& \frac{1}{i\hbar}\int_{-\infty}^{t} d\lambda[e^{iH\lambda/\hbar}H_{\rm ext}(\lambda)e^{-iH\lambda/\hbar},\rho] \\ & + \left(\frac{1}{i\hbar}\right)^2 \int_{-\infty}^{t} d\lambda \int_{-\infty}^{\lambda} d\lambda' \\ & \times [e^{iH\lambda/\hbar}H_{\rm ext}(\lambda)e^{-iH\lambda/\hbar}, [e^{iH\lambda'/\hbar}H_{\rm ext}(\lambda')e^{-iH\lambda'/\hbar},\rho]] + \cdots\end{aligned} \tag{8.51}$$

In the theory of the linear reaction of the system on the external perturbation, usually the only first term is retained

$$\Delta\rho(t) = \frac{1}{i\hbar}\int_{-\infty}^{t} d\tau e^{-iH(t-\tau)/\hbar}[H_{\rm ext}(\tau),\rho]e^{iH(t-\tau)/\hbar}\,. \tag{8.52}$$

The average value of observable A is

$$\langle A\rangle_t = \mathrm{Tr}(A\rho(t)) = \mathrm{Tr}(A\rho_0) + \mathrm{Tr}(A\Delta\rho(t)) = \langle A\rangle + \Delta\langle A\rangle_t\,. \tag{8.53}$$

From this, we find

$$\begin{aligned}\Delta\langle A\rangle_t &= \frac{1}{i\hbar}\int_{-\infty}^{t} d\tau \\ &\quad \times \mathrm{Tr}(e^{iH(t-\tau)/\hbar}Ae^{-iH(t-\tau)/\hbar}H_{\rm ext}(\tau)\rho - H_{\rm ext}(\tau)e^{iH(t-\tau)/\hbar}Ae^{-iH(t-\tau)/\hbar}\rho) \\ &\quad + \cdots \\ &= \frac{1}{i\hbar}\int_{-\infty}^{t} d\tau\langle[A(t-\tau),H_{\rm ext}(\tau)]_-\rangle + \cdots\end{aligned} \tag{8.54}$$

Introducing under the integral the sign function

$$\theta(t-\tau) = \begin{cases} 1 & \text{if } \tau < t\,, \\ 0 & \text{if } \tau > t\,, \end{cases} \tag{8.55}$$

and extending the limit of integration to $-\infty < \tau < +\infty$, we finally find

$$\Delta\langle A\rangle_t = \int_{-\infty}^{\infty} d\tau \frac{1}{i\hbar}\theta(\tau)\langle[A(\tau),H_{\rm ext}(t-\tau)]_-\rangle + \cdots \tag{8.56}$$

Let us consider an adiabatic switching on a periodic perturbation of the form

$$H_{\mathrm{ext}}(t) = B \exp \frac{1}{i\hbar}(E + i\varepsilon)t\,.$$

The presence in the exponential function of the infinitesimal factor $\varepsilon > 0$, $\varepsilon \to 0$ make for the adiabatic switching of the perturbation. Then we obtain

$$\Delta\langle A\rangle_t = \exp \frac{1}{i\hbar}(E + i\varepsilon)t \int_{-\infty}^{\infty} d\tau \exp \frac{-1}{i\hbar}(E + i\varepsilon)\tau \frac{1}{i\hbar}\theta(\tau)\langle[A(\tau), B]_-\rangle\,. \tag{8.57}$$

It is clear that the last expression can be rewritten as

$$\begin{aligned}\Delta\langle A\rangle_t &= \exp \frac{1}{i\hbar}(E + i\varepsilon)t \int_{-\infty}^{\infty} d\tau \exp \frac{-1}{i\hbar}(E + i\varepsilon)\tau G^{\mathrm{ret}}(A, B; \tau)\\ &= \exp \frac{1}{i\hbar}(E + i\varepsilon)t G^{\mathrm{ret}}(A, B; E)\\ &= \exp \frac{1}{i\hbar}(E + i\varepsilon)t\langle\langle A|B\rangle\rangle_{E+i\varepsilon}\,.\end{aligned} \tag{8.58}$$

Here $E = \hbar\omega$ and $\langle\langle A|B\rangle\rangle_{E+i\varepsilon}$ is the Fourier component of the *retarded* Green function $\langle\langle A(t); B(\tau)\rangle\rangle$.

The change in the average value of an operator when a periodic perturbation is switched on adiabatically can thus be expressed in terms of the Fourier components of the retarded Green functions which connect the perturbation operator and the observed quantity.

In the case of an instantaneous switching on of the interaction

$$H_{\mathrm{ext}}(t) = \begin{cases} 0 & \text{if } t < t_0\,,\\ \sum\limits_{\Omega} \exp(\Omega t/i\hbar)V_\Omega & \text{if } t > t_0\,,\end{cases} \tag{8.59}$$

where V_Ω is an operator which does not explicitly depend on the time, we get

$$\Delta\langle A\rangle_t = \sum_{\Omega} \int_{t_0}^{\infty} d\tau \langle\!\langle A(t); V_\Omega(\tau)\rangle\!\rangle \exp \frac{1}{i\hbar}(\Omega + i\varepsilon)\tau\,, \tag{8.60}$$

i.e., the reaction of the system can also be expressed in terms of the retarded Green functions.

Now we can define the generalized susceptibility of a system on a perturbation $H_{\mathrm{ext}}(t)$ as

$$\begin{aligned}\chi(A, B; E) &= \chi(A, zB; E)\\ &= \lim_{z\to 0} \frac{1}{z}\Delta\langle A\rangle_t \exp \frac{-1}{i\hbar}(E + i\varepsilon)t\\ &= \langle\!\langle A|B\rangle\!\rangle_{E+i\varepsilon}\,.\end{aligned} \tag{8.61}$$

In the time representation, the above expression reads

$$\chi(A, B; E) = \frac{1}{i\hbar}\int_{-\infty}^{\infty} dt \exp \frac{-1}{i\hbar}(E + i\varepsilon)t\theta(t)\langle[A(t), B]_-\rangle\,. \tag{8.62}$$

This expression is an alternative form of the fluctuation–dissipation theorem, which show explicitly the connection of the relaxation processes in the system with the dispersion of the physical quantities.

The particular case where the external perturbation is periodic in time and contains only one harmonic frequency ω is of interest. Putting in that case $\Omega = \pm\hbar\omega$ in Eq. (8.60), since

$$H_{\text{ext}}(t) = -h_0 \cos\omega t e^{\varepsilon t} B\,, \tag{8.63}$$

where h_0, the amplitude of the periodic force, is a c-number and where B is the operator part of the perturbation, we get

$$\begin{aligned}\Delta\langle A\rangle_t = {} & -h_0 \exp\left(\frac{1}{i\hbar}\omega t + \varepsilon t\right) \langle\langle A|B\rangle\rangle_{E=\hbar\omega} \\ & - h_0 \exp\left(\frac{-1}{i\hbar}\omega t + \varepsilon t\right) \langle\langle A|B\rangle\rangle_{E=-\hbar\omega}\,.\end{aligned} \tag{8.64}$$

Taking into account that $\langle A\rangle_t$ is a real quantity, we can write it as follows

$$\Delta\langle A\rangle_t = \mathrm{Re}(\chi(E) h_0 e^{\frac{1}{i\hbar}Et + \varepsilon t})\,. \tag{8.65}$$

Here $\chi(E)$ is the complex admittance, equal to

$$\chi(E) = -2\pi\langle\langle A|B\rangle\rangle_{E=\hbar\omega}\,. \tag{8.66}$$

These equations elucidate the physical meaning of the Fourier components of the Green function $\langle\langle A|B\rangle\rangle_{E=\hbar\omega}$ as being the complex admittance that describes the influence of the periodic perturbation on the average value of the quantity A.

8.3. *The electrical conductivity tensor*

When a uniform electric field of strength $\boldsymbol{\mathcal{E}}$ is switched on then the perturbation acting upon the system of charged particles assumes the form $H_{\text{ext}} = -\boldsymbol{\mathcal{E}} \cdot \mathbf{d}(t)$, where $\mathbf{d}(t)$ is the total dipole moment of the system. In this case, the average operator $A(t)$ is the current density operator $\mathbf{j}$ and the function χ is the complex electrical conductivity tensor denoted by $\sigma_{\alpha\beta}(\omega)$. If the volume of the system is taken to be equal to unity, then we have

$$\frac{d}{dt} d_\alpha(t) = j_\alpha(t)\,. \tag{8.67}$$

The Kubo formula (8.65) relates the linear response of a system to its equilibrium correlation functions. Here we consider the connection between the electrical conductivity tensor and Green functions.[42,260] Let us start with a simplified treatment when there be switched on adiabatically an electrical field $\boldsymbol{\mathcal{E}}(t)$, uniform in space and changing periodically in time with a frequency ω

$$\boldsymbol{\mathcal{E}}(t) = \boldsymbol{\mathcal{E}} \cos\omega t\,. \tag{8.68}$$

The corresponding perturbation operator is equal to

$$H_{\rm ext}(t) = -e\sum_j (\boldsymbol{\mathcal{E}}\mathbf{r}_j)\cos\omega t e^{\varepsilon t}\,. \tag{8.69}$$

Here e is the charge of an electron, and the summation is overall particle coordinates $\mathbf{r}_j$. Under the influence of the perturbation, there arises in the system an electrical current

$$j_\alpha(t) = \int_{-\infty}^{\infty} d\tau\langle\langle j_\alpha(t); H_{\rm ext}(\tau)\rangle\rangle\,, \tag{8.70}$$

where

$$\begin{gathered} H_{\rm ext}(\tau) = H^1_\tau(\tau)\cos\omega\tau e^{\varepsilon\tau}\,, \\ H^1_\tau(\tau) = -e\sum_{j\alpha}\mathcal{E}_\alpha r^\alpha_j(\tau)\,, \quad j_\alpha(t) = e\sum_j \dot{r}^\alpha_j(t)\,. \end{gathered} \tag{8.71}$$

Here j_α is the current density operator, if the volume of the system is taken to be unity. Equation (8.70) can be transformed to the following form

$$\begin{aligned} j_\alpha(t) = -\mathrm{Re}\Bigg\{&\int_{-\infty}^{\infty} d\tau\langle\langle j_\alpha(t); H^1_\tau(\tau)\rangle\rangle\frac{e^{\frac{i}{\hbar}\omega t+\varepsilon\tau}}{i\omega+\varepsilon} \\ &+ \langle[j_\alpha(0), H^1_\tau(0)]_-\rangle e^{\frac{i}{\hbar}\omega t+\varepsilon t}\frac{1}{\omega - i\varepsilon}\Bigg\}\,. \end{aligned} \tag{8.72}$$

Noting that

$$\dot{H}^1_\tau(\tau) = -(\boldsymbol{\mathcal{E}}\mathbf{j}(\tau))\,, \quad [r^\alpha_i, r^\beta_j] = \frac{1}{i\hbar m}\delta_{\alpha\beta}\delta_{ij}\,, \tag{8.73}$$

we get from this equation

$$j_\alpha(t) = \mathrm{Re}\{\sigma_{\alpha\beta}(\omega)\boldsymbol{\mathcal{E}}_\beta\exp(i\omega t + \varepsilon t)\}\,, \tag{8.74}$$

where

$$\sigma_{\alpha\beta}(\omega) = -\frac{ie^2n}{m\omega}\delta_{\alpha\beta} + \int_{-\infty}^{\infty} d\tau\langle\langle j_\alpha(0); j_\beta(\tau)\rangle\rangle\frac{\exp(i\omega t+\varepsilon t)}{i\omega+\varepsilon} \tag{8.75}$$

is the conductivity tensor, and n the number of electrons per unit volume. The first term in Eq. (8.75) corresponds to the electrical conductivity of a system of free charges and is not connected with the interparticle interaction. As $\omega \to \infty$, the second term decreases more strongly than the first one

$$\lim_{\omega\to\infty}\mathrm{Im}\,\omega\sigma_{\alpha\beta}(\omega) = -\frac{e^2n}{m\omega}\delta_{\alpha\beta}\,,$$

and the system behaves as a collection of free charges.

Let us discuss the derivation of the conductivity tensor in general form. Consider a system of charged particles in electrical field $\boldsymbol{\mathcal{E}}$, which is directed along the axis β ($\beta = x, y, z$). The corresponding electrostatic potential $\varphi^{(\beta)}$

$$\boldsymbol{\mathcal{E}}^{(\beta)} = -\nabla\varphi^{(\beta)}$$

has the following form

$$\varphi^{(\beta)}(\mathbf{r},t) = \sum_{\Omega} \frac{1}{V} \sum_{q} \varphi^{(\beta)}(\mathbf{q},\Omega) \exp((\Omega t + i\varepsilon t)/i\hbar - i\mathbf{qr})\,. \tag{8.76}$$

In the momentum representation, the above expression reads

$$\mathcal{E}_{\alpha}^{(\beta)}(\mathbf{q},\Omega) = \frac{i}{\hbar} q_{\alpha} \varphi^{(\beta)}(\mathbf{q},\Omega) = \delta_{\alpha\beta}\mathcal{E}_{\beta}(\mathbf{q},\Omega)\,. \tag{8.77}$$

Consider the case when the perturbation H^{ext} has the form

$$H^{\text{ext}}_{\mathbf{q}\Omega} = \frac{1}{V} e\varphi^{(\beta)}(\mathbf{q},\Omega)\eta_q^{\dagger} \exp((\Omega t + i\varepsilon t)/i\hbar) \tag{8.78}$$

Here

$$\eta_q = \sum_p a^{\dagger}_{p+q} a_p\,, \quad \eta_q^{\dagger} = \eta_{-q}\,.$$

is the particle density operator.

A reaction of the system on the perturbation is given by

$$\begin{aligned} I_{\alpha}^{(\beta)}(\mathbf{q},\Omega) &= \Delta\langle e j_{\alpha}(\mathbf{q})\rangle \\ &= \frac{1}{V}\langle\langle e j_{\alpha}(\mathbf{q}) | e\varphi^{(\beta)}(\mathbf{q},\Omega)\eta_q^{\dagger}\rangle\rangle_{\Omega+i\varepsilon} \\ &= e^2\varphi^{(\beta)}(\mathbf{q},\Omega)\frac{1}{V}\int_{-\infty}^{\infty} d\omega J(\eta_q^{\dagger}, j_{\alpha}(\mathbf{q});\omega)\frac{e^{\omega/\theta}-1}{\Omega-\omega+i\varepsilon}\,, \end{aligned} \tag{8.79}$$

where $I_{\alpha}^{(\beta)}(\mathbf{q},\Omega)$ denotes the component of the density of the current in the α-direction when external electric field directed along the β-axis.

8.4. *Linear response theory: pro et contra*

It was shown in the previous sections that the formulation of the linear response theory can be generalized so as to be applied to a rather wide class of the problems. It is worth to note that the "exact" linear expression for electrical conductivity for an arbitrary system was derived originally by Kubo[240] in a slightly different form than Eq. (8.75)

$$\sigma_{\mu\nu} = \lim_{\varepsilon\to 0}\frac{1}{\varepsilon}\left(\phi_{\mu\nu}(0) + \int_{-\infty}^{\infty} dt e^{-\varepsilon t}\dot{\phi}_{\mu\nu}(t)\right), \tag{8.80}$$

where

$$\phi_{\mu\nu}(t) = \frac{1}{i\hbar}\mathrm{Tr}\left(n, \sum_i e_i x_{i\nu}\right)\sum_i e_i \dot{x}_{i\nu}(t) \tag{8.81}$$

is the current response in the μ-direction when a pulse of electric field $\mathcal{E}(t)$ is applied in the ν-direction at $t = 0$; e_i is the charge of the ith particle with position vector $\mathbf{r}_i$

and n is a density operator. In the one-electron approximation, Eq. (8.80) reduces to (cf. Ref. 233)

$$\sigma_{ij} = 2\pi e^2 h \sum_{nm} \langle m|v_i|n\rangle \langle n|v_j|m\rangle \left(\frac{\partial f}{\partial E} \right)_n . \tag{8.82}$$

Here v_i is the velocity operator and f is the Fermi function.

To clarify the general consideration of the above sections, it is of interest to consider here a simplified derivation of this formula, using only the lowest-order of time-dependent perturbation theory.[262] This approach is rooted in the method of derivation of Callen and Welton,[263] but takes explicitly into account degeneracy of the states. The linear response theory formulated by Kubo[240] was motivated in part[237,238] by the prior work of Callen and Welton,[263] who proposed a quantum-mechanical perturbative calculation with the external forces exerted on a dissipative system. They pointed out a general relationship between the power dissipation induced by the perturbation and the average of a squared fluctuation of the current of the system in thermal equilibrium.

Let us discuss first the role of dissipation. A system may be called to be dissipative if it absorbs energy when subjected to a time-periodic perturbation, and linear if the dissipation (rate of absorption of energy) is quadratic in the perturbation. For a linear system, an impedance may be defined and the proportionality constant between the power and the square of the perturbation amplitude is simply related to the impedance. In the case of electrical current in a material, one can write down that

$$\bar{W} = \frac{1}{2} \frac{R}{(\text{Impedance})^2} = V^2 ,$$

where $\bar{W}$ is the average power and V is the voltage. If we calculate the power microscopically in some way and find it quadratic in the applied force (voltage), then comparison with this equation will give the conductivity of the substance.

Consider a situation when an electron of charge e is situated a distance x from the end of a resistor of length L and then a voltage $V = V_0 \sin \omega t$ is applied in the x-direction.[262] The perturbation term in the Hamiltonian will be of the form

$$H_\omega^{\text{ext}} = V_0 e \frac{x}{L} \sin \omega t . \tag{8.83}$$

The Hamiltonian of a system in the absence of the field (but including all other interactions) is denoted by H_0 with corresponding wavefunction ψ_n such that

$$H_0 \psi_n = E_n \psi_n . \tag{8.84}$$

The total wavefunction may be expanded in terms of the ψ_n

$$\Psi_n = \sum_n a_n(t) \psi_n , \tag{8.85}$$

where the coefficients $a_n(t)$ may be approximately determined by first-order perturbation theory.[81] The rate of transition is then given by

$$\frac{dp_n}{dt} = \frac{1}{2}\frac{\pi e^2 V_0^2}{\hbar}\sum_{mn}|\langle m|x|n\rangle|^2[\delta(E_m-(E_n+\hbar\omega))+\delta(E_m-(E_n-\hbar\omega))]. \qquad (8.86)$$

The first term corresponds to a transition to a state $E_m = E_n + \hbar\omega$ in which energy $\hbar\omega$ is absorbed, whereas the second term corresponds to a transition to a state $E_m = E_n - \hbar\omega$ in which energy is emitted. Hence, the net rate of absorption of energy is given by

$$\frac{dE_n}{dt} = \frac{1}{2}\frac{\pi e^2 V_0^2}{\hbar}\hbar\omega\sum_{mn}|\langle m|x|n\rangle|^2[\delta(E_m-E_n-\hbar\omega)+\delta(E_m-E_n+\hbar\omega)]\,, \qquad (8.87)$$

which is quadratic in V_0.

This equation gives the absorption rate for a single, isolated electrons, but in a real system we are dealing with an ensemble of these, which we shall represent by the Fermi function. One must therefore find[262] the average absorption by averaging over all initial states $|n\rangle$ and taking the Pauli exclusion principle as well as the two spin directions into account. The result is[262]:

$$\begin{aligned}\left\langle\frac{dE_n}{dt}\right\rangle &= \pi e^2 V_0^2\omega\sum_{mn}|\langle m|x|n\rangle|^2 \\ &\quad\times\{f(E_n)\delta(E_m-E_n-\hbar\omega)(1-f(E_m)) \\ &\quad - f(E_n)\delta(E_m-E_n+\hbar\omega)(1-f(E_m))\} \\ &= \pi e^2 V_0^2\omega\left\{\sum_n|\langle n+\hbar\omega|x|n\rangle|^2[f(E_n)-f(E_n)f(E_n+\hbar\omega)]\right. \\ &\quad\left.-\sum_{n'}|\langle n'|x|n'+\hbar\omega\rangle|^2[f(E_{n'}+\hbar\omega)-f(E_{n'}+\hbar\omega)f(E_{n'})]\right\}, \end{aligned} \qquad (8.88)$$

where we have put $n' = n - \hbar\omega$. The above formula can be transformed to the form

$$\begin{aligned}\left\langle\frac{dE_n}{dt}\right\rangle &= \pi e^2 V_0^2\omega\sum_{mn}|\langle m|x|n\rangle|^2 \\ &\quad\times[f(E_n)-f(E_m)]\delta(E_m-E_n-\hbar\omega)\,. \end{aligned} \qquad (8.89)$$

This expression may be simplified by introducing the matrix-element of the velocity operator

$$\frac{dx}{dt} = \frac{i}{\hbar}[H, x]\,. \qquad (8.90)$$

In principle, on the right-hand side of Eq. (8.90), the total Hamiltonian

$$\mathcal{H} = H + H_{\text{ext}} \qquad (8.91)$$

should be written. In this case, however, the terms of higher than quadratic order in V_0 appear. For a linear system, one can neglect these and use Eq. (8.90). Thus, we have

$$|\langle m|\dot{x}|n\rangle| = \frac{i}{\hbar}\langle m|[H,x]|n\rangle = \frac{i}{\hbar}(E_m\langle m|x|n\rangle - E_n\langle m|x|n\rangle) \tag{8.92}$$

and

$$|\langle m|\dot{x}|n\rangle|^2 = \frac{-1}{\hbar^2}(E_m - E_n)^2|\langle m|x|n\rangle|^2 = \omega^2|\langle m|x|n\rangle|^2\,. \tag{8.93}$$

Therefore

$$\left\langle \frac{dE_n}{dt} \right\rangle = -\frac{\pi e^2}{\omega}V_0^2\sum_{mn}|\langle m|\dot{x}|n\rangle|^2[f(E_n) - f(E_n + \hbar\omega)]\delta(E_m - E_n - \hbar\omega)\,. \tag{8.94}$$

If we now assume the current to be in phase with the applied voltage, the average energy dissipation becomes

$$\text{Power} = \frac{1}{2}\frac{V_0^2}{R(\omega)} \tag{8.95}$$

as the resistance $R(\omega)$ is now equal to the impedance $Z(\omega)$. Referring everything to unit volume and noting that the resistance per unit volume is the resistivity, we get for the conductivity σ

$$\begin{aligned}\sigma_{xx}(\omega) = -\frac{2\pi e^2}{\omega}\sum_{mn}&|\langle m|v|n\rangle\langle n|v|m\rangle| \\ &\times [f(E_n) - f(E_n + \hbar\omega)]\delta(E_m - E_n - \hbar\omega)\,.\end{aligned} \tag{8.96}$$

A straightforward generalization of this procedure, using a perturbation

$$H_{\text{ext}} = \sum_i V_0 e x_i/L\sin(\omega t)\,, \tag{8.97}$$

leads to the definition of an impedance matrix and a conductivity tensor

$$\sigma_{ij} = \frac{2\pi e^2}{\omega}\sum_{nm}|\langle m|v_i|n\rangle\langle n|v_j|m\rangle|[f(E_n) - f(E_n + \hbar\omega)]\delta(E_m - E_n - \hbar\omega)\,, \tag{8.98}$$

which is the Kubo–Greenwood equation.[233,240] The derivation[262] presented here confirms that fact that the linear response theory is based on the fluctuation–dissipation theorem, i.e., that the responses to an external perturbation are essentially determined by fluctuations of relevant physical quantities realized in the absence of the perturbation. Thus, the linear response theory has a special appeal since it deals directly with the quantum mechanical motion of a process.

The linear response theory (or its equivalent) soon became a very popular tool of the transport theory.[264,265] As was expressed by Langer,[266] the Kubo formula "probably provides the most rigorous possible point of departure for transport theory. Despite its extremely formal appearance, it has in fact proved amenable to direct evaluation for some simple models." Edwards[267] and Chester and Thellung[234] have used the Kubo formula to calculate the impurity resistance of a system of independent electrons and have recovered the usual solution of the linearized Boltzmann equation. Verboven[268] has extended this work to higher-orders in the concentration of impurities and has found corrections to the conductivity not originally derived via Boltzmann techniques. It was concluded that the Kubo formula might be most fruitfully applied in the full many-body problem, where it is not clear that any Boltzmann formulation is valid. However, Izuyama[269] casted doubt on the Kubo formula for electrical conductivity. He claimed that it is not, in fact, an exact formula for electrical conductivity, but is rather a coefficient relating current to an "external" field, the coefficient of which is equal to the conductivity only in special case. A correlation-function formula for electrical conductivity was derived by Magan[270] by a formalism which gives prominence to the total electric field, including fields which may arise from the charged particles that are part of the system being studied.

Langer[266] evaluated the impurity resistance of an interacting electron gas on the basis of the Kubo formula at low but finite temperatures. The calculations are exact to all orders in the electron–electron interactions and to lowest-order in the concentration of impurities. In the previous papers,[271,272] the impurity resistance of this gas was computed at absolute zero-temperature. It was shown[266] that the zero-temperature limit of this calculation yields the previous result. In Ref. 228, Kubo formula for thermal conductivity was evaluated for the case of an interacting electron gas and random, fixed, impurities. The heat flux was examined in some detail and it was shown that in a normal system where the many-body correlations are sufficiently weak, the Wiedemann–Franz law remains valid. The relationships between the transport coefficients of a metal in a strong magnetic field and at very low temperatures were discussed by Smrcka and Streda.[273] Formulae describing the electron coefficients as functions of the conductivity were derived on the basis of the linear response theory. As was mentioned earlier, examples of such relations are the Wiedemann–Franz law for the heat conductivity κ and the Mott rule[207] for the thermopower S. It was shown that that the Wiedemann–Franz law and the Mott rule are obeyed even in the presence of a quantized magnetic field $\omega\tau > 1$ if the scattering of electrons is elastic and if $\hbar\omega \gg kT$.

A theoretical analysis, based on Kubo formalism, was made for the ferromagnetic Hall effect by Leribaux[274] in the case of transport limited by electron–phonon scattering. The antisymmetric, off-diagonal conductivity was, to first-order in magnetization, found to be of order zero in the electron–phonon interaction (assumed to be weak) and, to this order, was equivalent to Karplus and Luttinger results.[275] Tanaka, Moorjani, and Morita[276] expressed the nonlinear transport coefficients in terms of many-time Green functions and made an attempt to calculate the higher-order transport coefficients. They applied their theory to the calculation of the nonlinear susceptibility of a Heisenberg ferromagnet and nonlinear polarizability problem. Schotte[277]reconsidered the linear response theory to show the closeness of it and kinetic equations.

At the same time, several authors[278–280] raised an important question as to the general validity of the correlation formulae for transport coefficients. The relation for the electrical conductivity was, in principle, not questioned as in this case (as was shown above) one may obtain it by a straightforward application of basic statistical mechanical principles and perturbation techniques. One simply calculates the response of the system to an electric field. What has been questioned, however, was the validity of the correlation relations for the transport coefficients of a fluid — the diffusion constant, the thermal conductivity, and the viscosity — where no such straightforward procedure, as was used for the electrical conductivity was available.[281]

However, Jackson and Mazur[282] presented a derivation of the correlation formula for the viscosity which is similar in spirit, and as free of additional assumptions, as that for the electrical conductivity. The correlation formula for the viscosity was obtained by calculating statistically the first-order response of a fluid, initially in equilibrium, to an external shearing force. It was shown that on the basis of this derivation, the correlation formula for the viscosity, the exactness of which had been questioned, was placed on as firm a theoretical basis as the Kubo relation for the electrical conductivity. In addition, Resibois[283,284] demonstrated the complete equivalence between the kinetic approach developed by Prigogine[285] and the correlation function formalism for the calculation of linear thermal transport coefficients. It was shown that in both cases these transport coefficients are determined by the solution of an inhomogeneous integral equation for a one-particle distribution function which is the generalization to strongly coupled system of the Chapman–Enskog first approximation of the Boltzmann equation.[45,286] Interesting remarks concerning the comparison of the linear response theory and Boltzmann equation approach were formulated by Peierls.[225,287] Schofield[288,289] elaborated a general derivation of the transport coefficients and thermal equilibrium correlation functions for a classical system having arbitrary number of microscopic conservation laws. This derivation gives both the structure of the correlation functions in the hydrodynamic (long wavelength) region and a generalized definition of the transport coefficients for all wavelengths and frequencies.

A number of authors have given the formulation of nonlinear responses.[258,290–295] It was shown that since in a nonlinear system fluctuation sources and transport coefficients may considerably depend on a nonequilibrium state of the system, nonlinear nonequilibrium thermodynamics should be a stochastic theory. From the other side, the linearity of the theory itself was a source of many doubts. The most serious criticism of the Kubo linear response theory was formulated by van Kampen.[296] He argued strenuously that the standard derivation of the response functions are incorrect. In his own words, "the basic linearity assumption of linear response theory … is completely unrealistic and incompatible with basic ideas of statistical mechanics of irreversible processes." The main question raised by van Kampen concerned the logic of the linear response theory, not the results. As van

Kampen[296] expressed it, "the task of statistical mechanics is not only to provide an expression for this (transport) coefficient in term of molecular quantities, but also to understand how such a linear dependence arises from the microscopic equations of motion."

van Kampen's objections[296] to Kubo linear response theory can be reduced to the following points. In the linear response theory, one solves the Liouville equation to first-order in the external field $\mathbf{E}$ (electric field). This is practically equivalent to following a perturbed trajectory in phase space in a vicinity of the order of $|\mathbf{E}|$ of unperturbed trajectory. In the classical case, trajectories are exponentially unstable and the corresponding field $\mathbf{E}$ should be very small. Kubo's derivation supposed nonexplicitly that macroscopic linearity (Ohm law, etc.) is the consequence of microscopic linearity, but these two notions are not identical. Macroscopic linearity is the result of averaging over many trajectories and is not the same as linear deviations from any one trajectory. In other words, van Kampen's argument was based on the observation that due to the Lyapunov instability of phase-space trajectories, even a very small external field will rapidly drive any trajectory far away from the corresponding trajectory without field. Hence, linear response theory which is based on the proportionality of the trajectory separation with the external field could only be expected to hold for extremely short times, of no physical interest. Responses to van Kampen's objections were given by many authors.[46,214,297–301] The main arguments of these responses were based on the deep analysis of the statistical mechanical behavior of the many-body system under the external perturbation. It was shown that in statistical mechanical calculations, one deals with the probability distributions for the behavior of the many particles than an individual particle. An analysis of the structural stability of hyperbolic dynamics-averaging and some other aspects of the dynamical behavior shows that the linear separation of trajectories goes on long enough for Green–Kubo integrals to decay. Moreover, Naudts, Pule and Verbeure[302] analyzed the long-time behavior of correlations between extensive variables for spin-lattice systems and showed that the Kubo formula, expressing the relaxation function in terms of of the linear response function, is exact in the thermodynamic limit.

It was mentioned above that in the 1950s and 1960s, the fluctuation relations, that is, the so-called Green–Kubo relations,[45,46,303–305] were derived for the causal transport coefficients that are defined by causal linear constitutive relations such as Fourier law of heat flow or Newton law of viscosity. Later it was shown also that it was possible to derive an exact expression for linear transport coefficients which is valid for systems of arbitrary temperature, T, and density. The Green–Kubo relations give exact mathematical expression for transport coefficients in terms of integrals of time correlation functions.[45,46,303–305] More precisely, it was shown that linear transport coefficients are exactly related to the time dependence of equilibrium fluctuations in the conjugate flux. For a more detailed discussion of these questions, see Refs. 45, 46, 302–305.

To summarize, close to equilibrium, linear response theory and linear irreversible thermodynamics provide a relatively complete treatment. However, in systems where local thermodynamic equilibrium has broken down, and thermodynamic properties are not the same local functions of thermodynamic state variables such that they are at equilibrium, serious problems may appear.[45,46]

9. The Nonequilibrium Statistical Operator Method and Kinetic Equations

The method of the nonequilibrium statistical order (NSO)[42,43,211,212,306] was reviewed already in detail[45] by us. In this section, we remind very briefly the main ideas of the NSO approach[42,43,45,211,212,306,307] for the sake of a self-contained formulation. The precise definition of the nonequilibrium state is quite difficult and complicated and is not uniquely specified. Thus, the method of reducing the number of relevant variables was proposed. A large and important class of transport processes can reasonably be modeled in terms of a reduced number of macroscopic relevant variables.[42,215] It was supposed that the equations of motion for the "relevant" variables (the space- and time-dependent thermodynamic "coordinates" of a many-body nonequilibrium system), can be derived directly from the Liouville equation. This can be done by defining a generalized canonical density operator depending only upon present values of the thermodynamic "coordinates". According to Zubarev,[42,43] the NSO method permits one to generalize the Gibbs ensemble method to the nonequilibrium case and to construct an NSO which enables one to obtain the transport equations and calculate the kinetic coefficients in terms of correlation functions, and which, in the case of equilibrium, goes over to the Gibbs distribution. The basic hypothesis is that after small time-interval τ, the nonequilibrium distribution is established. Moreover, it is supposed that it is weakly time-dependent by means of its parameter only. Then the statistical operator ρ for $t \geq \tau$ can be considered as an "integral of motion" of the quantum Liouville equation

$$\frac{\partial \rho}{\partial t} + \frac{1}{i\hbar}[\rho, H] = 0\,. \tag{9.1}$$

Here $\partial\rho/\partial t$ denotes time differentiation with respect to the time variable on which the relevant parameters F_m depend. It is important to note once again that ρ depends on t by means of $F_m(t)$ only. We may consider that the system is in thermal, material, and mechanical contact with a combination of thermal baths and reservoirs maintaining the given distribution of parameters F_m. For example, it can be the densities of energy, momentum and particle number for the system which is macroscopically defined by given fields of temperature, chemical potential and velocity. It is assumed that the chosen set of parameters is sufficient to characterize macroscopically the state of the system. The set of the relevant parameters is dictated by the external conditions for the system under consideration and, therefore, the term $\partial\rho/\partial t$ appears as the result of the external influence upon the system; this influence causes that the system is nonstationary.

In order to describe the nonequilibrium process, it is also necessary to choose the reduced set of relevant operators P_m, where m is the index (continuous or discrete). In the quantum case, all operators are considered to be in the Heisenberg representation

$$P_m(t) = \exp\left(\frac{iHt}{\hbar}\right) P_m \exp\left(\frac{-iHt}{\hbar}\right), \tag{9.2}$$

where H does not depend on the time. The relevant operators may be scalars or vectors. The equations of motions for P_m will lead to the suitable "evolution equations".[42,45] In the quantum case,

$$\frac{\partial P_m(t)}{\partial t} - \frac{1}{i\hbar}[P_m(t), H] = 0\,. \tag{9.3}$$

The time argument of the operator $P_m(t)$ denotes the Heisenberg representation with the Hamiltonian H independent of time. Then we suppose that the state of the ensemble is described by an NSO which is a functional of $P_m(t)$

$$\rho(t) = \rho\{\cdots P_m(t)\cdots\}\,. \tag{9.4}$$

Then $\rho(t)$ satisfies the Liouville equation (9.1). Hence the quasi-equilibrium (local equilibrium) Gibbs-type distribution will have the form

$$\rho_q = Q_q^{-1} \exp\left(-\sum_m F_m(t) P_m\right), \tag{9.5}$$

where the parameters $F_m(t)$ have the sense of time-dependent thermodynamic parameters, e.g., of temperature, chemical potential and velocity (for the hydrodynamic stage), or the occupation numbers of one-particle states (for the kinetic stage). The statistical functional Q_q is defined by demanding that the operator ρ_q be normalized and equal to

$$Q_q = \mathrm{Tr}\, \exp\left(-\sum_m F_m(t) P_m\right). \tag{9.6}$$

The kinetic equations are of great interest in the theory of transport processes. In the NSO approach,[42,45,307] the main quantities involved are the following thermodynamically conjugate values:

$$\langle P_m\rangle = -\frac{\delta\Omega}{\delta F_m(t)}\,; \quad F_m(t) = \frac{\delta S}{\delta\langle P_m\rangle}\,. \tag{9.7}$$

The generalized transport equations that describe the time evolution of variables $\langle P_m\rangle$ and F_m follow from the equation of motion for the P_m, averaged with the NSO (9.4). It reads

$$\langle \dot{P}_m\rangle = -\sum_n \frac{\delta^2\Omega}{\delta F_m(t)\delta F_n(t)} \dot{F}_n(t)\,; \quad \dot{F}_m(t) = \sum_n \frac{\delta^2 S}{\delta\langle P_m\rangle \delta\langle P_n\rangle}\langle \dot{P}_n\rangle\,. \tag{9.8}$$

10. Generalized Kinetic Equations and Electroconductivity

10.1. *Basic formulas*

Let us consider a many-particle system in the quasi-equilibrium state. It is determined completely by the quasi-integrals of motion, which are the internal parameters of the system. In this and following sections, we will use the notation A_j for the relevant observables to distinguish it from the momentum operator $\mathbf{P}$. Here, for the sake of simplicity, we shall mainly treat the simplest case of mechanical perturbations acting on the system. The total Hamiltonian of the system under the influence of homogeneous external perturbation, depending on time as $\sim \exp(i\omega t)$ is written in the following form

$$\mathcal{H}(t) = H + H_F(t)\,, \quad H_F(t) = -\sum_j A_j F_j \exp(i\omega t)\,. \tag{10.1}$$

In the standard approach the statistical operator ρ can be considered as an "integral of motion" of the quantum Liouville equation

$$\frac{\partial\rho(t)}{\partial t} + \frac{1}{i\hbar}[\rho(t), \mathcal{H}(t)] = 0\,. \tag{10.2}$$

Using the ideas of the method of the NSO, as it was described above, we can write

$$\rho(t) = \varepsilon \int_{-\infty}^{t} dt_1 e^{-\varepsilon(t-t_1)} U(t,t_1)\rho(t_1)U^\dagger(t,t_1)\,. \tag{10.3}$$

The time-evolution operator $U(t,t_1)$ satisfy the conditions

$$\frac{\partial}{\partial t}U(t,t_1) = \frac{1}{i\hbar}\mathcal{H}(t)U(t,t_1)\,,$$

$$\frac{\partial}{\partial t_1}U(t,t_1) = -\frac{1}{i\hbar}\mathcal{H}(t)U(t,t_1)\,, \quad U(t,t) = 1\,.$$

If we consider the special case in which $\rho(t_1) \to \rho_0$, where ρ_0 is an equilibrium solution of the quantum Liouville equation (10.2), then we can find the NSO from the following equation:

$$\frac{\partial\rho_\varepsilon^K(t)}{\partial t} + \frac{1}{i\hbar}[\rho_\varepsilon^K, \mathcal{H}(t)] = -\varepsilon(\rho_\varepsilon^K - \rho_0)\,. \tag{10.4}$$

In the $\lim_{\varepsilon\to 0^+}$ the NSO will corresponds to the Kubo density matrix

$$\rho_\varepsilon^K(t) = \rho_0 = \frac{1}{i\hbar}\int_{-\infty}^{t} dt_1 e^{-\varepsilon(t-t_1)} U(t,t_1)[\rho_0, H_F(t_1)]U^\dagger(t,t_1)\,. \tag{10.5}$$

An average of the observable B_j are defined as

$$\lim_{\varepsilon\to 0^+} \mathrm{Tr}(\rho_\varepsilon^K(t)B_j) = \langle B_j\rangle_t\,.$$

The linear response approximation for the statistical operator is given by

$$\rho_\varepsilon^K(t) = \rho_0 - \frac{1}{i\hbar}\sum_j A_j F_j \exp(i\omega t)\int_{-\infty}^0 dt_1 e^{(\varepsilon+i\omega)t_1}$$

$$\times \exp\left(\frac{iHt_1}{\hbar}\right)[\rho_0, A_j]\exp\left(\frac{-iHt_1}{\hbar}\right). \tag{10.6}$$

Using the obtained expression for the statistical operator, the mean values of the relevant observables B_i can be calculated. To simplify notation, only observables will be considered for which the mean value in the thermal equilibrium vanishes. In other words, in general, the B_i will be replaced by $B_i - \langle B_i\rangle_0$, where $\langle B_i\rangle_0 = \mathrm{Tr}(\rho_0 B_i)$. We find

$$\langle B_i\rangle_t \equiv \mathrm{Tr}(\rho_\varepsilon^K(t)B_i) = \sum_j L_{ij}(\omega)F_j\exp(i\omega t)\,, \tag{10.7}$$

where the linear response coefficients (linear admittances) are given by

$$L_{ij}(\omega) = \langle \dot{A}_j; B_i\rangle_{\omega - i\varepsilon}\,, \quad (\varepsilon \to 0^+)\,. \tag{10.8}$$

This expression vanish for operators A_j commuting with the Hamiltonian H of the system, i.e., the Kubo expressions for $L_{ij}(\omega)$ vanish for all ω where for $\omega = 0$ the correct result is given by

$$\langle B_i\rangle = \beta\sum_j F_j \mathrm{Tr}(\rho_0 A_j B_i) = \sum_j L_{ij}(\omega)F_j\exp(i\omega t)\,. \tag{10.9}$$

The scheme based on the NSO approach starts with the generalized Liouville equation

$$\frac{\partial\rho_\varepsilon(t)}{\partial t} + \frac{1}{i\hbar}[\rho_\varepsilon(t), \mathcal{H}(t)] = -\varepsilon(\rho_\varepsilon(t) - \rho_q(t))\,. \tag{10.10}$$

For the set of the relevant operators P_m, it is follow that

$$\frac{d}{dt}\mathrm{Tr}(\rho_\varepsilon(t)P_m) = 0\,. \tag{10.11}$$

Here notation are

$$\rho_q(t) = Q^{-1}\exp\left[-\beta\left(H - \mu N - \sum_m F_m(t)P_m\right)\right], \tag{10.12}$$

$$F_m(t) = F_m\exp(i\omega t)\,, \quad P_m \to P_m - \langle P_m\rangle_0\,.$$

To find the approximate evolution equations, the $\rho_\varepsilon(t)$ can be linearized with respect to the external fields F_j and parameters F_m

$$\rho(t) = \rho_q(t) - \exp(i\omega t)\rho_0\left(\int_{-\infty}^0 dt_1 e^{(\varepsilon+i\omega)t_1}\int_0^\beta d\tau\right.$$

$$\times\left[-\sum_j F_j\dot{A}_j(t-i\tau)+\sum_m F_m\dot{P}_m(t-i\tau)+i\omega\sum_m F_mP_m(t-i\tau)\right]\Bigg)\,. \tag{10.13}$$

As a result, we find

$$\sum_n F_n(\langle\dot{P}_n;P_m\rangle_{\omega-i\varepsilon}+i\omega\langle P_n;P_m\rangle_{\omega-i\varepsilon})=\sum_j F_j\langle\dot{A}_j;P_m\rangle_{\omega-i\varepsilon}\,. \tag{10.14}$$

In other notation, we obtain

$$\begin{aligned}&\sum_n F_n((\dot{P}_n|P_m)+\langle\dot{P}_n;\dot{P}_m\rangle_{\omega-i\varepsilon}+i\omega[(P_n|P_m)+\langle P_n;\dot{P}_m\rangle_{\omega-i\varepsilon}])\\ &\qquad=\sum_j F_j((\dot{A}_j|P_m)+\langle\dot{A}_j;\dot{P}_m\rangle_{\omega-i\varepsilon})\,,\end{aligned} \tag{10.15}$$

where

$$\begin{aligned}\langle A;B\rangle_{\omega-i\varepsilon}&=\int_{-\infty}^{\infty}dte^{(\omega-i\varepsilon)t}(A(t)|B)\,;\\ (A|B)&=\int_0^{\beta}d\lambda\mathrm{Tr}(\rho_0A(-i\lambda)B)\,,\quad \rho_0=\frac{1}{Q}e^{-\beta H}\,;\\ \chi_{ij}&=(A_i|A_j)\,,\quad \sum_k\chi_{ik}(\chi^{-1})_{kj}=\delta_{ij}\,.\end{aligned} \tag{10.16}$$

Thus, our generalized transport equation can be written in the following abbreviated form

$$\sum_n F_nP_{nm}=\sum_j F_jK_{jm}\,. \tag{10.17}$$

10.2. *Electrical conductivity*

The general formalism of the NSO has been the starting point of many calculations of transport coefficients in concrete physical systems. In the present section, we consider some selected aspects of the theory of electron conductivity in transition metals and disordered alloys.[308–310] We put $\hbar=1$ for simplicity of notation. Let us consider the dc electrical conductivity

$$\sigma=\frac{e^2}{3m^2\Omega}\langle\mathbf{P};\mathbf{P}\rangle=\frac{e^2}{3m^2\Omega}\int_{-\infty}^{0}dte^{\varepsilon t}\int_0^{\beta}d\lambda\mathrm{Tr}(\rho P(t-i\lambda)\mathbf{P})\,,\quad \varepsilon\to 0 \tag{10.18}$$

where $\mathbf{P}$ is the total momentum of the electrons. Representing $\mathbf{P}$ 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[308]

$$\sum_k\left(i\varepsilon\delta_{ik}-i\sum_l(\dot{A}_l|A_l)(\chi^{-1})_{lk}+i\sum_l\Pi_{il}(\chi^{-1})_{lk}\right)\langle A_k;A_j\rangle=i\chi_{ij}\,, \tag{10.19}$$

where

$$\chi_{ij} = (A_i|A_j)\,, \quad \sum_k \chi_{ik}(\chi^{-1})_{kj} = \delta_{ij}\,; \tag{10.20}$$

$$(A_i|A_j) = \int_0^\beta d\lambda \mathrm{Tr}(\rho A_i(-i\lambda)A_j)\,, \quad \rho = \frac{1}{Q}e^{-\beta H}\,; \tag{10.21}$$

$$\Pi_{ij} = \langle \dot{A}_i\tilde{C}|C\dot{A}_j\rangle^C\,, \quad \dot{A}_l = i[H, A_l]\,. \tag{10.22}$$

The operator $\tilde{C} = 1 - \tilde{P}$ is a projection operator[308] with $\tilde{P} = \sum_{ij}|A_i)(\chi^{-1})_{ij}(A_i|$ and $\langle\cdots\rangle^C$ denotes that in the time-evolution of this correlation function, operator $L = i[H,\ldots]$ is to be replaced by CLC. By solving the set of equations (10.19), the correlation functions $\langle A_i; A_j\rangle$ which we started from are replaced by the correlation functions Π_{ij} (10.22), and with a proper choice of the relevant observables these correlation functions can be calculated in a fairly simple approximation.[308] It is, however, difficult to go beyond this first approximation and, in particular, to take into account the projection operators. Furthermore, this method is restricted to the calculation of transport coefficients where the exact linear response expressions are known; generalization to thermal transport coefficients is not trivial. In Ref. 307, we described a kind of general formalism for the calculation of transport coefficients which includes the approaches discussed above and which can be adapted to the problem investigated.

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

$$\rho_{LR} = \frac{e\mathbf{E}}{m}\int_{-\infty}^t dt' e^{\varepsilon(t'-t)}\int_0^\beta d\lambda\rho\mathbf{P}(t'-t-i\lambda)\,, \quad \varepsilon \to 0\,, \tag{10.23}$$

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 statistical operator of the form

$$\rho_q = \frac{1}{Q_q}e^{-\beta(H - \sum_i \alpha_i A_i)}\,, \tag{10.24}$$

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 statistical operator (10.24) is not a solution of the Liouville equation, but an exact solution can be found starting from (10.24) as an initial condition:

$$\rho_s = \rho_q - i\int_{-\infty}^o dt' e^{\varepsilon(t'-t)}\exp(iH_s(t'-t))\rho_q\exp(-iH_s(t'-t))\,, \tag{10.25}$$

where $H_s = H - e\mathbf{E}\sum_i \mathbf{r}_i$. 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.,

$$\mathrm{Tr}(\rho_s A_i) = \mathrm{Tr}(\rho_q A_i)\,. \tag{10.26}$$

This condition is equivalent to the stationarity condition

$$\frac{d}{dt}\mathrm{Tr}(\rho_s A_i) = 0\,.$$

For a sufficiently complete set of operators A_i, the condition (10.26) ensures that ρ_q describes the system with a sufficient accuracy. Linearizing Eq. (10.26) with respect to the parameters α_i and the external field E, one obtains the set of equations

$$\sum_j \alpha_j(-i\,\mathrm{Tr}(\rho[A_j, A_i]) + \langle \dot{A}_j; \dot{A}_i\rangle) = \frac{e\mathbf{E}}{m}((\mathbf{P}|A_i) + \langle \mathbf{P}; \dot{A}_i\rangle)\,. \tag{10.27}$$

This set of equations can be shown to be equivalent to Eq. (10.19); whereas in the higher orders of interaction the Eqs. (10.27) are more convenient to handle because the time dependence is given here in an explicit form without any projection.

With the parameters α_i, the current density is given by

$$\mathbf{J} = \frac{e}{m\Omega}\mathrm{Tr}(\rho_q \mathbf{P}) = \frac{e}{m\Omega}\sum_j \alpha_j (A_j|\mathbf{P})\,. \tag{10.28}$$

Supposing that the total momentum $\mathbf{P}$ of the electrons can be built up by the operators A_i, it can be shown that Eqs. (10.27) and (10.28) include the Kubo expression for the conductivity (see below). In order to solve the system of equations (10.27), 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.

11. Resistivity of Transition Metal with Nonspherical Fermi Surface

The applicability of the transport equations (10.27) and (10.28) derived above to a given problem depends strongly on the choice of the relevant operators A_i. The first condition to be fulfilled is that the mean values of the occupation numbers of all quasiparticles involved in the transport process should be time-independent, i.e.,

$$\mathrm{Tr}(\rho_s(\alpha_i) n_k) = \mathrm{Tr}(\rho_q(\alpha_i) n_k)\,, \quad \frac{d}{dt}\mathrm{Tr}(\rho_s(\alpha_i) n_k) = 0\,. \tag{11.1}$$

Of course, this condition is fulfilled trivially for $A_i \to n_k$, but in this case the equations (10.27) cannot be solved in practice. In the most cases, however, a reduced set of operators can be found which is 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 one relaxation time only and then the set of relevant operators reduces to the total momentum of the electrons describing a homogeneous shift of the Fermi body in the Bloch (momentum) space. These conditions are fulfilled for a spherical Fermi body at temperatures that are 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, Eqs. (10.27) are reduced to the so-called resistivity formula.[308] For nonspherical 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. Our aim is to develop a theory of electron conductivity for the one-band model of a transition metal. The model considered is the modified Hubbard model, which include the electron–electron interaction as well as the electron–lattice interaction within MTBA. The nonspherical Fermi surface is taken into account.

The studies of the electrical resistivity of many transition metals revealed some peculiarities. It is believed that these specific features are caused by the fairly complicated dispersion law of the carriers and the existence of the two subsystems of the electrons, namely the broad s–p band and relatively narrow d-band. The Fermi surface of transition metals is far from the spherical form. In addition, the lattice dynamics and dispersion relations of the phonons are much more complicated than in simple metals. As a result, it is difficult to attribute the observed temperature dependence of the resistivity of transition metals to definite scattering mechanisms.

Here we investigate the influence of the electron dispersion on the electrical resistivity within a simplified but workable model. We consider an effective single-band model of transition metal with tight-binding dispersion relation of the electrons. We take into account the electron–electron and electron–lattice interactions within the extended Hubbard model. The electron–lattice interaction is described within the MTBA. For the calculation of the electrical conductivity, the generalized kinetic equations are used which were derived by the NSO method. In these kinetic equations, the shift of the nonspherical Fermi surface and its deformation by the external electrical field are taken into account explicitly. By using the weak scattering limit, the explicit expressions for the electrical resistivity are obtained and its temperature dependence is estimated.

We consider a transition metal model with one nonspherical Fermi body shifted in the k-space and deformed by the external electrical field. Hence, the Fermi surface equation $E(\mathbf{k}) = E_F$ is transformed into $\tilde{E}(\mathbf{k}) = E_F$, where

$$\tilde{E}(\mathbf{k}) = E(\mathbf{k}) + m\mathbf{v}_1 \frac{\partial E}{\partial \mathbf{k}} + m \sum_{i=1\sigma}^{n} \mathbf{v}_i \Phi^i(\mathbf{k}) \frac{\partial E}{\partial \mathbf{k}} + \cdots \tag{11.2}$$

The term proportional to $\mathbf{v}_1$ describes a homogeneous shift of the Fermi surface in the k-space and the last terms allow for deformations of the Fermi body. The polynomials $\Phi^i(\mathbf{k})$ have to be chosen corresponding to the symmetry of the crystal[96,311–313] and in consequence of the equality $\tilde{E}(\mathbf{k}+\mathbf{G}) = \tilde{E}(\mathbf{k})$ (which is fulfilled in our tight-binding model), they should satisfy the relation

$$\Phi^i(\mathbf{k}+\mathbf{G}) = \Phi^i(\mathbf{k})\,,$$

where $\mathbf{G}$ is a reciprocal lattice vector. Thus the relevant operators are given by

$$A_i \to m\sum_{k\sigma}\Phi^i(\mathbf{k})\frac{\partial E}{\partial \mathbf{k}}n_{k\sigma}\,, \quad \Phi^1 = 1\,. \tag{11.3}$$

For our tight-binding model we are restricting by the assumption that $\Phi^i \to 0$ for $i \geq 3$.

11.1. *Generalized kinetic equations*

The quantum-mechanical many-body system is described by the statistical operator ρ_s obeying the modified Liouville equation of motion Eq. (10.10)

$$\frac{\partial \rho_s}{\partial t} + \frac{1}{i\hbar}[\rho_s, H_s] = -\varepsilon(\rho_s - \rho_q)\,, \tag{11.4}$$

where $H_s = H + H_E$ is the total Hamiltonian of the system, including the interaction with an external electrical field $H_E = -e\mathbf{E}\sum_i \mathbf{r_i}$, and ρ_q is the quasi-equilibrium statistical operator. According to the NSO formalism, the relevant operators P_m should be selected. These operators include all the relevant observables which describe the reaction of the system on the external electrical field. These relevant operators satisfy the condition

$$\mathrm{Tr}(\rho_s(t,0)P_m) = \langle P_m\rangle = \langle P_m\rangle_q\,; \quad \mathrm{Tr}\rho_s = 1\,. \tag{11.5}$$

This condition is equivalent to the stationarity condition

$$\frac{d}{dt}\langle P_m\rangle = 0 \to \langle [H_s, P_m]\rangle + \langle [H_E, P_m]\rangle = 0\,. \tag{11.6}$$

In the framework of the linear response theory, the operators ρ_s and ρ_q in Eqs. (11.5) and (11.6) should be expanded to the first-order in the external electrical field $\mathbf{E}$ and in the parameters F_m. Thus Eq. (11.6) becomes[308]

$$\sum_n F_n(-i\,\mathrm{Tr}(\rho[P_n, P_m]) + \langle \dot{P}_n; \dot{P}_m\rangle) = \frac{eE}{m}(\mathrm{Tr}(\rho\mathbf{P}(-i\lambda)P_m) + \langle \mathbf{P}; \dot{P}_m\rangle)\,, \tag{11.7}$$

where

$$\dot{P}_m = i[H_s, P_m]\,, \tag{11.8}$$

$$\langle A; B\rangle = \int_{-\infty}^{0} dt e^{\varepsilon t}\int_0^\beta d\lambda\,\mathrm{Tr}(\rho A(t-i\lambda)B)\,, \tag{11.9}$$

$$A(t) = \exp(iHt)A\exp(-iHt)\,; \quad \rho = Q^{-1}\exp(-\beta H)\,,$$

and P is the total momentum of the electrons.

Equations (11.7) is a generalized kinetic equation in which the relaxation times and particle numbers are expressed via the correlation functions. It will be shown below that these equations can be reduced to the Kubo formula for the electrical conductivity provided a relation $\mathbf{P}_e = \sum \alpha_i P_i$ can be found.

The generalized kinetic equation (11.7) can be solved and the parameters F_m can be determined by using a variational principle. The current density is given by

$$\mathbf{j} = \frac{e}{m\Omega}\mathrm{Tr}(\rho_s \mathbf{P}_e) = \frac{e}{m\Omega}\mathrm{Tr}(\rho_q \mathbf{P}_e)\,, \tag{11.10}$$

where the conditions in (11.5) have been used and Ω is the volume of the system. Linearizing Eq. (11.10) in the parameter F_m, we find

$$\mathbf{j} = \frac{e}{m\Omega}\sum_m F_m \int_0^\beta d\lambda\,\mathrm{Tr}(\rho P_m(t-i\lambda)\mathbf{P}_e) \equiv \frac{1}{R}\mathbf{E}\,, \tag{11.11}$$

where the proportionality of the F_m to the external electrical field has been taken into account. For the tight-binding model Hamiltonian (4.65) and (4.66), the proper set of operators P_m is given by

$$P_e = P_1 = m\sum_{k\sigma}\frac{\partial E}{\partial k}a^\dagger_{k\sigma}a_{k\sigma}\,, \tag{11.12}$$

$$P_i = m\sum_{k\sigma}\Phi^i(\mathbf{k})\frac{\partial E}{\partial k}a^\dagger_{k\sigma}a_{k\sigma}\,, \quad (i = 2\ldots n)\,. \tag{11.13}$$

The parameters F_m are replaced by the generalized drift velocities. Then the quasi-equilibrium statistical operator ρ_q take the form

$$\rho_q = \frac{1}{Q_q}\exp\left(-\beta\left[H + mv_1\sum_{k\sigma}\frac{\partial E}{\partial k}a^\dagger_{k\sigma}a_{k\sigma} + \sum_{i=2\ldots n} mv_i\Phi^i(\mathbf{k})\frac{\partial E}{\partial k}a^\dagger_{k\sigma}a_{k\sigma}\right]\right). \tag{11.14}$$

It should be mentioned here that in general in ρ_q, the redistribution of the scatterers by collisions with electrons should be taken into consideration. For the electron–phonon problem, e.g., the phonon drag can be described by an additional term $\mathbf{v}_{ph}\mathbf{P}_{ph}$ in Eq. (11.2), where $\mathbf{v}_{ph}$ is the mean drift velocity and $\mathbf{P}_{ph}$ is the total momentum of the phonons. Here it will be supposed for simplicity, that due to phonon-phonon *Umklapp* processes, etc., the phonon subsystem remains near thermal equilibrium. In the same way, the above consideration can be generalized to many-band case. In the last case, the additional terms in (11.2), describing shift and deformation of other Fermi bodies should be taken into account.

For the tight-binding model Hamiltonian (4.65) and (4.66), the time derivatives of the generalized momenta (generalized forces) in Eq. (11.7) are given by

$$\dot{P}_n \to \dot{P}_j = \dot{P}^{ee}_j + \dot{P}^{ei}_j\,, \tag{11.15}$$

$$\begin{aligned}\dot{P}^{ee}_j &= i[H_{ee}, P_j]\\ &= \frac{iUm}{N}\sum_{k_1k_2}\sum_{k_3k_4G}\left(\Phi^j(\mathbf{k}_4)\frac{\partial E}{\partial k_4} + \Phi^j(\mathbf{k}_2)\frac{\partial E}{\partial k_2} - \Phi^j(\mathbf{k}_3)\frac{\partial E}{\partial k_3} - \Phi^j(\mathbf{k}_1)\frac{\partial E}{\partial k_1}\right)\\ &\quad\times a^\dagger_{k_1\uparrow}a_{k_2\uparrow}a^\dagger_{k_3\downarrow}a_{k_4\downarrow}\delta(\mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3 - \mathbf{k}_4 + \mathbf{G})\,,\end{aligned} \tag{11.16}$$

$$\dot{P}_j^{ei} = m \sum_{k_1 k_2} \sum_{qG} \sum_{\sigma\nu} g^{\nu}_{k_1 k_2} \left(\Phi^j(\mathbf{k}_2) \frac{\partial E}{\partial k_2} - \Phi^j(\mathbf{k}_1) \frac{\partial E}{\partial k_1} \right)$$
$$\times a^{\dagger}_{k_2\sigma} a_{k_1\sigma} (b^{\dagger}_{q\nu} + b_{-q\nu}) \delta(\mathbf{k}_2 - \mathbf{k}_1 + \mathbf{q} + \mathbf{G}) \,. \tag{11.17}$$

We confine ourselves by the weak scattering limit. For this case the total Hamiltonian H in evolution $A(t) = \exp(iHt)A\exp(-iHt)$, we replace by the Hamiltonian of the free quasiparticles $H_e^0 + H_i^0$. With this approximation, the correlation functions in Eq. (11.7) can be calculated straightforwardly. We find that

$$\langle \dot{P}_j ; \dot{P}_l \rangle \approx \langle \dot{P}_j^{ee} ; \dot{P}_l^{ee} \rangle + \langle \dot{P}_j^{ei} ; \dot{P}_l^{ei} \rangle \,. \tag{11.18}$$

Restricting ourselves for simplicity to a cubic system, the correlation functions of the generalized forces are given by

$$\langle \dot{P}_j^{ee} ; \dot{P}_l^{ee} \rangle = \frac{U^2 m^2 \beta\pi}{N^2} \sum_{k_1 k_2} \sum_{k_3 k_4 G} A_j(k_1, k_2, k_3, k_4) A_l(k_1, k_2, k_3, k_4)$$
$$\times f_{k_1}(1 - f_{k_2}) f_{k_3}(1 - f_{k_4}) \delta(E(k_1) - E(k_2) + E(k_3) - E(k_4))$$
$$\times \delta(\mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3 - \mathbf{k}_4 + \mathbf{G}) \,, \tag{11.19}$$

$$\langle \dot{P}_j^{ei} ; \dot{P}_l^{ei} \rangle = 2\pi m^2 \beta \sum_{k_1 k_2} \sum_{q\nu G} (g^{\nu}_{k_1 k_2})^2 B_j(k_1, k_2) B_l(k_1, k_2)$$
$$\times f_{k_2}(1 - f_{k_1}) N(q\nu) \delta(E(k_2) - E(k_1) + \omega(q\nu))$$
$$\times \delta(\mathbf{k}_2 - \mathbf{k}_1 - \mathbf{q} + \mathbf{G}) \,, \tag{11.20}$$

where

$$A_j(k_1, k_2, k_3, k_4) = \left(\Phi^j(\mathbf{k}_4) \frac{\partial E}{\partial k_4} + \Phi^j(\mathbf{k}_2) \frac{\partial E}{\partial k_2} - \Phi^j(\mathbf{k}_3) \frac{\partial E}{\partial k_3} - \Phi^j(\mathbf{k}_1) \frac{\partial E}{\partial k_1} \right) , \tag{11.21}$$

$$B_j(k_1, k_2) = \left(\Phi^j(\mathbf{k}_2) \frac{\partial E}{\partial k_2} - \Phi^j(\mathbf{k}_1) \frac{\partial E}{\partial k_1} \right) \tag{11.22}$$

and

$$f(E(k)) = f_k = [\exp \beta(E(k) - E_F) + 1]^{-1} \,,$$
$$N(\omega(q\nu)) = N(q\nu) = [\exp \beta\omega(q\nu) - 1]^{-1} \,.$$

The correlation functions $\langle \mathbf{P}_1 ; \dot{\mathbf{P}}_l \rangle$ vanish in the weak scattering limit. The generalized electron numbers in Eq. (11.13) become

$$N_l = \frac{1}{m} \mathrm{Tr}(\rho \mathbf{P}_1(i\lambda); \mathbf{P}_l) = m\beta \sum_k \Phi^l(\mathbf{k}) \frac{\partial E}{\partial \mathbf{k}} f_k(1 - f_k) \,. \tag{11.23}$$

11.2. *Temperature dependence of R*

Let us consider the low-temperature dependence of the electrical resistivity obtained above. For this region, we have

$$\lim_{T\to 0} \beta f_k(1-f_k) \to \delta(E(k)-E_F)\,.$$

Thus the generalized electron numbers N_l in Eq. (11.23) do not depend on temperature, and the temperature dependence of R in Eq. (11.11) is given by the correlation functions (11.19) and (11.20). For the term arising from the electron–electron scattering, we find

$$\begin{aligned}\langle \dot{P}_j^{ee}; \dot{P}_l^{ee}\rangle &= \beta \int_0 \iint^{E_{\max}} dE(k_1)dE(k_2)dE(k_3)F^1_{jl}(E(k_1),E(k_2),E(k_3)) \\ &\quad \times f_{k_1}(1-f_{k_2})f_{k_3}[1-f(E(k_1)-E(k_2)+E(k_3))]\,,\end{aligned} \tag{11.24}$$

where

$$\begin{aligned}&F^1_{jl}(E(k_1),E(k_2),E(k_3)) \\ &\quad = \frac{U^2m^2\pi}{N^2}\frac{\Omega^3}{(2\pi)^9}\sum_G \int d^2S_1 \int d^2S_2 \int d^2S_3 \\ &\quad\quad \times \frac{A_j(k_1,k_2,k_3,k_1-k_2+k_3+G)A_l(k_1,k_2,k_3,k_1-k_2+k_3+G)}{\left|\frac{\partial E}{\partial k_1}\right|\left|\frac{\partial E}{\partial k_2}\right|\left|\frac{\partial E}{\partial k_3}\right|} \\ &\quad\quad \times \delta(E(k_1)-E(k_2)+E(k_3)-E(k_1-k_2+k_3+G))\,.\end{aligned} \tag{11.25}$$

With the substitution

$$x = \beta(E(k_1)-E_F)\,, \quad y=\beta(E(k_2)-E_F)\,, \quad z=\beta(E(k_3)-E_F)\,,$$

the expression (11.24) reads

$$\begin{aligned}\langle \dot{P}_j^{ee}; \dot{P}_l^{ee}\rangle &= \beta^{-2}\int_{-\beta E_F}\iint^{\beta E_{\max}-E_F} \frac{1}{1+\exp(x)}\frac{1}{1+\exp(-y)}\frac{1}{1+\exp(z)} \\ &\quad\quad \times \frac{dxdydz}{1+\exp(-x+y-z)}F^1\left(\frac{x}{\beta}+E_F, \frac{y}{\beta}+E_F, \frac{z}{\beta}+E_F\right) \\ &= \beta^{-2}A^{ee}_{jl}\,.\end{aligned} \tag{11.26}$$

It is reasonably to conclude from this expression, that in the limits

$$\lim \beta E_F \to \infty\,, \quad \lim \beta(E_{\max}-E_F)\to\infty\,,$$

the electron–electron correlation function for low temperatures becomes proportional to T^2 for any polynomial $\Phi^j(\mathbf{k})$.

For the electron–phonon contributions to the resistivity, the temperature dependence is given by the Bose distribution function of phonons $N(q\nu)$. Because of the quasimomentum conservation law $\mathbf{q} = \mathbf{k}_2 - \mathbf{k}_1 - \mathbf{G}$, the contribution of the electron–phonon *Umklapp* processes freezes out at low temperatures as $[\exp \beta\omega(q_{\min}) - 1]^{-1}$, where $q_{\min}$ is the minimal distance between the closed Fermi surfaces in the extended zone scheme. For electron–phonon normal processes as well as for electron–phonon *Umklapp* processes in metals with an open Fermi surface, the quasimomentum conservation law can be fulfilled for phonons with $q \to 0$ being excited at low temperatures solely. To proceed further, we use the relation $\omega(q\nu) = v_0^\nu(\mathbf{q}/q)$ and the periodicity of the quasiparticle dispersion relation with the reciprocal lattice vector $\mathbf{G}$. Taking into account the relation $\Phi^i(\mathbf{k} + \mathbf{G}) = \Phi^i(\mathbf{k})$, we find to the first nonvanishing order in q

$$g^\nu_{k,k+q+G} \approx q\left(\frac{\mathbf{q}}{q}\frac{\partial}{\partial k'}\right) g^\nu_{k,k'}|_{k'=k}\,, \tag{11.27}$$

$$B_j(k, k+q+G) \approx q(\frac{\mathbf{q}}{q}\frac{\partial}{\partial k'})B_j(k,k')|_{k'=k}\,, \tag{11.28}$$

$$\delta(E(k+q+G) - E(k) + \omega(q\nu)) \approx \frac{1}{q}\delta\left(\frac{\mathbf{q}}{q}\frac{\partial E}{\partial k} + v_0^\nu\right). \tag{11.29}$$

Hence, we have

$$\begin{aligned}\langle \dot{P}_j^{ei}; \dot{P}_l^{ei}\rangle &\cong m^2\beta\frac{\Omega^2}{(2\pi)^9}\sum_\nu \int_0^{q_{\max}} q^5 dq \\ &\quad\times \int \sin(\theta_q)d\theta_q \int d\varphi_q[\exp(\beta v_0^\nu q) - 1]^{-1} F^2_{jl}(\theta_q, \varphi_q)\,,\end{aligned} \tag{11.30}$$

where

$$\begin{aligned}F^2_{jl} = \int dk &\left(\left(\frac{\mathbf{q}}{q}\frac{\partial}{\partial k'}\right) g^\nu_{k,k'}|_{k'=k}\right)^2 \left(\left(\frac{\mathbf{q}}{q}\frac{\partial}{\partial k}\right) B_l(k,k')|_{k'=k}\right) \\ &\times \left(\left(\frac{\mathbf{q}}{q}\frac{\partial}{\partial k}\right) B_j(k,k')|_{k'=k}\right) f_k(1-f_k)\delta\left(\frac{\mathbf{q}}{q}\frac{\partial E}{\partial k} + v_0^\nu\right).\end{aligned} \tag{11.31}$$

In the k-integral in Eq. (11.30), the integration limits have to be chosen differently for normal and *Umklapp* processes. With the substitution $x = \beta v_0^\nu q$, we find

$$\begin{aligned}\langle \dot{P}_j^{ei}; \dot{P}_l^{ei}\rangle &= \beta^{-5}\frac{m\Omega^2}{(2\pi)^9}\sum_\nu \frac{1}{(v_0^\nu)^6}\int_0^{\beta v_0^\nu q_{\max}} dx \frac{x^5}{e^x - 1} \\ &\quad\times \int \sin(\theta_q)d\theta_q \int d\varphi_q F^2_{jl}(\theta_q,\varphi_q) \\ &= A^{ei}_{jl}T^5\,.\end{aligned} \tag{11.32}$$

Thus we can conclude that the electron–phonon correlation function is proportional to T^5 for any polynomial Φ^i_k. It is worthy to note that for an open Fermi surface, this proportionality follows for normal and *Umklapp* processes either. For a closed

Fermi surface, the *Umklapp* processes freeze out at sufficiently low temperatures, and the electron–phonon normal processes contribute to the electrical resistivity only. With the aid of the Eqs. (11.26) and (11.32), the generalized kinetic equations (11.7) becomes

$$\sum_{i=1}^{n} v_i(A_{ij}^{ee}T^2 + A_{ij}^{ei}T^5) = eEN_j\,. \tag{11.33}$$

For simplicity, we restrict our consideration to two parameters v_1 and v_2 describing the homogeneous shift and one type of deformation of the Fermi body. Taking into consideration more parameters is straightforward but does not modify the qualitative results very much. Finally, the expression for the electrical resistivity becomes[308,309]

$$R = \frac{\Omega}{3e^2}\frac{(A_{11}^{ee}T^2 + A_{11}^{ei}T^5)(A_{22}^{ee}T^2 + A_{22}^{ei}T^5) - (A_{12}^{ee}T^2 + A_{12}^{ei}T^5)^2}{N_1^2(A_{22}^{ee}T^2 + A_{22}^{ei}T^5) + N_2^2(A_{11}^{ee}T^2 + A_{11}^{ei}T^5) - 2N_1N_2(A_{12}^{ee}T^2 + A_{12}^{ei}T^5)}\,. \tag{11.34}$$

In general, a simple dependence $R \sim T^2$ or $R \sim T^5$ can be expected only if one of the scattering mechanisms dominate. For example, when $A_{ij}^{ee} \approx 0$, we find

$$R = \frac{\Omega}{3e^2}\frac{(A_{11}^{ei}A_{22}^{ei} - A_{12}^{ei})T^5}{N_1^2A_{22}^{ei} + N_2^2A_{11}^{ei} - 2N_1N_2A_{12}^{ei}}\,. \tag{11.35}$$

If, on the other hand, the deformation of the Fermi body is negligible ($v_2 = 0$), then from Eq. (11.34) it follows that

$$R = \frac{\Omega}{3e^2N_1^2}(A_{11}^{ee}T^2 + A_{11}^{ei}T^5)\,. \tag{11.36}$$

It is interesting to note that a somewhat similar in structure to expression (11.34) have been used to describe the resistivity of the so-called strong scattering metals. In order to improve our formula for the resistivity derived above the few bands and the interband scattering (e.g., *s*–*d* scattering) as well as the phonon drag effects should be taken into account.

11.3. *Equivalence of NSO approach and Kubo formalism*

Equivalence of the generalized kinetic equations to the Kubo formula for the electrical resistivity can be outlined as following. Let us consider the generalized kinetic equations

$$\sum_n F_n(-i\,\mathrm{Tr}(\rho[P_n, P_m]) + \langle \dot{P}_n; \dot{P}_m\rangle) = \frac{eE}{m}(\mathrm{Tr}(\rho\mathbf{P}_e(-i\lambda)P_m) + \langle \mathbf{P}_e; \dot{P}_m\rangle)\,. \tag{11.37}$$

To establish the correspondence of these equations with the Kubo expression for the electrical resistivity, it is necessary to express the operators of the total electron momentum $\mathbf{P_e}$ and the current density $\mathbf{j}$ in terms of the operators P_m. In other words, we suppose that there exists a suitable set of coefficients a_i with the properties

$$\mathbf{P}_e = \sum_i \mathbf{a}_i P_i \quad \mathbf{j} = \frac{e}{m\Omega}\mathbf{P}_e \,. \tag{11.38}$$

We get, by integrating Eq. (11.37) by parts, the following relation

$$\sum_n F_n \left(\int_0^\beta d\lambda \, \mathrm{Tr}(\rho P_n(-i\lambda)P_m) - \varepsilon\langle P_n; P_m\rangle \right) = \frac{eE}{m}\langle \mathbf{P}_e; P_m\rangle \,. \tag{11.39}$$

Supposing the correlation function $\langle P_n; P_m\rangle$ to be finite and using Eq. (11.38), we find in the limit $\varepsilon \to 0$

$$\sum_i \sum_n a_i F_n \int_0^\beta d\lambda \, \mathrm{Tr}(\rho P_n(-i\lambda)P_i) = \frac{eE}{m}\langle \mathbf{P}_e; \mathbf{P}_e\rangle \,. \tag{11.40}$$

From the equality (11.40), it follows that

$$\sum_n F_n \int_0^\beta d\lambda \, \mathrm{Tr}(\rho P_n(-i\lambda)P_e) = \frac{eE}{m}\langle \mathbf{P}_e; \mathbf{P}_e\rangle \,. \tag{11.41}$$

Let us emphasize again that the condition

$$\lim_{\varepsilon\to 0} \varepsilon\langle P_n; P_m\rangle = 0 \tag{11.42}$$

is an additional one for a suitable choice of the operators P_m. It is, in the essence, a certain boundary condition for the kinetic equations (11.37). Since the Kubo expression for the electrical conductivity

$$\sigma \sim \langle \mathbf{P}_e; \mathbf{P}_e\rangle \sim \langle P_n; P_m\rangle \tag{11.43}$$

should be a finite quantity, the condition (11.42) seems quite reasonable. To make a following step, we must take into account Eqs. (11.10) and (11.11). It is easy to see that the right-hand side of Eq. (11.41) is proportional to the current density. Finally, we reproduce the Kubo expression (10.18) (for cubic systems)

$$\sigma = \frac{j}{E} = \frac{e^2}{3m^2\Omega}\langle \mathbf{P}_e; \mathbf{P}_e\rangle \,, \tag{11.44}$$

where the proportionality of the F_m to the external electrical field has been taken into account.

It will be instructive to consider a concrete problem to clarify some points discussed above. There are some cases when the calculation of electrical resistivity is more convenient to be performed within the approach of the generalized transport equations (10.27) and (10.28) than within the Kubo formalism for the conductivity. We can use these two approaches as two complementary calculating scheme, depending on its convenience to treat the problem considered.[308] To clarify this, let us start from the condition

$$\mathrm{Tr}(\rho_{LR} B_i) = \mathrm{Tr}(\rho_s B_i) \,, \tag{11.45}$$

where the density matrices ρ_{LR} and ρ_s were given by Eqs. (10.23) and (10.25). For operators B_i which can be represented by linear combinations of the relevant observables A_i Eq. (11.45) is fulfilled exactly, where as for other operators, Eqs. (11.45) seems to be plausible if the relevant observables have been chosen properly. The conditions (11.45) 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 (11.45) even allow to calculate the correlation functions in (10.27) without resorting to another technique. As an example, we consider the one-band Hubbard model (4.14)

$$H = H_e + H_{ee} \tag{11.46}$$

in the strongly-correlated limit[62,99] $|t|/U \ll 1$. It well-known 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. The relevant operators will have the form

$$\mathbf{P}^{\alpha\beta} = m \sum_{k\sigma} \frac{\partial E}{\partial \mathbf{k}} n^{\alpha\beta}_{k\sigma} \,, \tag{11.47}$$

where

$$n^{\alpha\beta}_{k\sigma} = N^1 \sum_{ij} e^{i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j)} a^\dagger_{i\sigma} n^\alpha_{i-\sigma} a_{j\sigma} n^\beta_{j-\sigma} \tag{11.48}$$

with the projection operators

$$n^\alpha_{i-\sigma} = \begin{cases} n_{i-\sigma} & \text{if } \alpha = + \,, \\ (1 - n_{i-\sigma}) & \text{if } \alpha = + \,. \end{cases} \tag{11.49}$$

Here $\mathbf{P}^{\alpha\alpha}$ is the operator of the total momentum of the electrons in the sub-band α and $\mathbf{P}^{\alpha\beta}, (\alpha \neq \beta)$ describes kinematical transitions between the sub-bands. It can be shown that correlation functions $\langle \mathbf{P}^{\alpha\beta}; \mathbf{P}^{\gamma\delta} \rangle$ and $\langle \mathbf{P}^{\alpha\alpha}; \mathbf{P}^{\beta\beta} \rangle$ vanish for $\alpha \neq \beta$ in the limit $|t|/U \ll 1$. To make an estimation, it is necessary to decouple the higher correlation functions in $|t|/U$ and take into account nearest neighbor hopping terms only. Then the correlation functions $\langle \mathbf{P}^{\alpha\alpha}; \mathbf{P}^{\alpha\alpha} \rangle$ $(\alpha = \pm)$ can be calculated directly by means of Eq. (11.45), where $B_i \to \mathbf{P}^{\alpha\alpha}$. The conductivity becomes

$$\sigma = W T^{-1} \sum_\sigma \sum_\alpha \langle n^\alpha_\sigma \rangle^{-1/2} \langle n^\alpha_\sigma n^\alpha_{-\sigma} \rangle (\langle n^\alpha_\sigma \rangle - \langle n^\alpha_\sigma n^\alpha_{-\sigma} \rangle) \,, \tag{11.50}$$

where

$$W = \frac{e^2}{3m^2 \Omega k} \frac{1}{\sqrt{2z}} \frac{1}{|t|} \sum_{\mathbf{k}} \left(\frac{\partial E}{\partial \mathbf{k}} \right)^2 \tag{11.51}$$

and

$$\langle W \rangle = \mathrm{Tr}(\rho W) \,, \quad \rho = \frac{1}{Q} \exp(-\beta H) \,.$$

Here z is the number of nearest neighbors and t the nearest neighbor hopping matrix-element. With the well-known expressions for the mean values $\langle n^{\alpha}_{\sigma} n^{\alpha}_{-\sigma} \rangle$, we find the conductivity in dependence on the electron number in the form[308]

$$\sigma = WT^{-1} \frac{1}{2} \frac{n(1-n)}{\sqrt{1-n/2}} , \quad (0 \leq n < 1) , \tag{11.52}$$

$$\sigma = WT^{-1} \frac{1}{\sqrt{2}} \exp(-U/2kT) , \quad (n = 1) , \tag{11.53}$$

$$\sigma = WT^{-1} \sqrt{2} \frac{(1-n/2)(1-n)}{\sqrt{n}} , \quad (2 \geq n > 1) . \tag{11.54}$$

Thus, it was shown in this and in the preceding sections that the formalism of the generalized kinetic equations has certain convenient features and its own specific in comparison with Kubo formalism. The derived expressions are compact and easy to handle.

11.4. *High-temperature resistivity and MTBA*

At high temperatures, the temperature dependence of the electrical resistivity R of some transition metals and highly resistive metallic systems such as A15 compounds may deviate substantially from the linear dependence, which follows from the Bloch–Gruneisen law. These strong deviations from the expected behavior with a tendency to flatten to a constant resistivity value was termed by *resistivity saturation*[314] and have been studied both experimentally and theoretically by many authors.[315–327] The phenomenon of *resistivity saturation* describes a less-than-linear rise in dc electrical resistivity R when temperature T increases. It was found that this effect is common in transition metal compounds (with pronounced d-band structure) when R exceeds ~ 80 $\mu\Omega$cm, and that R seems bounded above by a value $R_{\max} \sim 150$ $\mu\Omega$cm which varies somewhat with material. In Ref. 326, in particular, it was formulated that the electrical resistivity, R, of a metal is usually interpreted in terms of the mean free path (the average distance, l, an electron travels before it is scattered). As the temperature is raised, the resistivity increases and the apparent mean free path is correspondingly reduced. In this semi-classical picture, the mean free path cannot be much shorter than the distance, a, between two atoms. This has been confirmed for many systems and was considered to be a universal behavior. Recently, some apparent exceptions were found, including alkali-doped fullerenes and high-temperature superconductors.[328] However, there remains the possibility that these systems are in exotic states, with only a small fraction of the conduction electrons contributing to the conductivity; the mean free path would then have to be correspondingly larger to explain the observed resistivity. The authors of Ref. 325 performed a model calculation of electron conduction in alkali-doped fullerenes, in which the electrons are scattered by intramolecular vibrations. The resistivity at large temperatures implies $l \sim a$, demonstrating that there is no fundamental principle requiring $l > a$. At high temperatures, the semiclassical picture breaks down, and the electrons cannot be described as quasiparticles. Recent review of theoretical and experimental investigations in this field was given in Refs. 328–330 (for discussion of the electronic thermal conductivity at high temperatures, see Ref. 331).

The nature of saturation phenomenon of electrical resistivity is not fully understood. Resistivity of a metallic system as a function of temperature reflects an overall electron–phonon interaction effects as well as certain contribution effects of disorder.[332–334] There have been some attempts to explain the saturation phenomenon in the framework of of the Boltzmann transport theory using special assumptions concerning the band structure, etc. The influence of electron–phonon scattering on electrical resistivity at high temperatures was investigated in Refs. 323 and 324 in the framework of Fröhlich–Hamiltonian for the electron–phonon interaction. In Ref. 323, the authors calculated a temperature-dependent self-energy to the lowest nonvanishing order of the electron–phonon interaction.

However, as it was shown above, for transition metals and their disordered alloys, the MTBA is more adequate. Moreover, the anisotropic effects are described better within MTBA. Here we consider a single-band model of transition metal with the Hamiltonian

$$H = H_e + H_i + H_{ei} \,. \tag{11.55}$$

The electron subsystem is described by the Hubbard model (4.14) in the Hartree–Fock approximation

$$H_e = \sum_{k\sigma} E(k\sigma) a^{\dagger}_{k\sigma} a_{k\sigma} \,, \quad E(k\sigma) = E(k) + \frac{U}{N} \sum_{p} \langle n_{k-\sigma} \rangle \,. \tag{11.56}$$

For the tight-binding electrons in crystals, we use $E(k) = 2\sum_\alpha t^0(\mathbf{R}_\kappa)\cos(\mathbf{k}\mathbf{R}_\kappa)$, where $t^0(\mathbf{R}_\kappa)$ is the hopping integral between nearest neighbors, and $\mathbf{R}_\kappa$ ($\kappa = x, y, z$) denotes the lattice vectors in a simple lattice in an inversion centre. For the electron–phonon interaction, we use the Hamiltonian (4.66)

$$H_{ei} = \sum_{\sigma} \sum_{kq} V(\mathbf{k}, \mathbf{k}+\mathbf{q}) Q_{\mathbf{q}} a^{+}_{k+q\sigma} a_{k\sigma} \,, \quad Q_{\mathbf{q}} = \frac{1}{\sqrt{2\omega(q)}} (b_q + b^{\dagger}_{-q}) \,, \tag{11.57}$$

where

$$V(\mathbf{k}, \mathbf{k}+\mathbf{q}) = \frac{iq_0}{(NM)^{1/2}} \sum_{\kappa\nu} t^0(\mathbf{R}_\kappa) \frac{\mathbf{R}_\kappa \mathbf{e}_\nu(\mathbf{q})}{|\mathbf{R}_\kappa|} [\sin \mathbf{R}_\kappa \mathbf{k} - \sin \mathbf{R}_\kappa (\mathbf{k}+\mathbf{q})] \,. \tag{11.58}$$

The one-electron hopping $t^0(\mathbf{R}_\kappa)$ is the overlap integral between a given site $\mathbf{R}_m$ and one of the two nearby sites lying on the lattice axis $\mathbf{R}_\kappa$. Operators $b^{\dagger}_q$ and b_q are creation and annihilation phonon operators and $\omega(q)$ is the acoustical phonon frequency. N is the number of unit cells in the crystal and M is the ion mass. The $\mathbf{e}_\nu(\mathbf{q})$ are the polarization vectors of the phonon modes.

For the ion subsystem, we have

$$H_i = \sum_{q} \omega(\mathbf{q}) \left(b^{\dagger}_q b_q + \frac{1}{2} \right) . \tag{11.59}$$

For the resistivity calculation, we use the following formula[323]

$$R = \frac{\Omega}{3e^2\mathcal{N}^2}\frac{\langle \mathbf{F};\mathbf{F}\rangle}{1+(1/3m\mathcal{N})\langle \mathbf{P};\mathbf{F}\rangle}\,. \tag{11.60}$$

Here $\mathcal{N}$ is the effective number of electrons in the band considered

$$\mathcal{N} = \frac{1}{3m}\int_0^\beta d\lambda\,\mathrm{Tr}(\rho\mathbf{P}(-i\hbar\lambda)\mathbf{P}) \tag{11.61}$$

and $\mathbf{P}$ is the total momentum operator

$$\mathbf{P} = \frac{m}{\hbar}\sum_{\mathbf{k}}\left(\frac{\partial E(\mathbf{k}\sigma)}{\partial \mathbf{k}}\right)n_{k\sigma}\,,\quad n_{k\sigma} = a^\dagger_{k\sigma}a_{k\sigma}\,. \tag{11.62}$$

The total force $\mathbf{F}$ acting on the electrons is giving by

$$\mathbf{F} = \frac{i}{\hbar}[H,\mathbf{P}] = -\frac{im}{\hbar}\sum_{\mathbf{kq}\sigma}V(\mathbf{k},\mathbf{k}+\mathbf{q})(\mathbf{v}_{k+q,\sigma}-\mathbf{v}_{k,\sigma})Q_q a^\dagger_{k+q\sigma}a_{k\sigma}\,, \tag{11.63}$$

with the velocity defined as $\mathbf{v}_{k,\sigma} = \partial E(\mathbf{k}\sigma)/\hbar\partial\mathbf{k}$. It is convenient to introduce a notation

$$\frac{V(\mathbf{k},\mathbf{k}+\mathbf{q})}{\sqrt{2\omega(q)}} = \frac{i\Lambda F_q}{\sqrt{\Omega}}\,.$$

Correlation functions in Eq. (11.60) can be expressed in terms of the double-time thermodynamic Green functions

$$\langle \mathbf{F};\mathbf{F}\rangle = \frac{2\pi i}{\hbar}\langle\langle \mathbf{F}|\mathbf{P}\rangle\rangle_{-i\hbar\varepsilon}\,, \tag{11.64}$$

$$\langle \mathbf{P};\mathbf{F}\rangle = \frac{2\pi mi}{\hbar}\langle\langle \mathbf{P}|\mathbf{F}\rangle\rangle_{-i\hbar\varepsilon}, \tag{11.65}$$

$$\langle\langle \mathbf{F}|A\rangle\rangle_{-i\hbar\varepsilon} = \frac{1}{2\pi}\int_{-\infty}^{\infty}dt e^{\varepsilon t}\theta(-t)\mathrm{Tr}(\rho[A,F(t)])\,, \tag{11.66}$$

where A represents either the momentum operator $\mathbf{P}$ or the position operator $\mathbf{R}$ with $\mathbf{P} = im[H,\mathbf{R}]/\hbar$.

We find the following relation

$$\langle \mathbf{F};\mathbf{F}\rangle = \frac{2\pi m}{\hbar^2}\sum_{\mathbf{kq}\sigma}\frac{V(\mathbf{k},\mathbf{k}+\mathbf{q})}{\sqrt{2\omega(q)}}(\mathbf{v}_{k+q,\sigma}-\mathbf{v}_{k,\sigma})\langle\langle a^+_{k+q\sigma}a_{k\sigma}(b_q+b^\dagger_{-q})|\mathbf{P}\rangle\rangle_{-i\hbar\varepsilon}\,. \tag{11.67}$$

Thus we obtain

$$\begin{aligned}\langle\langle \mathbf{F};\mathbf{A}\rangle\rangle_{-i\hbar\varepsilon} = -i\sum_{\mathbf{kq}\sigma}&\frac{V(\mathbf{k},\mathbf{k}+\mathbf{q})}{\sqrt{2\omega(q)}}(\mathbf{v}_{k+q,\sigma}-\mathbf{v}_{k,\sigma})(\langle\langle a^+_{k+q\sigma}a_{k\sigma}b_q|\mathbf{A}\rangle\rangle_{-i\hbar\varepsilon}\\ &-\langle\langle a^+_{k+q\sigma}a_{k\sigma}b^\dagger_{-q})|\mathbf{A}\rangle\rangle_{-i\hbar\varepsilon})\,.\end{aligned} \tag{11.68}$$

Calculation of the higher-order Green functions gives

$$\begin{aligned}
&(E(k+q\sigma) - E(k\sigma) - \Omega_q - i\hbar\varepsilon)\langle\langle a^\dagger_{k+q\sigma} a_{k\sigma} B_q|\mathbf{A}\rangle\rangle_{-i\hbar\varepsilon} \\
&\quad = T_{kq}(A) + \sum_{\mathbf{q}'}\Bigg(\frac{V(\mathbf{k}-\mathbf{q}',\mathbf{k})}{\sqrt{2\omega(q')}}\langle\langle a^\dagger_{k+q\sigma}a_{k-q'\sigma}(b_{q'} - b^\dagger_{-q'})B_q|\mathbf{A}\rangle\rangle_{-i\hbar\varepsilon} \\
&\qquad - \frac{V(\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}+\mathbf{q}')}{\sqrt{2\omega(q')}}\langle\langle a^\dagger_{k+q+q'\sigma}a_{k\sigma}(b_{q'}-b^\dagger_{-q'})B_q|\mathbf{A}\rangle\rangle_{-i\hbar\varepsilon}\Bigg) \\
&\qquad - \sum_{\mathbf{k}'}\frac{V(\mathbf{k}',\mathbf{k}'-\mathbf{q})}{\sqrt{2\omega(q)}}\langle\langle a^\dagger_{k+q\sigma}a_{k\sigma}a^\dagger_{k'-q\sigma}a_{k'\sigma}|\mathbf{A}\rangle\rangle_{-i\hbar\varepsilon}
\end{aligned} \tag{11.69}$$

with notation

$$\begin{aligned}
&\Omega_q = \hbar\omega(q) \to B_q = b_q\,; \quad E_q = -\hbar\omega(q) \to B_q = b^\dagger_{-q}\,, \\
&T_{kq}(\mathbf{P}) = \frac{im}{2\pi}(\mathbf{v}_{k+q,\sigma} - \mathbf{v}_{k,\sigma})\langle a^\dagger_{k+q\sigma}a_{k\sigma}B_q\rangle\,, \\
&T_{kq}(\mathbf{R}) = -\frac{1}{2\pi}\sum_{\mathbf{q}'}\frac{\partial}{\partial q'}\langle a^\dagger_{k+q+q'\sigma}a_{k+q'\sigma}B_q\rangle\delta_{q',0}\,, \\
&\mathcal{N} = \frac{m}{3\hbar}\sum_{kq'\sigma}\delta_{q',0}\mathbf{v}_{k,\sigma}\frac{\partial}{\partial q'}\langle a^\dagger_{k+q'\sigma}a_{k+q'\sigma}\rangle\,.
\end{aligned}$$

We find also

$$\begin{aligned}
&\langle\langle a^\dagger_{k+q\sigma}a_{k-q'\sigma}b_q b_{q'}|A\rangle\rangle_{-i\hbar\varepsilon} \\
&\quad = -\langle b^\dagger_{q'}b_{q'}\rangle_0\frac{V(\mathbf{k},\mathbf{k}-\mathbf{q}')}{\sqrt{2\omega(q')}} \\
&\qquad \times\frac{\langle\langle a^\dagger_{k+q\sigma}a_{k\sigma}b_q|A\rangle\rangle_{-i\hbar\varepsilon}}{(E(k+q\sigma) - E(k-q'\sigma) - E_{q'} - \hbar\omega(q') - i\hbar\varepsilon)}\,,
\end{aligned} \tag{11.70}$$

$$\begin{aligned}
&\langle\langle a^\dagger_{k+q+q'\sigma}a_{k\sigma}b_q b_{q'}|A\rangle\rangle_{-i\hbar\varepsilon} \\
&\quad = -\langle b^\dagger_{q'}b_{q'}\rangle_0\frac{V(\mathbf{k}+\mathbf{q}+\mathbf{q}',\mathbf{k}+\mathbf{q})}{\sqrt{2\omega(q')}} \\
&\qquad \times\frac{\langle\langle a^\dagger_{k+q\sigma}a_{k\sigma}b_q|A\rangle\rangle_{-i\hbar\varepsilon}}{(E(k+q+q'\sigma) - E(k\sigma) - E_{q'} - \hbar\omega(q') - i\hbar\varepsilon)}\,.
\end{aligned} \tag{11.71}$$

Here the symmetry relations

$$V(\mathbf{k}-\mathbf{q}',\mathbf{k}) = V^*(\mathbf{k},\mathbf{k}-\mathbf{q}')\,; \quad V(\mathbf{k}+\mathbf{q}+\mathbf{q}',\mathbf{k}+\mathbf{q}) = V^*(\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}+\mathbf{q}')$$

were taken into account.

Now the Green function of interest can be determined by introducing the self-energy[323]

$$\begin{aligned}&\langle\langle a^\dagger_{k+q\sigma}a_{k-q'\sigma}b_qB_q|A\rangle\rangle_{-i\hbar\varepsilon}\\&\quad=-\langle b^\dagger_{q'}b_{q'}\rangle_0\frac{T_{kq}(A)}{(E(k+q\sigma)-E(k-q'\sigma)-E_q-M_{kq\sigma}(E_q,-i\hbar\varepsilon)-i\hbar\varepsilon)}\,.\end{aligned}\tag{11.72}$$

The self-energy is given by

$$\begin{aligned}M_{kq\sigma}(E_q,-i\hbar\varepsilon)=&\sum_{q'}\frac{1}{2\omega(q')}\Bigg(\langle b^\dagger_{q'}b_{q'}\rangle\Bigg[\frac{|V(\mathbf{k},\mathbf{k}-\mathbf{q}')|^2}{E(k+q\sigma)-E(k-q'\sigma)-E_{q'}-\hbar\omega(q')-i\hbar\varepsilon}\\&+\frac{|V(\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}+\mathbf{q}')|^2}{E(k+q+q'\sigma)-E(k\sigma)-E_{q'}-\hbar\omega(q')-i\hbar\varepsilon}\Bigg]\\&+\langle b_{q'}b^\dagger_{q'}\rangle\Bigg[\frac{|V(\mathbf{k},\mathbf{k}-\mathbf{q}')|^2}{E(k+q\sigma)-E(k-q'\sigma)-E_{q'}+\hbar\omega(q')-i\hbar\varepsilon}\\&+\frac{|V(\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}+\mathbf{q}')|^2}{E(k+q+q'\sigma)-E(k\sigma)-E_{q'}+\hbar\omega(q')-i\hbar\varepsilon}\Bigg]\Bigg)\,.\end{aligned}\tag{11.73}$$

In Eq. (11.73), the energy difference $(E(k+q\sigma)-E(k-q\sigma)-E_q))$ is that for the scattering process of electrons on phonons, while emission or absorption of one phonon is possible, corresponding to E_q. These scattering processes are contained in the usual Boltzmann transport theory leading to the Bloch–Gruneisen law. The self-energy $M_{kq\sigma}$ describes multiple scattering corrections to the Bloch–Gruneisen behavior to second-order in V, which depends on the temperature via the phonon occupation numbers.

Furthermore, it is assumed that the averages of occupation numbers for phonons in the self-energy and for electrons in the effective particle number, are replaced by the Bose and Fermi distribution functions, respectively:

$$\langle b^\dagger_q b_q\rangle=N_q\,,\quad N_q=[\exp(\beta\hbar\omega(q))-1]^{-1}\,,\tag{11.74}$$

$$\langle a^\dagger_{k\sigma}a_{k\sigma}\rangle=f_k\,,\quad f_k=[\exp(\beta E(k\sigma)-E_F)+1]^{-1}\,.\tag{11.75}$$

This corresponds to neglecting the influence of multiple scattering corrections on the phonon and electron distribution functions.

In order to calculate the expectation values in the inhomogeneities, Eqs. (11.72) and (11.73), the spectral theorem should be used. In the lowest nonvanishing order of the electron–phonon interaction parameter V, we obtain

$$\begin{aligned}\langle a^\dagger_{k+q\sigma}a_{k\sigma}B_q\rangle=&\frac{V(\mathbf{k}+\mathbf{q},\mathbf{k})}{\sqrt{2\omega(q)}}f_{k+q}(1-f_k)\nu_q(E_q)\\&\times\frac{[\exp(\beta(E(k+q\sigma)-E(k\sigma)-E_q)]-1}{E(k+q\sigma)-E(k\sigma)-E_q}\,,\end{aligned}\tag{11.76}$$

with

$$\begin{aligned}\nu_q(E_q) &= \frac{1}{1-\exp(-\beta E_q)} \\ &= \begin{cases} 1+N_q & \text{if } B_q = b_q; \quad E_q = \hbar\omega(q) \\ N_q & \text{if } B_q = b^{\dagger}_{-q}; \quad E_q = -\hbar\omega(q)\,. \end{cases}\end{aligned} \tag{11.77}$$

Applying the approximation scheme discussed above, we have found the following expressions for the Green function with $A = P$

$$\begin{aligned}&\langle\langle a^{\dagger}_{k+q\sigma} a_{k\sigma} B_q | \mathbf{P} \rangle\rangle_{-i\hbar\varepsilon} \\ &\quad = \frac{im}{2\pi}\frac{V(\mathbf{k}+\mathbf{q},\mathbf{k})}{\sqrt{2\omega(q)}}(\mathbf{v}_{k+q,\sigma} - \mathbf{v}_{k,\sigma})\frac{P^1_{kq\sigma}(E_q)}{\Omega_{kq\sigma}(E_q) - M_{kq\sigma} - i\hbar\varepsilon}\,,\end{aligned} \tag{11.78}$$

and for the Green function with $A = R$

$$\begin{aligned}&\langle\langle a^{\dagger}_{k+q\sigma} a_{k\sigma} B_q | \mathbf{R} \rangle\rangle_{-i\hbar\varepsilon} \\ &\quad = \frac{\hbar}{2\pi}\frac{V(\mathbf{k}+\mathbf{q},\mathbf{k})}{\sqrt{2\omega(q)}}(\mathbf{v}_{k+q,\sigma} - \mathbf{v}_{k,\sigma})\frac{P^2_{kq\sigma}(E_q) - P^3_{kq\sigma}(E_q)}{\Omega_{kq\sigma}(E_q) - M_{kq\sigma} - i\hbar\varepsilon}\,.\end{aligned} \tag{11.79}$$

We have introduced in the above equations the following notation:

$$P^{(1)}_{kq\sigma}(E_q) = f_{k+q}(1-f_k)\nu_q(E_q)\gamma_1(\Omega_{kq\sigma}(E_q))\,, \tag{11.80}$$

$$P^{(2)}_{kq\sigma}(E_q) = (v_{k+q\sigma} - v_{k\sigma})f_{k+q}(1-f_k)\nu_q(E_q)\left(\gamma_2(\Omega_{kq\sigma}(E_q)) - \frac{\beta\exp(\beta\Omega_{kq\sigma}(E_q))}{\Omega_{kq\sigma}(E_q)}\right), \tag{11.81}$$

$$P^{(3)}_{kq\sigma}(E_q) = f_{k+q}(1-f_k)\nu_q(E_q)\beta\gamma_1(\Omega_{kq\sigma}(E_q))[f_k v_{k\sigma} - (1-f_{k+q})v_{k+q\sigma}]\,, \tag{11.82}$$

with

$$\gamma_n(\Omega_{kq\sigma}(E_q)) = \frac{\beta\exp(\beta\Omega_{kq\sigma}(E_q)) - 1}{(\Omega_{kq\sigma}(E_q))^n}\,, \tag{11.83}$$

and

$$\Omega_{kq\sigma}(E_q) = E(k+q\sigma) - E(k\sigma) - E_q\,. \tag{11.84}$$

For the effective particle number we find

$$\mathcal{N} = \frac{2}{3}m\beta\sum_k (v_k)^2 f_k(1-f_k)\,. \tag{11.85}$$

Before starting of calculation of the resistivity it is instructive to split the self-energy into real and imaginary part ($\varepsilon \to 0$)

$$\lim_{\varepsilon\to 0} M_{kq\sigma}(\hbar\omega(q) \pm i\hbar\varepsilon) = \mathrm{Re}\, M_{kq\sigma}(\hbar\omega(q)) \mp i\,\mathrm{Im} M_{kq\sigma}(\hbar\omega(q)) \tag{11.86}$$

and perform an interchange of variables $k + q \to k; q \to -q$. Now for the relevant correlation functions, we obtain the expressions

$$\langle \mathbf{F}; \mathbf{F} \rangle = \frac{2m^2}{\hbar} \sum_{kq\sigma} \frac{|V(\mathbf{k}, \mathbf{k}+\mathbf{q})|^2}{\sqrt{2\omega(q)}} (v_{k+q\sigma} - v_{k\sigma})^2 P^{(1)}_{kq\sigma}(\hbar\omega(q)) S_{kq\sigma}(\hbar\omega(q)) , \quad (11.87)$$

$$\langle \mathbf{P}; \mathbf{F} \rangle = -m^2 \sum_{kq\sigma} \frac{|V(\mathbf{k}, \mathbf{k}+\mathbf{q})|^2}{\sqrt{2\omega(q)}} (v_{k+q\sigma} - v_{k\sigma}) \times (P^{(2)}_{kq\sigma}(\hbar\omega(q)) + P^{(3)}_{kq\sigma}(\hbar\omega(q))) S_{kq\sigma}(\hbar\omega(q)) , \quad (11.88)$$

where

$$S_{kq\sigma}(\hbar\omega(q)) = \frac{\operatorname{Im} M_{kq\sigma}(\hbar\omega(q))}{(\Omega_{kq\sigma}(\hbar\omega(q)) - \operatorname{Re} M_{kq\sigma}(\hbar\omega(q)))^2 + (\operatorname{Im} M_{kq\sigma}(\hbar\omega(q)))^2} . \quad (11.89)$$

In order to obtain Eq. (11.89), the following symmetry relation for the self-energy was used

$$M_{kq\sigma}(\hbar\omega(q) - i\hbar\varepsilon) = -M_{kq\sigma}(\hbar\omega(q) + i\hbar\varepsilon) . \quad (11.90)$$

The inspection of both the correlation functions $\langle \mathbf{F}; \mathbf{F} \rangle$ and $\langle \mathbf{P}; \mathbf{F} \rangle$ shows that its include two dominant parts. The first one is the scattering part $S_{kq\sigma}(\hbar\omega(q))$, which contains all the information about the scattering processes. The second part describes the occupation possibilities before and after the scattering processes $(P^{(1)}_{kq\sigma}(\hbar\omega(q)), P^{(2)}_{kq\sigma}(\hbar\omega(q)), P^{(3)}_{kq\sigma}(\hbar\omega(q)))$, and includes both the Fermi and Bose distribution functions. The approximation procedure described above neglects the multiple scattering corrections in these factors for the occupation possibilities.

For further estimation of the correlation functions, the quasi-elastic approximation can be used. In this case, in the energy difference $\Omega_{kq\sigma}(\hbar\omega(q))$, the phonon energy $\hbar\omega(q)$ can be neglected $\Omega_{kq\sigma}(\hbar\omega(q)) \simeq \Omega_{kq\sigma}(0)$. The phonon wave number $\mathbf{q}$ only is taken into account via the electron dispersion relation. Furthermore, for the Bose distribution function, it was assumed that

$$\langle b^\dagger_q b_q \rangle = \langle b_q b^\dagger_q \rangle \simeq (\beta\hbar\omega(q))^{-1} . \quad (11.91)$$

This approximation is reasonable at temperatures which are high in comparison to the Debye temperature Θ_D.

It is well-known[2,38] from Bloch–Gruneisen theory that the quasi-elastic approximation does not disturb the temperature dependence of the electrical resistivity at high or low temperatures. The absolute value of the resistivity is changed, but the qualitative picture of the power law of the temperature dependence of the resistivity is not influenced.

In the framework of the quasi-elastic approximation, the scattering contribution can be represented in the form

$$S_{kq\sigma} = \frac{\operatorname{Im} M^e_{kq\sigma}}{(\Omega_{kq\sigma}(0) - \operatorname{Re} M^e_{kq\sigma})^2 + (\operatorname{Im} M^e_{kq\sigma}))^2} . \quad (11.92)$$

Here the real and imaginary parts of the self-energy have the following form

$$\operatorname{Re} M^e_{kq\sigma} = \frac{kT}{\hbar}\sum_p \left(\frac{|V(\mathbf{k},\mathbf{k}+\mathbf{p})|^2}{\omega(p)^2} P\left(\frac{1}{E(k+q\sigma)-E(k-p\sigma)}\right)\right.$$
$$\left. + \frac{|V(\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}+\mathbf{p})|^2}{\omega(p)^2} P\left(\frac{1}{E(k+q+p\sigma)-E(k\sigma)}\right)\right), \quad (11.93)$$

$$\operatorname{Im} M^e_{kq\sigma} = \frac{\pi kT}{\hbar}\sum_p \left(\frac{|V(\mathbf{k},\mathbf{k}+\mathbf{p})|^2}{\omega(p)^2} \delta(E(k+q\sigma)-E(k-p\sigma))\right.$$
$$\left. + \frac{|V(\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}+\mathbf{p})|^2}{\omega(p)^2} \delta(E(k+q+p\sigma)-E(k\sigma))\right). \quad (11.94)$$

The occupation possibilities given by $P^{(n)}_{kq\sigma}$ can be represented in the quasi-elastic approximation as[323]

$$P^{(1)e}_{kq\sigma} \simeq \frac{kT}{\hbar\omega(q)}\delta(E_F - E(k\sigma))\,; \quad (11.95)$$

$$P^{(2)e}_{kq\sigma} = P^{(3)e}_{kq\sigma} = 0\,. \quad (11.96)$$

In this approximation, the momentum–force correlation function disappears $\langle \mathbf{P};\mathbf{F}\rangle \simeq 0$. Thus we have

$$R \simeq \frac{\Omega}{3e^2N^2}\langle \mathbf{F};\mathbf{F}\rangle\,, \quad (11.97)$$

$$\langle \mathbf{F};\mathbf{F}\rangle = \frac{2m^2kT}{\hbar}\sum_{kq\sigma}\frac{|V(\mathbf{k},\mathbf{k}+\mathbf{q})|^2}{\omega(q)^2}(v_{k+q\sigma}-v_{k\sigma})^2\delta(E_F-E(k\sigma))$$
$$\times \frac{\operatorname{Im} M^e_{kq\sigma}}{(E(k+q\sigma)-E(k\sigma)-\operatorname{Re} M^e_{kq\sigma})^2 + (\operatorname{Im} M^e_{kq\sigma}))^2}\,. \quad (11.98)$$

The explicit expression for the electrical resistivity was calculated in Ref. 323. The additional simplifying assumptions have been made to achieve it. For the electrons and phonons, the following simple dispersion relations were taken

$$E(k) = \frac{\hbar^2k^2}{2m^*}; \quad \omega(q) = v_0|\mathbf{q}|, \quad V(\mathbf{k},\mathbf{k}+\mathbf{q}) \sim \sqrt{|\mathbf{q}|}\,.$$

It was shown that the estimation of $P^{(1)e}_{kq\sigma}$ is given by

$$P^{(1)e}_{kq\sigma} \simeq \frac{Tkm^*}{v_0\hbar^3k_Fq}\delta(k_F-k)\,. \quad (11.99)$$

Then, for the electrical resistivity, the following result was found

$$R \simeq \frac{3V^2m^*q_D}{2e^2k_F^5\hbar}\frac{T}{\Theta_D}\int_0^{q_D}dq\int_{-1}^{1}dzq^4$$
$$\times \frac{\operatorname{Im} M^e_{k_Fqz}}{[(\hbar^2q/m^*)(zk_F+q/2)-\operatorname{Re} M^e_{k_Fqz}]^2+[\operatorname{Im} M^e_{k_Fqz})]^2}\,. \quad (11.100)$$

This result shows that the usual Bloch–Gruneisen theory of the electrical resistivity can be corrected by including the self-energy in the final expression for the resistivity. The Bloch–Gruneisen theory can be reproduced in the weak scattering limit using the relation

$$\lim_{\mathrm{Re(Im)}M\to 0} \frac{\mathrm{Im}\, M^e_{k_F qz}}{[(\hbar^2 q/m^*)(zk_F + q/2) - \mathrm{Re}\, M^e_{k_F qz}]^2 + [\mathrm{Im}\, M^e_{k_F qz})]^2} = \frac{\pi m^*}{\hbar^2 q k_F}\delta\left(z + \frac{q}{2k_F}\right). \tag{11.101}$$

Inserting Eq. (11.101) in the resistivity expression equation (11.100) gives the electrical resistivity R_w in the weak scattering limit, showing a linear temperature dependence

$$R_w \simeq \frac{3\pi}{8}\frac{V^2(m^*)^2 q_D^5}{e^2 k_F^6 \hbar^3}\frac{T}{\Theta_D}. \tag{11.102}$$

In this form, the resistivity formula contains two main parameters that influence substantially. The first is the Debye temperature Θ_D characterizing the phonon system, and, the second, the parameter $\alpha = (Vm^*)^2$ describing the influence of both the electron system and the strength of the electron–phonon interaction. The numerical estimations[323] were carried out for Nb and gave the magnitude of the saturation resistivity as 207 $\mu\Omega$cm.

In the theory described above, the deviation from linearity in the high-temperature region of the resistivity may be caused by multiple scattering corrections. The multiple scattering processes which describe the scattering processes of electrons on the phonon system by emission or absorption of more than one phonon in terms of self-energy corrections become more and more important with increasing temperature. As was shown above, even for simple dispersion relation of electrons and phonons within one-band model, the thermally induced saturation phenomenon occurs. For the anisotropic model within MTBA, the extensive numerical calculations are necessary.

In a subsequent paper,[324] Christoph and Schiller considered the problem of the microscopic foundation of the empirical formula[314] (parallel resistor model)

$$\frac{1}{R(T)} = \frac{1}{R_{SBT}(T)} + \frac{1}{R_{\max}(T)} \tag{11.103}$$

within the framework of the transport theory of Christoph and Kuzemsky.[308] The parallel resistor formula describing the saturation phenomenon of electrical resistivity in systems with strong electron–phonon interaction was derived. In Eq. (11.103), $R_{SBT}(T)$ is the resistivity given by the semiclassical Boltzmann transport theory $R_{SBT}(T) \sim T$ and the saturation resistivity $R_{\max}$ corresponds to the maximum metallic resistivity.[335] The higher-order terms in the electron–phonon interaction were described by a self-energy was determined self-consistently. They found for the saturation resistivity, the formula[324]

$$R_{\max} = \frac{3\pi^3}{32}\frac{\hbar}{e^2}\frac{q_D^4}{k_F^5}\frac{1}{|P(q_D/2k_F)|}\,. \qquad (11.104)$$

Within the framework of this approach, the saturation behavior of the electrical resistivity was explained by the influence of multiple scattering processes described by a temperature-dependent damping term of one-electron energies. In the standard picture, the conventional linear temperature dependence of the resistivity $R \sim T(T \gg \Theta_D)$ is explained by taking into account that the number of phonons is proportional to the temperature and, moreover, assuming that the electron momentum is dissipated in single-phonon scattering processes only. For an increasing number of phonons, however, the multiple scattering processes become more important and the single scattering event becomes less effective. This argument coincides in some sense with the Yoffe–Regel criterion[332–334] stating that an increase in the number of scatterers does not result in a corresponding increase of the resistivity if the the mean free path of the electrons becomes comparable with the lattice distance. Indeed, the saturation resistivity (11.104) coincides roughly with the inverse minimal metallic conductivity which can be derived using this criterion.

12. Resistivity of Disordered Alloys

In the present section, a theory of electroconductivity in disordered transition metal alloys with the proper microscopic treatment of the nonlocal electron–phonon interaction is considered. It was established long ago that any deviation from perfect periodicity will lead to a resistivity contribution, which will depend upon the spatial extent and lifetime of the disturbance measured in relation to the conduction electron mean free path and relaxation time. It is especially important to develop a theory for the resistivity of concentrated alloys because of its practical significance. The electrical resistivity of disordered metal alloys and its temperature coefficient is of considerable practical and theoretical interest.[22,59,167–172,235,325,336–339] The work in this field has been considerably stimulated by Mooij paper,[168] where it has been shown that the temperature coefficient of the resistivity of disordered alloys becomes negative if their residual resistivity exceeds a given critical value. To explain this phenomenon, one has to go beyond the weak-scattering limit and take into account the interference effects between the static disorder scattering and the electron–phonon scattering.[338–345]

In the weak-scattering limit,[346] the contributions of impurity and phonon scattering add to the total resistivity without any interference terms (Matthiessen rule). For disordered systems, many physical properties can be related to the configuration-averaged Green functions.[347] A few methods for calculation of these averaged Green functions were formulated. It vas found that the single-site coherent potential approximation (CPA)[348–352] provides a convenient and accurate approximation for it.[353–360] The CPA is a self-consistent method[353–360] that predicts alloy electronic properties, interpolating between those of the pure constituents over the entire range of concentrations and scattering strengths. The self-consistency condition is introduced by requiring that the coherent potential, when placed at each lattice site of the ordered lattice, reproduces all the average properties of the actual crystal. The coherent-potential approximation has been developed within the framework of the multiple-scattering description of disordered systems.[347] A given scatterer in the alloy can be viewed as being embedded in an effective medium with a complex energy-dependent potential whose choice is open and can be made self-consistently such that the average forward scattering from the real scatterer is the same as free propagation in the effective medium. The strong scattering has been first considered by Velicky[351] in the framework of the single-site CPA using the Kubo–Greenwood formula. These results have been extended later to a more general models.[353–367]

The first attempt to include the electron–phonon scattering in the CPA calculations of the resistivity was given by Chen *et al.*[340] A model was introduced in which phonons were treated phenomenologically while electrons were described in CPA. The electron–phonon interaction was described by a local operator. Chen, Weisz and Sher[340] (CWS) have performed a model calculation on the temperature dependence of the electronic density of states and the electrical conductivity of disordered binary alloys, based on CPA solutions by introducing thermal disorder in the single-band model. They found that the effect of thermal disorder is to broaden and smear the static alloy density of states. The electrical conductivity in weak scattering alloys always decreases with temperature. However, in the strong-scattering case, the temperature coefficient of conductivity can be negative, zero or positive, depending on the location of the Fermi energy. Brouers and Brauwers[368] have extended the calculation to an *s*–*d* two-band model that accounts for the general behavior of the temperature dependence of the electrical resistivity in concentrated transition metal alloys. In Ref. 358, a generalization of CWS theory[340] was made by including the effect of uniaxial strain on the temperature variation of the electronic density of states and the electrical conductivity of disordered concentrated binary alloys. The validity of the adiabatic approximation in strong-scattering alloys was analyzed by CSW.[359] It was shown that the electron screening process in the moving lattice may be modified by lattice motion in disordered alloys. If this modification is significant, not only the effective Hamiltonian but also the whole adiabatic approximation would need to be reconsidered.

A consistent theory of the electroconductivity in disordered transition metal alloys with the proper microscopic treatment of the electron–phonon interaction was carried out by Christoph and Kuzemsky.[310] They used the approach of paper,[180] where a self-consistent microscopic theory for the calculation of one-particle Green functions for the electron–phonon problem in disordered transition metal alloys was developed. However, this approach cannot be simply generalized to the calculation of two-particle Green functions needed for the calculation of the conductivity by the Kubo formula. Therefore, for the sake of simplicity, in their study Christoph and Kuzemsky[310] neglected the influence of disorder on the phonons. Thus, in the model investigated here, in contrast to the GWS approach,[340] the dynamics of the phonons is taken into account microscopically, but they are treated as in a virtual reference crystal.

For a given configuration of atoms, the total Hamiltonian of the electron-ion system in the substitutionally disordered alloy can be written in the form[180,310]

$$H = H_e + H_i + H_{ei}\,, \tag{12.1}$$

where

$$H_e = \sum_{i\sigma} \epsilon_i a^\dagger_{i\sigma} a_{i\sigma} + \sum_{ij\sigma} t_{ij} a^\dagger_{i\sigma} a_{j\sigma} \tag{12.2}$$

is the one-particle Hamiltonian of the electrons. For our main interest is the description of the electron–phonon interaction, we can suppose that the electron–electron correlation in the Hubbard form has been taken here in the Hartree–Fock approximation in analogy with Eq. (11.56).

For simplicity, in this paper the vibrating ion system will be described by the usual phonon Hamiltonian

$$H_i = \sum_{q\nu} \omega(\mathbf{q}\nu) \left(b^\dagger_{q\nu} b_{q\nu} + \frac{1}{2} \right). \tag{12.3}$$

The electron–phonon interaction term is taken in the following form[180]

$$H_{ei} = \sum_{ij} \sum_{\alpha\sigma} T^\alpha_{ij} (u^\alpha_i - u^\alpha_j) a^\dagger_{i\sigma} a_{j\sigma}\,, \tag{12.4}$$

where u^α_i $(\alpha = x, y, z)$ is the ion displacement from the equilibrium position $\mathbf{R}_i$.

In terms of phonon operators this expression can be rewritten in the form

$$H_{ei} = \sum_{i \neq j} \sum_{q\nu\sigma} A_{q\nu}(ij)(b_{q\nu} + b^\dagger_{-q\nu}) a^\dagger_{i\sigma} a_{j\sigma}\,, \tag{12.5}$$

where

$$A_{q\nu}(ij) = \frac{q_0}{\sqrt{2\langle M \rangle N \omega(\mathbf{q}\nu)}} t^0_{ij} \frac{\mathbf{R}_j - \mathbf{R}_i}{|\mathbf{R}_j - \mathbf{R}_i|} \mathbf{e}_\nu(\mathbf{q}) (e^{i\mathbf{q}\mathbf{R}_i} - e^{i\mathbf{q}\mathbf{R}_j})\,. \tag{12.6}$$

Here $\omega(\mathbf{q}\nu)$ are the acoustic phonon frequencies, $\langle M \rangle$ is the average ion mass, $\mathbf{e}_\nu(\mathbf{q})$ are the polarization vectors of the phonons, and q_0 is the Slater coefficient originated in the exponential radial decrease of the tight-binding electron wavefunction. It is convenient to rewrite this expression in the form

$$H_{ei} = \sum_{i \neq j} \sum_{q} A_q(ij)(b_q + b^\dagger_{-q}) a^\dagger_i a_j\,, \tag{12.7}$$

where the spin and phonon polarization indices are omitted for brevity.

The electrical conductivity will be calculated starting with the Kubo expression for the dc conductivity:

$$\sigma(i\varepsilon) = -\langle\langle \mathbf{J}|\mathbf{P}\rangle\rangle_{i\varepsilon}\,, \quad (\varepsilon \to 0^+)\,, \tag{12.8}$$

where $\mathbf{P} = e\sum_i \mathbf{R}_i a_i^\dagger a_i$ and $\mathbf{R}_i$ is the position vector; $m/e\mathbf{J} = m/e\dot{\mathbf{P}}$ is the current operator of the electrons. It has the form

$$\mathbf{J} = -ie\sum_{ij}(\mathbf{R}_i - \mathbf{R}_j)t_{ij}a_i^\dagger a_j\,. \tag{12.9}$$

Then the normalized conductivity becomes

$$\sigma^{\alpha\beta} = \frac{ie^2}{\Omega}\sum_{ij}\sum_{l}(\mathbf{R}_i - \mathbf{R}_j)^\alpha \mathbf{R}_l^\beta t_{ij}\langle\langle a_i^\dagger a_j|a_l^\dagger a_l\rangle\rangle_{i\varepsilon}\,, \tag{12.10}$$

where Ω is the volume of the system. It should be emphasized here that $\sigma^{\alpha\beta}$ depends on the configuration of the alloy. A realistic treatment of disordered alloys must involve a formalism to deal with one-electron Hamiltonians that include both diagonal and off-diagonal randomness.[353–360] In the present study, for the sake of simplicity, we restrict ourselves to a diagonal disorder. Hence we can rewrite hopping integral t_{ij} as

$$t_{ij} = \frac{1}{N}\sum_{k} E(\mathbf{k})\exp[i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j)]\,. \tag{12.11}$$

Thus to proceed it is necessary to find the Green function $G_{ij,lm} = \langle\langle a_i^\dagger a_j|a_l^\dagger a_m\rangle\rangle$. It can be calculated by the equation of motion method. Using the Hamiltonian (12.1), we find by a differentiation with respect to the left-hand side

$$\begin{aligned}\sum_{nr} H_{ij,rn}G_{nr,lm}(\omega) &= \langle a_i^\dagger a_m\rangle\delta_{lj} - \langle a_l^\dagger a_j\rangle\delta_{mi}\\ &\quad + \sum_{qn}(A_q(j-n)e^{i\mathbf{q}\mathbf{R}_j}\langle\langle a_i^\dagger a_n(b_q + b_{-q}^\dagger)|a_l^\dagger a_m\rangle\rangle\\ &\quad - A_q(n-i)e^{i\mathbf{q}\mathbf{R}_n}\langle\langle a_n^\dagger a_j(b_q + b_{-q}^\dagger)|a_l^\dagger a_m\rangle\rangle)\,,\end{aligned} \tag{12.12}$$

where

$$H_{ij,rn} = (\omega - \epsilon_n + \epsilon_r)\delta_{ni}\delta_{rj} - t_{jr}\delta_{ni} + t_{ni}\delta_{rj}\,. \tag{12.13}$$

We define now the zeroth-order Green functions $G^0_{ij,lm}$ that obey the following equations of motion

$$\sum_{nr} H_{ij,rn}G^0_{nr,lm} = \langle a_i^\dagger a_m\rangle\delta_{lj} - \langle a_l^\dagger a_j\rangle\delta_{mi}\,, \tag{12.14}$$

$$\sum_{nr} H_{rn,lm}G^0_{ij,nr} = \langle a_i^\dagger a_m\rangle\delta_{lj} - \langle a_l^\dagger a_j\rangle\delta_{mi}\,, \tag{12.15}$$

where Eq. (12.15) has been obtained by a differentiation with respect to the right-hand side of $G^0_{ij,lm}$. Using these definitions it can be shown that

$$\begin{aligned}
&\sum_{nr}(\langle a_s^\dagger a_n\rangle\delta_{rt} - \langle a_r^\dagger a_t\rangle\delta_{sn})G_{nr,lm}(\omega)\\
&\quad = \sum_{ij}(\langle a_i^\dagger a_m\rangle\delta_{lj} - \langle a_l^\dagger a_j\rangle\delta_{mi})G^0_{st,ji}(\omega)\\
&\quad\quad + \sum_{ijn}\sum_q (A_q(j-n)e^{i\mathbf{qR}_j}\langle\!\langle a_i^\dagger a_n(b_q + b^\dagger_{-q})|a_l^\dagger a_m\rangle\!\rangle\\
&\quad\quad - A_q(n-i)e^{i\mathbf{qR}_n}\langle\!\langle a_n^\dagger a_j(b_q + b^\dagger_{-q})|a_l^\dagger a_m\rangle\!\rangle)G^0_{st,ji}(\omega)\,.
\end{aligned} \tag{12.16}$$

The right-hand side higher-order Green functions can be calculated in a similar way. To proceed we approximate the electron–phonon Green function as

$$\langle\!\langle a_n^\dagger a_r b_q^\dagger b_q|B\rangle\!\rangle \simeq N(q)\langle\!\langle a_n^\dagger a_r|B\rangle\!\rangle\,. \tag{12.17}$$

Here $N(q)$ denotes the Bose distribution function of the phonons.

As a result we find

$$\begin{aligned}
&\sum_{nr}(\langle a_s^\dagger a_n\rangle\delta_{rt} - \langle a_r^\dagger a_t\rangle\delta_{sn})\langle\!\langle a_n^\dagger a_r b_q|a_l^\dagger a_m\rangle\!\rangle\\
&\quad = \omega(q)\sum_{ij}\langle\!\langle a_i^\dagger a_j b_q|a_l^\dagger a_m\rangle\!\rangle G^0_{st,ji}(\omega)\\
&\quad\quad - \sum_{ijn}(1+N(q))(A_{-q}(j-n)e^{-i\mathbf{qR}_j}G_{in,lm}(\omega)\\
&\quad\quad - A_{-q}(n-i)e^{-i\mathbf{qR}_n}G_{nj,lm}(\omega))G^0_{st,ji}(\omega)\\
&\quad\quad - \sum_{ij}\sum_{np}A_{-q}(n-p)e^{-i\mathbf{qR}_n}(\langle a_p a_i^\dagger\rangle G_{nj,lm} - \langle a_p^\dagger a_j\rangle G_{ip,lm})G^0_{st,ji}(\omega)
\end{aligned} \tag{12.18}$$

and a similar equation for $\langle\!\langle a_n^\dagger a_r b_{-q}|a_l^\dagger a_m\rangle\!\rangle$.

In the above equations the Green functions G and G^0 as well as the mean values $\langle a_i^\dagger a_j\rangle$ which can be expressed by one-particle Green functions depend on the atomic configuration. For the configuration averaging (which we will denote by $\bar{G}$), we use the simplest approximation

$$\overline{G\cdot G} \sim \bar{G}\cdot\bar{G}\,, \tag{12.19}$$

i.e., in all products the configurational-dependent quantities will be averaged separately. Taking into account Eqs. (12.14) and (12.19), the averaged zeroth-order Green function $\overline{G^0_{ij,lm}}$ is given by the well-known CPA solution for two-particle Green function in disordered metallic alloy[351]

$$\overline{G^0_{ij,lm}}(\omega) = \frac{1}{N^2}\sum_{k_1k_2}e^{i\mathbf{k}_1(\mathbf{R}_m - \mathbf{R}_i)}e^{i\mathbf{k}_2(\mathbf{R}_j - \mathbf{R}_l)}F_2(\mathbf{k}_1,\mathbf{k}_2)\,, \tag{12.20}$$

where $F_2(\mathbf{k}_1, \mathbf{k}_2)$ is given by

$$\begin{gathered} F_2(\mathbf{k}_1, \mathbf{k}_2) \approx i(E(\mathbf{k}_2) - E(\mathbf{k}_1)) \int d\omega \frac{\partial f}{\partial \omega} \left[\mathrm{Im} \left(\frac{1}{\omega - \Sigma(\omega) - E(\mathbf{k}_1)} \right) \right]^2 , \\ \text{for} \quad |E(\mathbf{k}_1) - E(\mathbf{k}_2)| \ll |\Sigma(E(\mathbf{k}_1))| , \end{gathered} \tag{12.21}$$

$$\begin{gathered} F_2(\mathbf{k}_1, \mathbf{k}_2) \approx \tfrac{f(E(\mathbf{k}_1)) - f(E(\mathbf{k}_2))}{E(\mathbf{k}_1) - E(\mathbf{k}_2)} , \\ \text{for} \quad |E(\mathbf{k}_1) - E(\mathbf{k}_2)| \gg |\Sigma(E(\mathbf{k}_1))| . \end{gathered} \tag{12.22}$$

Here $\Sigma(\omega)$ denotes the coherent potential and $f(\omega)$ is the Fermi distribution function. The configurational averaged terms $\overline{\langle a_s^\dagger a_n \rangle}$ are given by

$$\begin{aligned} \overline{\langle a_s^\dagger a_n \rangle} &= \sum_k e^{i\mathbf{k}(\mathbf{R}_n - \mathbf{R}_s)} F_1(\mathbf{k}) , \\ F_1(\mathbf{k}) &= -\frac{1}{\pi} \int d\omega f(\omega) \mathrm{Im} \left(\tfrac{1}{\omega - \Sigma(\omega) - E(\mathbf{k})} \right) . \end{aligned} \tag{12.23}$$

After the configurational averaging equations (12.16) and (12.18) can be solved by Fourier transformation and we find

$$\overline{G_{ij,lm}(\omega)} = \frac{1}{N^2} \sum_{k_1 k_2} \sum_{k_3 k_4} e^{-i\mathbf{k}_1 \mathbf{R}_i} e^{i\mathbf{k}_2 \mathbf{R}_j} e^{-i\mathbf{k}_3 \mathbf{R}_l} e^{i\mathbf{k}_4 \mathbf{R}_m} G(\mathbf{k}_1, \mathbf{k}_2; \mathbf{k}_3, \mathbf{k}_4) , \tag{12.24}$$

where

$$\begin{aligned} G(\mathbf{k}_1, \mathbf{k}_2; \mathbf{k}_3, \mathbf{k}_4) \equiv G(\mathbf{k}_1, \mathbf{k}_2) &= F_2(\mathbf{k}_1, \mathbf{k}_2) \delta(\mathbf{k}_4, \mathbf{k}_1) \delta(\mathbf{k}_3, \mathbf{k}_2) - \frac{F_2(\mathbf{k}_1, \mathbf{k}_2)}{F_1(\mathbf{k}_1) - F_1(\mathbf{k}_2)} \\ &\times \sum_q \left(\frac{X(\mathbf{q}, \mathbf{k}_2) G(\mathbf{k}_1, \mathbf{k}_2) + Y(\mathbf{q}, \mathbf{k}_1, \mathbf{k}_2) G(\mathbf{k}_1 - \mathbf{q}, \mathbf{k}_2 - \mathbf{q})}{[F_1(\mathbf{k}_1) - F_1(\mathbf{k}_2 - \mathbf{q}) - \omega(\mathbf{q}) F_2(\mathbf{k}_1, \mathbf{k}_2 - \mathbf{q})](F_2(\mathbf{k}_1, \mathbf{k}_2 - \mathbf{q}))^{-1}} \right. \\ &+ \frac{X_1(\mathbf{q}, \mathbf{k}_1, \mathbf{k}_2) G(\mathbf{k}_1 - \mathbf{q}, \mathbf{k}_2 - \mathbf{q}) - Y_1(\mathbf{q}, \mathbf{k}_1) G(\mathbf{k}_1, \mathbf{k}_2)}{[F_1(\mathbf{k}_1 - \mathbf{q}) - F_1(\mathbf{k}_2) - \omega(\mathbf{q}) F_2(\mathbf{k}_1 - \mathbf{q}, \mathbf{k}_2)](F_2(\mathbf{k}_1 - \mathbf{q}, \mathbf{k}_2))^{-1}} \\ &\left. - 2 \ \text{terms with} \ \omega(\mathbf{q}) \to -\omega(\mathbf{q}), N(q) \to (-1 - N(q)) \right) , \end{aligned} \tag{12.25}$$

and

$$A(q, k) = \frac{1}{N} \sum_k e^{-i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j)} A_q(i - j) . \tag{12.26}$$

Here the following notation were introduced

$$X(\mathbf{q}, \mathbf{k}_2) = A(\mathbf{q}, \mathbf{k}_2 - \mathbf{q}) A(-\mathbf{q}, \mathbf{k}_2)(F_1(\mathbf{k}_2 - \mathbf{q}) - 1 - N(q)) , \tag{12.27}$$

$$Y(\mathbf{q}, \mathbf{k}_1, \mathbf{k}_2) = A(\mathbf{q}, \mathbf{k}_2 - \mathbf{q}) A(-\mathbf{q}, \mathbf{k}_1)(F_1(\mathbf{k}_1) + N(q)) , \tag{12.28}$$

$$X_1(\mathbf{q}, \mathbf{k}_1, \mathbf{k}_2) = A(\mathbf{q}, \mathbf{k}_1) A(-\mathbf{q}, \mathbf{k}_2 - \mathbf{q})(1 + N(q) - F_1(\mathbf{k}_2)) , \tag{12.29}$$

$$Y_1(\mathbf{q}, \mathbf{k}_1) = A(\mathbf{q}, \mathbf{k}_1) A(-\mathbf{q}, \mathbf{k}_1 - \mathbf{q})(F_1(\mathbf{k}_1 - \mathbf{q}) + N(q)) . \tag{12.30}$$

Equation (12.25) is an integral equation for the Green function $G(\mathbf{k}_1, \mathbf{k}_2)$ to be determined.

The structural averaged conductivity can be obtained, in principle, by using Eq. (12.10), where the Green function $\langle\langle a_i^\dagger a_j | a_l^\dagger a_l \rangle\rangle$ is to be replaced by $\overline{G_{ij,ll}(\omega)}$ as given by Eq. (12.24). It is, however, more convenient to start with the Kubo formula in the following form[310]

$$\sigma = \frac{ie^2}{\Omega} \lim_{p\to 0} \sum_k \frac{1}{p^2} \left(\frac{\partial E(k)}{\partial k} p \right) \langle\langle a_k^\dagger a_{k+p} | \eta_{-p} \rangle\rangle_{i\varepsilon} \,, \tag{12.31}$$

where $\eta_{-p} = \sum_k a_k^\dagger a_{k-p}$ is the electron density operator. To find the Green function $\langle\langle a_k^\dagger a_{k+p} | \eta_{-p} \rangle\rangle$, the integral equation (12.25) has to be solved. In general, this can be done only numerically, but we can discuss here two limiting cases explicitly. At first we consider the weak-scattering limit being realized for a weak disorder in the alloy, and second, we investigate the temperature coefficient of the conductivity for a strong potential scattering.

In the weak-scattering limit, the CPA Green function is given by the expression

$$\begin{gathered} F_2(\mathbf{k}_1, \mathbf{k}_2) \approx i(E(\mathbf{k}_2) - E(\mathbf{k}_1)) \frac{df}{dE(k_1)} \cdot \frac{1}{\Sigma(E(k_1))} \,, \\ \text{for} \quad |E(\mathbf{k}_2) - E(\mathbf{k}_1)| \ll |\Sigma(E(\mathbf{k}_1))| \,. \end{gathered} \tag{12.32}$$

Corresponding to this limit, the following solution ansatz for the Green function $G(k, k+p)$ can be used

$$G(k, k+p) = \langle\langle a_k^\dagger a_{k+p} | \eta_{-p} \rangle\rangle_{i\varepsilon} \simeq i \left(\frac{\partial E(k)}{\partial k} p \right) \frac{df}{dE(k)} \cdot \frac{1}{\Sigma(E(k)) + \gamma(E(k))} \,, \tag{12.33}$$

where γ describes the contribution of the electron–phonon scattering to the coherent potential. Taking into account that in the weak-scattering limit $|\Sigma| \ll \omega(\mathbf{q})$, the terms $F_2(k, k-q)$ in the right-hand side denominators of Eq. (12.25) can be replaced by the expression (12.32), and then the integral equation (12.25) becomes for $\lim p \to 0$

$$\begin{aligned} & i \frac{\partial f(E(k))}{\partial E(k)} \left(\frac{\partial E(k)}{\partial k} p \right) \frac{1}{\Sigma(E(k)) + \gamma(E(k))} \\ & \quad \simeq i \frac{\partial f(E(k))}{\partial E(k)} \left(\frac{\partial E(k)}{\partial k} p \right) \frac{1}{\Sigma(E(k))} \\ & \qquad - \frac{1}{\Sigma(E(k))} \frac{1}{N} \sum_q A(\mathbf{q}, \mathbf{k}-\mathbf{q}) A(-\mathbf{q}, \mathbf{k}) \left[\frac{Z_1(k,q) + Z_2(k,q)}{E(k) - E(k-q) - \omega(q) + i\varepsilon} \right. \\ & \qquad + \frac{Z_3(k,q) - Z_4(k,q)}{E(k) - E(k-q) + \omega(q) + i\varepsilon} \\ & \qquad \left. - \, 2 \ \text{terms with} \ \omega(\mathbf{q}) \to -\omega(\mathbf{q}), N(q) \to (-1 - N(q)) \right] . \end{aligned} \tag{12.34}$$

Here the following notation were introduced

$$Z_1(k,q) = (f(E(k-q)) - 1 - N(q))\frac{df}{dE(k)} \cdot \frac{\left(\frac{\partial E(k)}{\partial k}p\right)}{\Sigma(E(k)) + \gamma(E(k))}\,, \tag{12.35}$$

$$Z_2(k,q) = (f(E(k)) + N(q))\frac{df}{dE(k-q)} \cdot \frac{\left(\frac{\partial E(k-q)}{\partial (k-q)}p\right)}{\Sigma(E(k-q)) + \gamma(E(k-q))}\,, \tag{12.36}$$

$$Z_3(k,q) = (1 - f(E(k)) + N(q))\frac{df}{dE(k-q)} \cdot \frac{\left(\frac{\partial E(k-q)}{\partial (k-q)}p\right)}{\Sigma(E(k-q)) + \gamma(E(k-q))}\,, \tag{12.37}$$

$$Z_4(k,q) = (f(E(k-q)) + N(q))\frac{df}{dE(k)} \cdot \frac{\left(\frac{\partial E(k)}{\partial k}p\right)}{\Sigma(E(k)) + \gamma(E(k))}\,. \tag{12.38}$$

Approximating the self-energy terms $\Sigma(E(k))$ and $\gamma(E(k))$ by $\Sigma(E_F) \equiv \Sigma$ and $\gamma(E_F) \equiv \gamma$, respectively, the terms proportional to Σ cancel and γ can be calculated by

$$\begin{aligned}
\gamma\frac{df}{dE(k)} \cdot \left(\frac{\partial E(k)}{\partial k}p\right) = {}& -\frac{\pi}{N}\sum_q A(\mathbf{q},\mathbf{k}-\mathbf{q})A(-\mathbf{q},\mathbf{k}) \\
& \times\Bigg(\Bigg[(f(E(k)) + N(q))\frac{df}{dE(k-q)} \cdot \left(\frac{\partial E(k-q)}{\partial (k-q)}p\right) \\
& - (1 - f(E(k-q)) + N(q))\frac{df}{dE(k-q)} \\
& \times \left(\frac{\partial E(k)}{\partial k}p\right)\Bigg]\delta(E(k) - E(k-q) - \omega(q))\Bigg) \\
& - \frac{\pi}{N}\sum_q A(\mathbf{q},\mathbf{k}-\mathbf{q})A(-\mathbf{q},\mathbf{k}) \\
& \times\Bigg(\Bigg[(f(E(k-q)) + N(q))\frac{df}{dE(k)} \cdot \left(\frac{\partial E(k)}{\partial k}p\right) \\
& - (1 - f(E(k)) + N(q))\frac{df}{dE(k-q)} \\
& \times \left(\frac{\partial E(k-q)}{\partial (k-q)}p\right)\Bigg]\delta(E(k) - E(k-q) + \omega(q))\Bigg).
\end{aligned} \tag{12.39}$$

Using the approximations

$$\frac{\partial E(k)}{\partial k} \simeq \frac{1}{m^*}k, \quad A(\mathbf{q},\mathbf{k}-\mathbf{q})A(-\mathbf{q},\mathbf{k}) \simeq A^2 q, \quad q \to 0\,,$$

where effective mass $m^* = m^*(E_F)$, we find

$$\gamma = \beta \frac{\Omega}{2\pi N} \frac{A^2 m^*}{2(2m^* E_F)^{3/2}} \int dq q^4 \omega(q) N(q)(1+N(q)) \tag{12.40}$$

and

$$\gamma \sim \begin{cases} T^5 & \text{if } T \ll \theta_D \,, \\ T & \text{if } T \gg \theta_D \,. \end{cases} \tag{12.41}$$

For a binary alloy $A_x B_{1-x}$ with concentrations of the constituents c_A and c_B and the corresponding atomic energies ϵ_A and ϵ_B, in the weak-scattering limit the coherent potential is given by[340]

$$\Sigma = c_A c_B (\epsilon_A - \epsilon_B)^2 D(E_F) \,. \tag{12.42}$$

Then the conductivity becomes

$$\sigma = \frac{e^2}{3(2\pi)^3} \int dk \left(\frac{\partial E(k)}{\partial k} \right)^2 \frac{df}{dE(k)} \cdot \tau \,, \tag{12.43}$$

where

$$\tau^{-1} = \Sigma + \gamma \,, \tag{12.44}$$

in correspondence with the Matthiessen, Nordheim and Bloch–Gruneisen rules.

Now we estimate temperature coefficient of the conductivity for a strong potential scattering. For a strongly disordered alloy, the electron–phonon interaction can be considered as a small perturbation and the Green functions $G(k,k')$ on the right-hand side of Eq. (12.25) can be replaced by CPA Green functions $F(k,k')$. For simplicity, on the right-hand side of Eq. (12.25), we take into consideration only terms proportional to the Bose distribution function giving the main contribution to the temperature dependence of the conductivity. Then $\langle\langle a_k^\dagger a_{k_1} | \eta_{k-k_1} \rangle\rangle$ becomes $(k_1 = k + p \simeq k)$

$$\begin{aligned} &\langle\langle a_k^\dagger a_{k_1} | \eta_{k-k_1} \rangle\rangle \\ &= F_2(k,k_1) \Bigg(1 - \frac{2}{F_1(k) - F_1(k_1)} \sum_q A(\mathbf{q}, \mathbf{k}-\mathbf{q}) A(-\mathbf{q}, \mathbf{k}) N(q) \\ &\quad \times \Bigg\{ \frac{F_2(k,k-q)[F_2(k-q,k_1-q) - F_2(k,k_1)](F_1(k) - F_1(k-q))}{[F_1(k) - F_1(k-q)]^2 - \omega^2(q) F_2^2(k,k-q)} \\ &\quad + \frac{F_2(k-q,k)[F_2(k-q,k_1-q) - F_2(k,k_1)](F_1(k-q) - F_1(k))}{[F_1(k-q) - F_1(k)]^2 - \omega^2(q) F_2^2(k-q,k)} \Bigg\} \Bigg) . \end{aligned} \tag{12.45}$$

Neglecting at low temperatures, the terms $\omega^2(q) F_2^2(k_1 - q, k_1) \sim q^4$ as compared to $[F_1(k_1) - F_1(k_1 - q)]^2 \sim q^2$ and using Eq. (12.21) for $\omega(q) \ll |\Sigma|$, we find for small

q and $p \to 0$

$$\langle\langle a_k^\dagger a_{k+p} | \eta_{-p} \rangle\rangle \simeq F_2(k, k+p) \left[1 + \left(\frac{dF_1}{dE(k)} \right)^{-2} \sum_q (\Delta(q, k-q) - \Delta(q,k)) \right] . \tag{12.46}$$

Here $\Delta(q,k)$ is the temperature-dependent correction terms to the CPA Green function are given by

$$\Delta(q,k) = 2A^2 qN(q) \left(\int d\omega \frac{df(\omega)}{d\omega} \left[\mathrm{Im} \left(\frac{1}{\omega - \Sigma(\omega) - E(k)} \right) \right]^2 \right)^2 . \tag{12.47}$$

For temperatures $k_B T \ll E_F$, we can write

$$\int d\omega \frac{df(\omega)}{d\omega} S(\omega, E(k)) \cong -S(E_F, E(k)) \tag{12.48}$$

and the conductivity becomes

$$\sigma = \sigma_{CPA} + \Delta\sigma(T) \,, \tag{12.49}$$

where

$$\sigma_{CPA} = \frac{e^2}{\Omega} \sum_k \left(\frac{\partial E(k)}{\partial k} \right)^2 \left[\mathrm{Im} \left(\frac{1}{E_F - \Sigma(E_F) - E(k)} \right) \right]^2 \tag{12.50}$$

is the standard CPA expression for the conductivity and

$$\begin{aligned} \Delta\sigma(T) = \frac{2e^2 A^2}{\Omega} \sum_k \left(\frac{\partial E(k)}{\partial k} \right)^2 \sum_q qN(q) \\ \times \left(\left[\mathrm{Im} \left(\frac{1}{E_F - \Sigma(E_F) - E(k-q)} \right) \right]^4 \right. \\ \left. - \left[\mathrm{Im} \left(\frac{1}{E_F - \Sigma(E_F) - E(k)} \right) \right]^4 \right) . \end{aligned} \tag{12.51}$$

Introducing the effective mass of the electrons with $E(k) \simeq E_F$, the temperature-dependent correction to the conductivity becomes

$$\Delta\sigma(T) \cong \frac{2e^2 A^2}{\Omega} \frac{1}{(m^*)^2} \sum_k \sum_q q^3 N(q) \left[\mathrm{Im} \left(\frac{1}{E_F - \Sigma(E_F) - E(k-q)} \right) \right]^4 . \tag{12.52}$$

Here the quantity $\Delta\sigma(T)$ is positive definite and increasing with increasing temperature. Hence, in strongly disordered alloys where the electron–phonon scattering is weak as compared with the disorder scattering, the temperature coefficient of the resistivity is negative. It should be mentioned, however, that the concrete temperature dependence of the correction term (12.52) is a crude estimation only because in the derivation of (12.52) the influence of the disorder on the lattice vibrations has been neglected.

One more remark is appropriate for the above consideration. For the calculation of transport coefficients in disordered $3d$ systems, the classical approaches such as the Boltzmann equation, become useless if the random fluctuations of the potential are too large.[235,337] The strong potential fluctuations force the electrons into localized states. In order to investigate the resistivity of metallic alloys near the metal–insulator transition,[235,337] the corresponding formula for the resistivity can be deduced along the line described above. For a binary transition metal alloy, the corresponding Hamiltonian is given by

$$H = \sum_i \epsilon_i a_i^\dagger a_i + \sum_{ij} t_{ij} a_i^\dagger a_j \tag{12.53}$$

(with $\epsilon_i = \epsilon_A$, ϵ_B depending on the occupation of the lattice site i). A corresponding integral equation for the Green function $\langle\langle a_j | a_i^\dagger \rangle\rangle_\omega$ can be written down. Using a simple ensemble averaging procedure and approximating the averaged Green function by the expression

$$\overline{\langle\langle a_j | a_i^\dagger \rangle\rangle_\omega} \approx \frac{1}{N} \sum_k \exp[ik(R_i - R_j)] \frac{1}{\omega - \epsilon_k} \exp(-\alpha(\epsilon_k)|R_i - R_j|)\,, \tag{12.54}$$

the integral equation transforms into an equation for the parameter $(\alpha(\epsilon_k))^{-1}$ which is proportional to the averaged mean free path of the electrons. It can be shown then, by solving this equation for electrons at the Fermi surface E_F, that $(\alpha(E_F))^{-1}$ and the conductivity σ drop in a discontinued way from $(\alpha)^{-1}_{\min}$ and $\sigma_{\min}$, respectively, to zero as the potential fluctuations exceed a critical value. Note that $(\alpha)^{-1}_{\min}$ is of the order $1/d$, where d is the lattice parameter.

13. Discussion

In the foregoing sections, we have discussed some selected statistical mechanics approaches to the calculation of the electrical conductivity in metallic systems like transition metals and their disordered alloys within a model approach.

Electrons in metals are scattered by impurities and phonons. The theory of transport processes for ordinary metals was based on the consideration of various types of scattering mechanisms and, as a rule, has used the Boltzmann equation approach. The aim of the present review was to describe an alternative approach to the calculation of electroconductivity, which can be suitable for transition metals and their disordered alloys. There is an important aspect of this consideration. The approximations used here are the tight-binding and modified tight-binding, which are admittedly not ideally precise but does give (at least as the first approximation) reasonable qualitative results for paramagnetic transition metals and their disordered alloys. We studied the electronic conduction in a model of transition metals and their disordered alloys utilizing the method of generalized kinetic equations. The reasonable and workable expressions for the electrical conductivity were established and analyzed. We discussed briefly various approaches for computing electrical conductivity as well.

We hope that these considerations have been worked out with sufficient details to bring out their scope and workability. In this paper, we have considered the idealized Hubbard model which is the simplest (in the sense of formulation, but not solution) and most popular model of correlated lattice fermions.[62,99] We believe that this technique can be applied to other model systems (e.g., multi-band Hubbard model, periodic Anderson model, etc.). As it is seen, this treatment has some advantages in comparison with the standard methods of computing electrical conductivity within the Boltzmann equation approach, namely, the very compact form. The physical picture of electron–electron and electron–phonon scattering processes in the interacting many-particle systems is clearly seen at every stage of calculations, which is not the case with the standard methods. This picture of interacting many-particle system on a lattice is far richer and gives more possibilities for the analysis of phenomena which can actually take place in real metallic systems. We believe that our approach offers a convenient way for approximate considerations of the resistivity of the correlated electron systems on a lattice. We believe that in view of the great difficulty of developing a first principles microscopic theory of transport processes in solids, the present approach is a useful alternative for description the influence of electron–electron, electron–phonon and disorder scattering effects on the transport properties of transition metals and their disordered alloys.

In the confines of a review of this nature many topics of great practical and theoretical interest have necessarily to be omitted (see e.g., Refs. 369–371). In recent years the field of mesoscopic physics is developing rapidly.[337,372–375] It deals with systems under experimental conditions where several quantum-length scales for electrons are comparable. The physics of transport processes in such systems is rich of quantum effects, which is typically characterized by interplay of quantum interference and many-body interactions. It would be of interest to generalize the present approach to quantum transport phenomena.

In conclusion, the foregoing analysis suggests that the method of the generalized kinetic equations is an efficient and useful formalism for the studying of some selected transport processes in metallic systems.

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