VARIATIONAL METHODS IN THE CONDUCTION THEORY OF METALS

THESIS

Submitted in partial fulfilment of
the requirements for the degree of
M.Sc.

by

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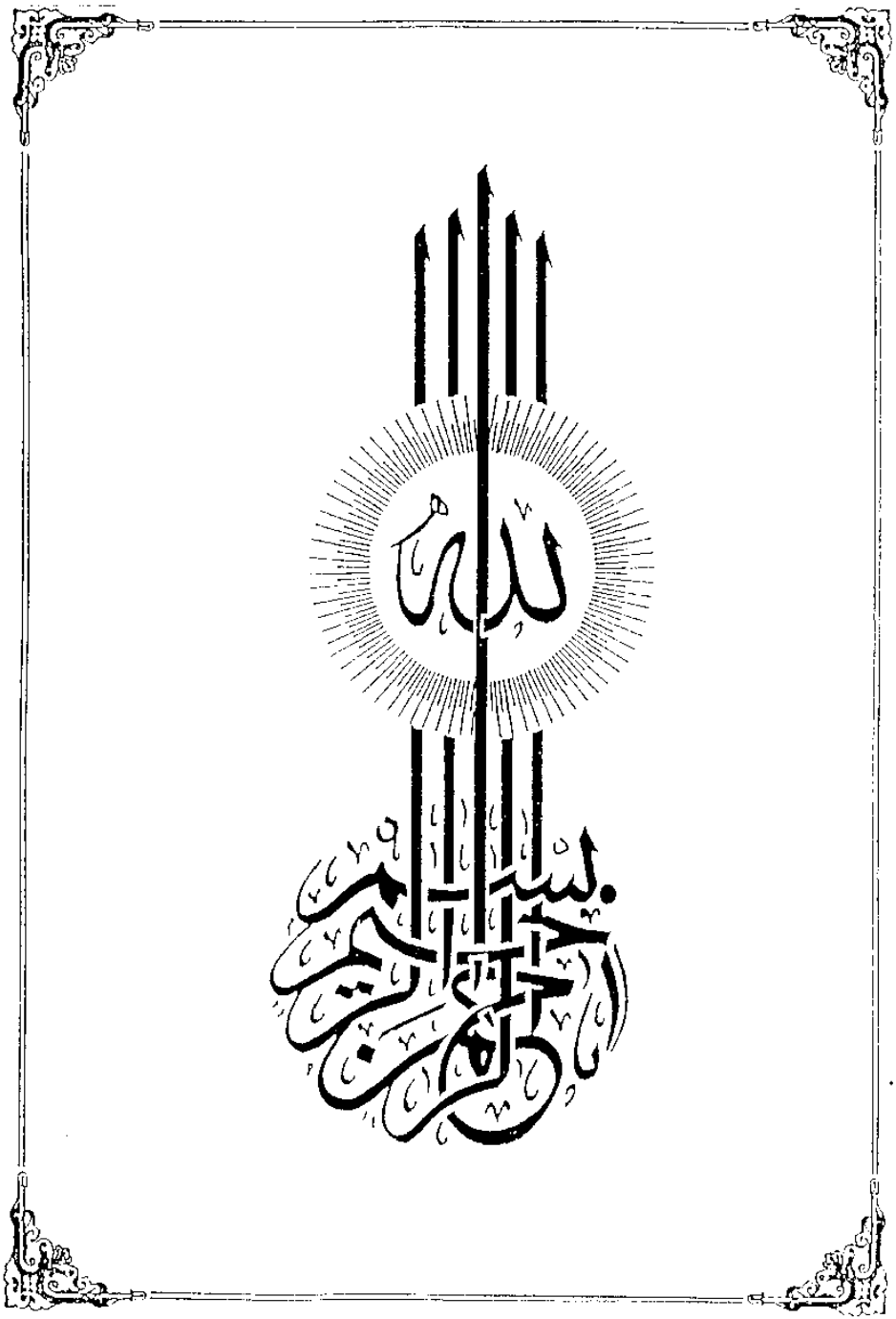
February 1971

A C K N O W L E D G E M E N T

I wish to record my sincere thanks to Dr. I.I. Hanna for suggesting the problem treated in this work, and for his helpful guidance, invaluable criticism, and kind encouragement during my course of study under his supervision.

I am also greatly indebted to him for his useful help during writing the thesis.



C O N T E N T S

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I N T R O D U C T I O N

Chapter One

The first idea for explaining the transport phenomena in metals was given by Weber (1875). He imagined the molecule of a metal to consist of a number of electically charged particles in relative motion to one another and that each molecule is not completely stable so that from time to time one or more particles would leave the molecule and move through the metal until they are captured by another molecule and once more ejected to continue their journey through the metal. This attempt did not really, give any rigid explanation of the transport phenomenae until the discovery of the electron by J.J. Thomson in 1897. This discovery presented, a better foundation to every attempt in this field to build up the mechanism of metallic conduction. The first contribution was made by Rieche in 1898, and was soon superceded by Drude in 1900.

According to Drude's theory, in a metal there are free electrons forming a kind of "Electron Gas". These electrons have an average velocity and pursue random motions through the metal due to collisions with the metallic ions assumed to be at rest. As an electric field $\underline{\mathcal{E}}$ is imposed, the motion of the electrons are no longer entirely random and an electric current will be set up in the direction of the electric field.

Drude obtained formulae for the electrical and thermal conductivities, but his results are far to give any explanation of known experimental results. The best result of his theory is that it gave a theoretical explanation of the empirical law discovered by Wiedmann and Franz in 1853, namely that the ratio of the electrical and thermal conductivities at a given temperature is the same for all metals, and inagreement with Lorentz (1872) rule that the Weidmann-Franz ratio is proportional to the absolute temperature.

A great disadvantage of Drude's theory, which lead to its failure, is that it makes the concentration n of the free electrons varies as $T^{-1/2}$, and it is very difficult to see how the number of free electrons could decrease with increasing temperature. It was left to Lorentz (1905) to reinvestigate the problem using the full statistical theory derived by Maxwell and Boltzmann which give the distribution function $f_o(E)$ of the free electrons as

$$f_o(E) = n(m/2\pi kT)^{\frac{3}{2}} \exp(-E/kT), \qquad (1.1)$$

where m is the mass of the electron, k Boltzmann's constant and n the number of free electrons per unit volume.

Lorentz solved the Boltzmann equation (see chapter II) by assuming a relaxation time.

$$\tau = \mu |\underline{V}|^{p}, \qquad (1.2)$$

where $\underline{V}$ is the velocity of the electron, μ and p are two constants to be adjusted according to experimental data. Inspite of the fact that with these two-parameters. Lorentz theory is so much simplified, detailed comparison with experiment has shown serious deviations from experimental data. The most serious objection to this theory is that it leads to the assumption that each atom in the solid will give approximately one electron to the "Electron Gas". The specific heat for such a solid (ion-electron combination) will be 9 calories/deg./mol. in contradiction with the law of Dulong and Petit.

The application of the Drude-Lorentz theory to all magnetic and thermal effects lead to a few apparent successes coupled with a large number of failures and the subject became a very confused one, as is well explained by the report to the Solvay Conference held in 1923. No real advance was made until the birth of Pauli's (1925) exclusion principle, and the new form of statistical mechanics derived independently by Fermi and Dirac in1926. According to this Fermi-Dirac Statistics, the new form of the distribution function $f_o(E)$ is given by

$$f_o(E) = 1/\left[\exp(E-\zeta)/kT + 1\right], \qquad (1.3)$$

which in the limit of low particle densities will reduce to the Maxwellian forms indicated by equation (1.1).

Soon afterwards, Sommerfeld (1928) presented his model in which he imagined a metal to consist of a number of electrons, without mutual attraction, moving in a region of constant negative potential energy ($-K$). The number n of free electrons per unit volume and the potential energy ($-K$) were treated as parameters. The motion of these free electrons is governed by Schrodinger equation

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E + K)\psi = 0$$

and by certain boundary conditions.

The most important feature of Sommerfeld's theory, is that it puts forward a new concept concerning the conduction electrons. It states that not all free electrons, but those in the range in which $\frac{\partial f_o}{\partial E}$ is not zero, are conduction electrons. For the Fermi distribution (1.3) this range is small, extending over a range of order kT round the energy

$$\zeta_o = \frac{h^2}{8m}(3n/\pi)^{\frac{2}{3}} \qquad (1.4)$$

It is along this line, that Sommerfeld was able to show that the specific heat of the free electrons is very small in

comparison with the specific heat of the lattice at normal temperatures and was, thus, successful to reveal one of the paradoxes of the theory of free electrons. A second, but an important advantage of this theory is that the theoretical values of the second-order galvanomagnetic and thermomagnetic effects come into excellent alinement with the experimental values, whereas there was previously a wide divergence.

The real development in the theory of conduction of solids is due to Bloch (1928), according to whom electrons move freely through a perfect crystal lattice without resistance. Conductivity becomes finite when we take into account the irregularities in the lattice structure produced by the thermal vibrations of the lattice itself, by impurities, strains, ... etc. According to his analysis all electrons in a metal are considered as free electrons but not necessarily as conduction electrons. Since then, the theory of electronic conduction in solids has drawn the attention of a large number of physists and mathematicians. In the following parts of the present chapter we give a brief summary of the mathematical treatment of the problem.

Any theoretical study of the transport phenomena in solids depends upon the solution of Boltzmann equation,

sometimes called the transport equation, which is an integro-differential equation and may be turned to an integral equation of the velocity distribution (see chapter II). The first attempt for the solution of this equation was given by Wilson (1936, 1937) for the simplest model in which electrons are assumed to be quasi free. His solution, which was not satisfactory and generally valid, was obtained for the two relatively high ($T \gg \Theta$) and low ($T \ll \Theta$) ranges of temperature, (see Wilson, 1953; chapters VIII and IX). The case of an impure metal, at very low temperatures, was also treated by Wilson (1937) and Dube (1938) using a method of successive approximations which amounts to an expansion in descending powers of the residual resistance, but the high order terms become very complicated and the method cannot be applied to the case of an ideally pure metal.

So far the Boltzmann equation, in the absence of a magnetic field, had resisted any correct solution in the usual sense. More complications are to be expected in the presence of a magnetic field. The first acceptable work done on the galvanomagnetic and thermomagnetic effects is due to Sommerfeld (1931). In his work, which is an extension to his non-magnetic conduction effects, he considered the

simplest possible case in which electrons are assumed to be quasi free and the energy surfaces to be spherical. Further developments, but along the same line, were done by Sommerfeld and Bethe (1933), Boreluis (1935), Meissner (1935), Jones (1936), Ariyama (1938) and Gruneisen and Erfling (1939). According to these calculations, the free electron model is incapable to account for the magneto-resistance effects, and more complicated energy surfaces are needed for further discussions.

To obtain non-zero magnetic effects, Wilson and Sondheimer (1947) and Sondheimer (1948) presented a model in which they assumed two overlapping energy bands, an s-band containing some conduction electrons and a d-band containing some unoccupied levels. In each band the energy is assumed to be proportional to the square of the wave-vector, i.e. spherical energy surfaces. Using this model which is considered artificial, they obtained non-zero values of the magnetic effects sometimes in agreement with experimental values.

The methods of solution, so far used, are underlined under the name "Successive Approximations". They depend mainly upon the properties of the transport equation as related to temperature and the mean free paths of the

electrons being scattered by different scattering mechanisms. The first method applicable, in principle, to the whole temperature range was given by Kroll (1933a, b & 1938), in which the integral equation is transformed into an infinite set of linear equations and a solution using infinite determinants was obtained.

The most powerful method for the solution of these equations is the Variational Method.

The first attempt in that direction was carried out by Kohler (1948, 1949). In his trial he expanded the distribution function (see eq. 2.5.1) as a power series, the coefficients of which are determined by the variational principle (details are given in Chapter II). He succeeded to obtain explicit approximations of the lowest order and his results lead to expressions for the electrical and thermal conductivities identical with the interpolation formulae previously obtained by Wilson (1937) for a pure metal.

Further developments of Kohler's method was given by Umeda and Toya (1949); Umeda and Yamamota (1949); Sondheimer and Wilson (1949) and by Sondheimer (1950). The latter completed the work for a degenerate electron gas and obtained formulae for the conductivities and thermoelectric power as

ratios of two infinite determinants. Thus exact expressions valid for all temperatures are obtained for the transport coefficients which may be calculated to any degree of approximation required. Kohn (1952) formulated a variational principle for periodic lattice in terms of the crystal orbital in one of the unit cells and used the Bloch boundary conditions. His formulation led subsequently to the variation interaction method for solving crystal problems. Further extension was made by Hanna (1957) and Dorn (1957) to include the phonon-drag effect.

It is the purpose of the present thesis to discuss the role of the variational theory in studying transport phenomena in electronic conductors. A complete review of the existing theories which consider the problem in presence of an electric field only, has led to a general treatment of the problem when a magnetic field together with the electric field are both present.

In chapter two we examined and re-formulated the existing theories for the case of an electric field using modern analysis. The results obtained for the zero-order approximation are exactly similar to those obtained before by Sondheimer (1950). As a matter of fact our formalism has helped in the further development of the theory to include