Electrical Conductivity in Superionic Conductors and Narrow-Band Materials.

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ELECTRICAL CONDUCTIVITY IN SUPERIONIC
CONDUCTORS AND NARROW-BAND MATERIALS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
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in

The Department of Physics and Astronomy

by

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To my parents
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td>ii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vi</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>vii</td>
</tr>
<tr>
<td>CHAPTER I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>A. Superionic Conductivity</td>
<td>1</td>
</tr>
<tr>
<td>B. Narrow-Band Materials</td>
<td>14</td>
</tr>
<tr>
<td>CHAPTER II. THE MOMENT METHOD FOR CALCULATING</td>
<td>25</td>
</tr>
<tr>
<td>ELECTRICAL CONDUCTIVITY</td>
<td></td>
</tr>
<tr>
<td>A. Formalism</td>
<td>25</td>
</tr>
<tr>
<td>B. Evaluation of Moments</td>
<td>33</td>
</tr>
<tr>
<td>CHAPTER III. TEST OF APPROXIMATIONS AND PRELIMINARY APPLICATIONS</td>
<td>50</td>
</tr>
<tr>
<td>A. Two-Site Problem</td>
<td>50</td>
</tr>
<tr>
<td>B. Planar Antiferromagnet</td>
<td>56</td>
</tr>
<tr>
<td>CHAPTER IV. THE RANDOM-SPIN HUBBARD LATTICE</td>
<td>68</td>
</tr>
<tr>
<td>CHAPTER V. MODEL OF SUPERIONIC CONDUCTION AND ISOTOPE EFFECT IN SUPERIONIC CONDUCTIVITY</td>
<td>76</td>
</tr>
<tr>
<td>A. The Model</td>
<td>76</td>
</tr>
<tr>
<td>B. Isotope Separation</td>
<td>83</td>
</tr>
<tr>
<td>CHAPTER VI. SUMMARY AND CONCLUSION</td>
<td>90</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>93</td>
</tr>
<tr>
<td>FIGURE CAPTIONS</td>
<td>101</td>
</tr>
<tr>
<td>FIGURES</td>
<td>103</td>
</tr>
</tbody>
</table>
APPENDICES

A. Contribution to Moments 111
B. Disconnected Diagrams 145

VITA 148
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hole-Walk in an Antiferromagnet</td>
<td>103</td>
</tr>
<tr>
<td>2</td>
<td>Examples of Paths Involved in the Calculation of Moments</td>
<td>104</td>
</tr>
<tr>
<td>3</td>
<td>Electrical Conductivity in a Ferromagnet</td>
<td>105</td>
</tr>
<tr>
<td>4</td>
<td>Impurity-Resistivity in a Ferromagnet</td>
<td>106</td>
</tr>
<tr>
<td>5</td>
<td>Electrical Conductivity in the Random-Spin Hubbard Lattice</td>
<td>107</td>
</tr>
<tr>
<td>6</td>
<td>Deviation from Matthiessen's Rule</td>
<td>108</td>
</tr>
<tr>
<td>7</td>
<td>Electrical Conductivity in a Superionic Conductor</td>
<td>109</td>
</tr>
<tr>
<td>8</td>
<td>Ratio of Isotope Mobilities in a Superionic Conductor</td>
<td>110</td>
</tr>
</tbody>
</table>
ABSTRACT

A calculation of the d.c. conductivity in superionic conductors and narrow-band materials is presented. A generalized moment method allows for the calculation of the conductivity for arbitrary carrier and impurity concentrations and, in the case of narrow-band materials, for random magnetization.

In narrow-band materials, the electronic conductivity vanishes for a half-filled band, and in the absence of impurities it increases approximately linearly with the number of empty or doubly occupied lattice sites. In the absence of electron-electron scattering, the impurity limited conductivity varies as the product of the hole and electron concentrations. Numerical results indicate that to within 3% a generalized Matthiessen's rule holds; the resistivities due to impurities and electron-electron interactions are additive. An upper bound on the conductivity of strongly interacting electrons in narrow-band materials is obtained. The model of a planar antiferromagnet is used to explain the anisotropic conductivity of nickel sulfide below the Neél temperature.

A model for superionic conductors is set up and the d.c. conductivities of these materials obtained. The quantum statistics of the nuclear spins of the mobile ions is seen to play an important role in superionic conduction.
The effect of the presence of two isotopes of the mobile ion on the conductivity is investigated. A significant difference, arising from correlation effects, is seen to exist in the conductivities of the isotopes. This difference could, in principle, lead to isotope separation.
CHAPTER I
INTRODUCTION

The purpose of this dissertation is two-fold:

1. to report an investigation and theoretical calculation of the anomalously large electrical conductivities found in some ionic crystals ("superionic conductors"),

2. to present our work on the electrical conductivity in narrow-band materials.

We set up a model for superionic conductors and develop a method for calculating their conductivities. The Hamiltonian of our model reduces, in a special case, to one that is frequently used to describe electronic motion in narrow-band materials. Consequently, the calculation of the electrical conductivities of superionic conductors and of narrow-band materials run on parallel lines. This chapter is separated into two sections. In the first section we introduce the subject of superionic conductivity and in the second we present an introduction to narrow-band materials.

A. Superionic Conductivity

It has been known for a long time that in many ionic crystals electrical conduction takes place via the transport of ions. In normal ionic crystals the conductivity usually is very small. For example, the ionic...
conductivity of NaCl around 250°K is ~10^{-17} (ohm-cm)^{-1}.

However, there are certain classes of crystals in which the ionic conductivities are ~1 (ohm-cm)^{-1}, almost as high as those of good liquid electrolytes. Such ionic conductors with anomalously high conductivities are called "superionic conductors". Sometimes they are also referred to as solid electrolytes. Barring a few exceptions, the predominant contribution to the electrical conductivity of superionic conductors comes from the motion of ions; the electronic contribution is entirely negligible. In recent years there has been a surge of interest in these materials because of their potential utility in energy storage devices.

In a perfect crystal, free from irregularities and defects, no ionic conduction can take place. Crystal imperfections are necessary if ionic conduction is to be at all possible. Ion interchange which preserves the perfect lattice requires an amount of energy that is prohibitive. Some of the conduction mechanisms operative in ionic crystals are as follows:

(i) Due to thermal vibrations some ions in the crystal are promoted from their normal sites to interstitial positions (Frenkel defects). Under the influence of an electric field these ions move from one interstitial position to another, thereby contributing to the electrical conductivity of the crystal.

(ii) Vacancies are produced in the crystal when some ions are removed from their normal sites to the crystal
surface (Schottky defects). It is energetically favorable for an ionic crystal to have an equal number of cation and anion vacancies because local charge neutrality is maintained. The migration of such vacancies in an electric field gives rise to electrical conductivity.

In an ionic crystal, there are always a certain number of Frenkel and Schottky defects present at finite temperatures because disorder increases the entropy of the system. The number of defects present at any temperature is such that the free energy of the system is a minimum.

(iii) Ionic conductivity can also occur by what is known as the interstitialcy mechanism. In this process an interstitial ion displaces another ion from a normal to an interstitial site and occupies the vacancy thus created.

In ionic as well as superionic conduction, the variation of electrical conductivity, $\sigma(T)$, with temperature, $T$, is experimentally seen to be described over a large range of temperature by the Arrhenius formula:

$$\sigma(T) = \frac{C}{T} e^{-\Delta/k_B T},$$

where $C$ is a constant independent of the temperature, $k_B$ is Boltzmann's constant and $\Delta$ is the "activation energy". $\Delta$ may be interpreted as the minimum energy required by the migrating ions in order to surmount the potential barrier offered by the surrounding ions. More rigorously, the
activation energy represents the minimum energy at which the probability of barrier penetration becomes appreciable.

In most superionic conductors, the ions responsible for electrical transport are the cations, which are usually much smaller than the anions in these materials. The anions form a more or less rigid lattice and the cations move between available positions determined by the network of anions. There are, however, some exceptional superionic conductors in which anions or anion-vacancies are the charge carriers.

Superionic conductors are generally characterized by the following properties:

1. The number of sites available to the cations is usually much larger than the number of cations present, so that each cation has many equivalent sites available to it. For example, in the superionic conductor AgI the two silver ions in each unit cell of the crystal have forty-two available sites, all of almost the same energy. Thus the silver ions can move with great ease from site to site, giving rise to a large ionic conductivity.

2. The cations are distributed over the available sites in a random fashion at temperatures higher than a critical value. In fact, in some superionic conductors there are two distinct phases. In the phase below the critical temperature, the cations are distributed over the available sites in an ordered or partially ordered manner. Above the transition temperature the cations are disordered,
and the conductor is said to be in the "cation disordered phase." The large conductivities of superionic conductors is partly due to the liquid-like disorder of the cations. The ionic conductivity would clearly not be very large if the mobile ions were constrained to maintain long range order of any kind.

3. The activation energies are much smaller than those for normal ionic conductors. (In most superionic conductors, $\Delta$ is of the order of a tenth of an electron-volt, an order of magnitude smaller than those for normal ionic crystals.) Consequently, the cations are thermally activated with relative ease and a large number of them are therefore "ready" for diffusion.

Some superionic conductors are also known to exhibit phase transitions, which generally are of two kinds.

I  First order phase transitions with a large discontinuity in the ionic conductivity. There is also a latent heat associated with these transitions.

II  Second order phase transitions with a divergence in the specific heat. The ionic conductivity, however, remains continuous through these transitions.

There is some doubt as to whether the order-disorder phase transition is of first order or of second order. Some authors claim that the discontinuity in the ionic conductivity occurs due to the transition to the
cation-disordered phase, i.e., that the order-disorder phase transition is of first order. Others\textsuperscript{19,20} claim that the ionic conductivity remains continuous through the order-disorder phase transition, implying that this phase transition is of second order.

The superionic conductors that have been studied in some detail can be broadly placed into three categories\textsuperscript{3}:

A. Ionic compounds in cation disordered phases, represented by silver halides and chalcogenides,\textsuperscript{17-22} e.g., AgI. The charge carriers in this type of conductors are cations.

B. Sodium $\beta$-alumina,\textsuperscript{23-26} with the ideal formula $\text{Na}_2\text{O.11Al}_2\text{O}_3$. The sodium ions can be substitutionally replaced by silver or other ions with practically no change in crystal structure. Cation conduction takes place in well-separated planes and the sites available to the cations ($\text{Na}^+$ or $\text{Ag}^+$) fall on a two-dimensional hexagonal lattice, i.e., honeycomb lattice, defined by the fixed anions ($\text{O}^{2-}$).

C. Materials with cation-impurities of valence lower than that of the host cations,\textsuperscript{27,28} e.g., CaO.$\text{ZrO}_2$. Charge neutrality requirements produce anion vacancies in the neighborhood of the impurities. Ionic conduction takes place by the motion of anions through these lattice vacancies.

There are many theories that have been put forward to explain the phenomenon of superionic conductivity. Though
these succeed in explaining some, though not all, of the
general characteristics of superionic conductors, there is
not yet a detailed theory which explains the conduction
process from a microscopic point of view. There is a great
diversity of opinion regarding the basic mechanisms that
are held responsible for the anomalously high conductivities
observed in these materials. Often the results of the
different theories are at variance.

The traditional approach to ionic and superionic
conductivity has been based on the so-called "hopping
model".2 A conducting ion is viewed as vibrating about its
mean position. Occasionally, it acquires enough energy to
surmount or tunnel through the potential barrier offered
by the surrounding ions to a vacant site in the neighbor-
hood. The probability per unit time that such a jump to
another site occurs is easily calculated as a function of
the temperature using statistical mechanics, and from that
the conductivity is obtained. The result is the Arrhenius
relation (1.1).

Rice and Roth3 have proposed a model in which the con-
ducting ions are assumed to have an energy gap below which
they are in localized states and consequently cannot con-
tribute to the ionic conductivity. It is supposed that
these ions are capable of being excited into free-ion-like
states in which the ions can propagate throughout the
crystal. Interactions with the rest of the solid are
assumed to give these free-ion states a finite lifetime. Using the Boltzmann transport equation an expression similar to (1.1) is derived for the ionic conductivity. The frequency dependent conductivity in this model is of the Drude type, i.e., like that of an electron gas when the electron states have a finite lifetime. A valid objection to this model is that it is not clear how the mobile ions can be considered to be "free".

Kikuchi and Sato\textsuperscript{29,30} have theoretically investigated the ionic conductivity in the lattice gas model. The model assumes a gas of cations which can sit on a fixed network of available sites. They have included nearest-neighbor cation-cation interactions. The free energy is expressed in terms of the possible cation configurations and the most probable configuration obtained by minimizing the free energy. They have shown that an order-disorder phase transition exists in this model. They also find that nearest-neighbor interactions between cations tends to lower the activation energy and enhance the conductivity.

The lattice gas model\textsuperscript{20,31} has also been recently applied to superionic conductors by Pardee and Mahan. Nearest-neighbor interaction between cations is included. Changes in the number of nearest (cation) neighbors of a cation produces discrete changes in the energy of the system. If these energy differences are supplied by incident photons, for example, then the cations can take part in the conduction process, giving rise to an "optical
absorption conductivity". In the lattice gas model, the energies needed are discrete and the absorption conductivity is theoretically a series of delta-function spikes. At low temperatures, it is shown by Pardee and Mahan that the cation-cation interaction gives rise to an activation energy -- a result which contradicts that of Kikuchi and Sato.\textsuperscript{29,30} They further show that the lattice gas model exhibits an order-disorder transition in which the activation energy changes at the transition temperature but the ionic conductivity does not. The quantitative results of this theory fit the experimental data on the optical absorption conductivity\textsuperscript{32} of such materials only for values of the cation-cation interaction which are too small to be credible.

A cation would tend to polarize the anions in its neighborhood. As the cation moves through the crystal one would expect that it would carry this polarization cloud along with it.\textsuperscript{33-34} Thus there will be an interaction between the cation and the lattice, giving rise to phonons. The effect of phonons has been included in model calculations by Pardee and Mahan.\textsuperscript{35} They find that the high temperature conductivity is due to phonon-assisted hopping of the cations. It is their view that the activation energy in superionic conductors arises out of dynamical processes such as cation-cation interactions (lattice gas) or cation-anion interactions (phonons). This is a departure from the traditional view\textsuperscript{2} that the activation energy represents
the height of the potential barrier over which the ion hops.

It has been found that in some superionic conductors in which electrical transport is a result of interstitial migration, the energy required to promote an ion to an interstitial site is much greater than the measured activation energy. This observation has led to the theory that superionic conduction is a cooperative phenomenon in which the motions of several ions are correlated. There is additional evidence that this may be true: If the motions of the ions are completely uncorrelated, then the d.c. conductivity, \( \sigma \), and the self-diffusion constant, \( D \), of the mobile ions would be related via the well-known Nernst-Einstein relation

\[
\sigma = \frac{nq^2}{k_B T} D 
\]  

(1.2)

where \( n \) is the number of charge carriers per unit volume, \( q \) being the charge on each carrier. Measurement of \( D \) using tracer diffusion techniques has shown that (1.2) does not hold in many superionic conductors, suggesting that the independent-particle approach in the theory of superionic conductivity may not be appropriate.

A numerical calculation has been done very recently by Wang et al. to obtain the potential energy curves for the cations in \( \beta \)-alumina. As mentioned earlier, the sites available to the cations in these materials fall on a
honeycomb network in well-separated planes. Electrical conduction in \(\beta\)-alumina, therefore, takes place essentially in two-dimensions. All the available cation-sites are not equivalent; half of them, called the Beevers-Ross (BR) sites, have a slightly lower energy than the other half, called the anti-Beevers-Ross (ABR) sites. In a perfectly stoichiometric crystal, all the BR sites are occupied while all the ABR sites are vacant. In non-stoichiometric \(\beta\)-alumina with an excess of sodium, the extra sodium atoms would be expected to occupy the vacant ABR sites. Instead, the calculations of Wang et al. show that it is energetically more favorable for the extra cations to displace the cations at the BR sites and then to form interstitial pairs with them around these BR sites. The activation energy for ionic conductivity through the correlated and "in-phase" motion of these interstitial pairs is seen to be close to the experimentally observed value. On the other hand, the activation energy for a single cation whose motion is uncorrelated with those of the rest is found to be an order of magnitude greater than the experimental value. These results seem to support the idea that superionic conductivity is a cooperative phenomenon, at least in \(\beta\)-alumina.

Van Gool and Bottleberghs\(^{44}\) have put forward a domain model of cooperative motion in superionic conductors. The crystal is assumed to be made up of a number of domains, the positions of the conducting ions being different in different domains. Ionic conduction is assumed to take
place by the motion of the domain walls. Simple electrostatic considerations show that the activation energy for such a conduction process is small for large domains, thereby favoring fast ionic conduction. Though this model is attractive in some respects, it appears unlikely that all the ions on the domain walls can consistently move in phase with one another.

Huberman$^{45,46}$ has suggested yet another theory of cooperative phenomena in superionic conductors with Frenkel defects. In addition to nearest-neighbor cation-cation interaction he has also included phonon energies and an attractive interaction between interstitial ions and vacancies. He has shown that depending on certain parameter values the number of carriers may exhibit a discontinuity at a critical value of the temperature. At this critical temperature occurs an order-disorder phase transition, a discontinuity in the ionic conductivity and also a divergence in the specific heat of the system.

Yokota$^{47}$ has attempted to explain the breakdown of the Nernst-Einstein relation (1.2) in some superionic conductors in terms of the so-called "caterpillar mechanism", which allows for the correlated jumps of two or more ions. In this mechanism, a cation is not only allowed to jump from one site onto a vacant site but also onto an already occupied cation-site, inducing the cation at a latter site to jump onto yet another site in (more or less) the same direction as the first jump. A single cation-jump can thus
induce a series of successively correlated hops. A n-step process of this type contributes n-steps to the electrical conductivity but only one step to the self-diffusion of a specified ion involved in the process. This results in a deviation from the Nernst-Einstein relation. However, the caterpillar mechanism is basically one-dimensional and it is not clear how effective such a process would be in three dimensions.

A more feasible explanation of the deviation of the Nernst-Einstein relation has been given very recently by Kimball, using some of the results presented in this dissertation.

In this dissertation we report an investigation of the anomalously high conductivities of superionic conductors. We set up a model for such systems, assuming that the ionic motions are strongly correlated. We develop a technique for calculating the conductivities of these materials and, in particular, study the effect of the presence of two isotopes of the cations on the conductivity. We discover that quantum statistics plays an important role in ionic conductivity, because the conduction process can involve interchange of (indistinguishable) cations. It is found that the difference in conductivities of the isotopes is significant enough to lead to isotope separation. Our results on the conductivity also yield considerable information on the diffusion constants of these materials.
In a special case, the model Hamiltonian we use to describe ionic motion in superionic conductors is isomorphic to one that is extensively used at present to describe electronic motion in narrow-band materials. We exploit this isomorphism to test the model and the technique developed to calculate the electrical conductivity by first applying them to narrow-band materials.

B. Narrow-Band Materials

By "narrow-band" materials we mean those in which the potential energy of the conduction electrons is at least as important as their kinetic energy. The electrical conductivity in materials with narrow bands has been of great interest over the past decade or so. Examples of this type of materials are the oxides of transition metals. Though there are many narrow-band materials, we restrict ourselves at the moment to transition metal oxides in order to be specific. The d electrons that are contributed by the transition metals dominate the electrical transport properties of transition metal oxides because the Fermi energy falls in the vicinity of the d bands. Since these d electrons are more or less localized, their energy bands are quite narrow.

A large number of the oxides of transition metals are insulators and most of them are antiferromagnetic. These materials are very peculiar in that band theory appears to be inapplicable to them. The Bloch-Wilson theory predicts
that a material will be a metal or an insulator depending on whether or not it has partially filled bands. Consider, for example, NiO, the most widely studied transition metal oxide. Symmetry arguments lead one to conclude that NiO has partially filled bands and so should be a metal. However, NiO is experimentally observed to be an insulator! The same is true of many other transition metal oxides.

It has been pointed out\textsuperscript{62} that the antiferromagnetic order in NiO and other transition metal oxides could be responsible for their insulating property. Antiferromagnetism essentially doubles the lattice periodicity, it has been argued, and consequently the Brillouin zone is reduced in half. Each energy band is therefore split into half with a gap in the middle. Thus a material which would otherwise have been a metal could become an insulator because of its antiferromagnetism. But if it is really true that the energy gap in these materials is due to their antiferromagnetism, then they must become metals above the Neél temperature. This is not always observed experimentally. NiO, for example, remains an insulator even after it loses its magnetic order. Other attempts\textsuperscript{63-65} have been made to apply band theory to such magnetic insulators, but they are at best unsatisfactory\textsuperscript{57} and at worst incorrect.

Attempts have also been made to apply small-polaron theory\textsuperscript{66-68} to narrow-band materials. It is known that a conduction electron can set up a lattice distortion and
become trapped in the resulting potential. A new quasiparticle, comprising of an electron and a phonon-cloud called a "polaron" is formed. In narrow-band materials, the lattice distortion is localized and one has a "small polaron". It has been shown that small polarons are capable of thermally activated hopping at room and higher temperatures and so can contribute to the electrical conductivity of the material. The low conductivity in narrow-band materials has often been attributed to this process. However, Hall effect measurements eliminate this possibility and suggest that the electrical conduction is due to holes in narrow d-bands.

Band theory fails when applied to narrow bands because it ignores correlations between the conduction electrons. Two Bloch-electrons in the same spatial orbital would have a large Coulomb repulsion energy as a result of their physical proximity. In reality two such electrons would tend to stay away from one another. This type of "correlation effect" -- not taken into account in band theory -- is most important in narrow-band materials. In contrast to the band picture one has the Heitler-London model, which pictures the electrons as being completely localized. But this view is extreme in that it altogether forbids the motion of electrons and so requires all materials to be insulators!

In dealing with electrons (or holes) in narrow bands, one requires a model that takes into account their kinetic
energy as well as their correlation energy, i.e., Coulomb repulsion energy. Such a model has been proposed\textsuperscript{74-82} and has come to be known as the Hubbard model. In this model, the electrons are pictured as "hopping" from site to site, the transfer matrix element being usually denoted by $t$. Two electrons are assumed to interact only when they are on the same lattice site, and their repulsion energy is denoted by $U$. It is also assumed that each lattice site can accommodate no more than two electrons.

Hubbard has shown\textsuperscript{77} that when the electrons are strongly interacting ($U \gg t$), the band splits into two distinct sub-bands, separated by an energy $\sim U$. The lower band accommodates electrons that are moving only through sites unoccupied by other electrons, so the electron-electron repulsion does not contribute to the energy in this band. The upper band belongs to electron states involving a doubly occupied site. Since the interaction between two electrons on the same site is $U$, the separation between the two bands is also $\sim U$.

It has become clear over the years that any attempt to study the transport properties of narrow-band materials must be based on a model at least as sophisticated as the Hubbard model. However, the Hubbard model is not free from inadequacies. For one, the electron-electron interaction considered is very short ranged. Further, the band is assumed to be an s-band whereas the model is usually applied to d bands, which are five-fold degenerate. But
in spite of these drawbacks the Hubbard model is attractive because it is exactly soluble in the two extreme limits, viz., the limit of no Coulomb repulsion (U=0), and the limit of no hopping (atomic limit). In these two limits the Hubbard model gives reasonable results and so one might expect that it would adequately describe situations in which both the kinetics and the correlations are important.

It is estimated that the transfer matrix element, t, in transition metal-oxides is \( -0.3 \text{ eV} \) and the Coulomb interaction energy, U, is \( -13 \text{ eV} \). As a consequence, most of the theoretical work done in narrow-band materials is based on the strong-interaction limit of the Hubbard model (U\( >t \)).

Bulaevskii and Khomskii investigated the electrical conductivity of antiferromagnets. They began from the atomic limit, i.e., zero bandwidth limit, of the Hubbard model. The hopping term of the Hamiltonian was treated as a perturbation. To second order in t, the energy shift is represented by an antiferromagnetic Heisenberg type exchange -- the so-called Anderson kinetic exchange of order \( t^2/U \). The introduction of the possibility of hopping increases the bandwidth by a factor which is strongly dependent on the magnetic order of the system. By examining this spin-dependent factor they have shown that a sharp broadening in the Hubbard sub-bands and a corresponding decrease in the forbidden gap occurs above the Neél temperature.
Pratt and Caron\textsuperscript{50} have used a self-consistent cluster treatment to analyze the conductivity in the Hubbard model as a function of the band occupancy. They have shown that in the regime $t/U \ll 1$, the d.c. conductivity is zero. In the case of an exactly half-filled band, i.e., one electron per lattice site, as the ratio $t/U$ is increased they claim that the system undergoes a Mott transition\textsuperscript{73} evidenced by an abrupt increase in the conductivity. On this matter, however, there is a great deal of controversy\textsuperscript{86–90} and the situation is not entirely resolved. Pratt and Caron also demonstrate that the conductivity in narrow-band materials is partially suppressed as a result of correlations between electrons. Basically, the electrons would tend to avoid lattice sites that are already occupied by other electrons because the Coulomb repulsion would render states with doubly occupied states energetically unfavorable. The motion of the electrons is consequently restricted and the conductivity tends to be suppressed.

Bari, Adler and Lange\textsuperscript{56} have verified the earlier result\textsuperscript{50} that for $t/U \ll 1$ the conductivity vanishes at $T=0$ for a band with one electron per site. In the atomic limit, the ground state of the system is extremely degenerate. This is clearly seen from the fact that there are a large number of spin configurations that have the same energy. For finite $t$ and $U$ the Anderson kinetic exchange\textsuperscript{85} mentioned earlier lifts this degeneracy. However, in the atomic limit $t^2/U \gg 0$ and there is a mixing of
states that are degenerate in zeroth order. There are serious problems associated with this degeneracy and this has been dealt with by several authors. In the case of a non-half-filled band this degeneracy plays a crucial role in yielding a non-zero conductivity.

Ohata and Kubo have investigated the d.c. conductivity of a small concentration of holes in the strong-interaction limit of the Hubbard model. The authors used the so-called path formulation method of Nagaoka, in which the problem is set up in terms of the number of possible paths a hole starting from a given lattice site can take and return to its starting point without altering the spin configuration of the system. The moments of the current-current correlation function were evaluated. Based on these moments, a plausible form of the correlation function was guessed and the hole conductivity calculated. In particular, the dependence of the conductivity on the magnetic ordering of the system was investigated. It was found that when all the spins are aligned, the conductivity is infinite. Introduction of spin disorder produces a finite conductivity because the motion of the holes is disturbed. The basic assumption made in this calculation is that the hole concentration is so small that two holes never collide. Consequently, their results are valid only for nearly half-filled bands. Within the same approximation, Ohata has also investigated the effect of vacancies in the lattice. It was found that for very small
spin disorders, the resistances arising from the vacancies and from spin disorder are independent and simply add. This additivity of the resistance is lost for greater spin disorders.

Brinkman and Rice\textsuperscript{55} have calculated the mobility of a single hole in the atomic limit of the Hubbard model. Again, the path formulation of Nagaoka\textsuperscript{95} was used but only those paths which are completely retraceable were assumed to be important. In spite of this approximation, they obtained a hole mobility ($\sim 1 \text{ cm}^2/\text{v}$) that agreed reasonably well with the experimental hole mobility measured in NiO.\textsuperscript{84} The reason for the low hole mobility is that the holes undergo Brownian motion through the lattice. The reasonable agreement with experiment of this calculation that did not include any small-polaron effects is further evidence that small-polarons are not of great importance in the transport properties of narrow-band materials -- contrary to earlier speculations\textsuperscript{68,84} on the matter. The authors have also investigated the effects of introducing more than one band. In this more realistic situation, intra-atomic exchange becomes important. It is found that intra-atomic exchange gives rise to a further narrowing in the band. It is also seen that a finite value of $t/U$ has relatively weak effects on the bulk of the band.

In a realistic calculation of the conductivity of NiO, Adler and Feinleib\textsuperscript{57} considered contributions from holes in narrow d-bands, small polarons and also from large
polarons (formed by the 2p electrons of oxygen). They concluded that the dominant contribution to the conductivity in the temperature region 150°K to 1000°K was from hole-like large polarons in the 2p band of oxygen.

The optical absorption conductivity in narrow s-bands at T=0°K has been calculated by Kubo. The frequency dependent conductivity is seen to have a δ-function peak at zero frequency, corresponding to the d.c. part of the conductivity. In addition, it has finite optical peaks at frequencies ~±U/ℏ. The optical peaks in the conductivity arise from transitions of electrons between the sub-bands split by the correlation effect. The transitions are accompanied by the absorption or emission of electromagnetic radiation of frequency ~U/ℏ.

Bari and Kaplan have studied the conductivity of a half-filled band in the regimes \( t^2/U < k_BT < U \) and \( k_BT \approx U \) (where \( T \) is the absolute temperature and \( k_B \) Boltzman's constant). They showed that the d.c. conductivity starts at small values at low \( T \) (due to small carrier concentrations) and rises to a smooth maximum around \( k_BT \approx \frac{1}{3} U \) and the slowly approaches zero as \( 1/T \) as \( T \to \infty \). At high temperatures the conductivity goes to zero because the (random) thermal velocities of the electrons dominate their drift velocity in an electric field.

In the next two chapters of this dissertation we present our work on the d.c. conductivity of narrow-band materials based on the strong-interaction limit of the
Hubbard model. We assume a simple cubic lattice, though our results are easily generalizable to other simple crystal structures. The conductivity is worked out for an arbitrary concentration of holes, using a generalization of the moment method used by Ohata and Kubo. The dependence of the conductivity on the magnetic ordering of the system is investigated. In order to obtain realistic results, we include the effect of impurities. The impurities are simply taken to be vacancies produced by removing atomic sites from the lattice.

Our calculation of the d.c. conductivity is strictly valid only at high temperatures $\beta^{-1} \gg t$, (where $\beta = 1/k_B T$, and $k_B$ is Boltzmann's constant). However, we present numerical evidence which suggests that the high temperature results can be unambiguously extended to lower temperatures and remain at least qualitatively correct.

We obtain an upper bound of about $10^4 \text{ (ohm-cm)}^{-1}$ on the conductivity of all narrow-band materials. This is in agreement with most of the experimental data available on the transition metal oxides. We find, in addition, that at intermediate temperatures -- temperatures small compared to the bandwidth but larger than the magnetic ordering temperature -- the conductivity is independent of the hopping integral, $t$. Simple examples which can be calculated more or less exactly bear this result out.

A planar antiferromagnetic order is shown to produce an anisotropic conductivity even if the hopping matrix
elements are isotropic, i.e., if the energies associated with the hopping of electrons in the \( x \), \( y \) and \( z \) directions are all the same. This model of a planar antiferromagnet is of interest in materials like NiS and \( V_2O_3 \).

We have found that to a very good accuracy, the resistivities that arise from electron-electron interaction and impurities are additive, thereby giving a generalized Mattheissen's rule.

The plan of the dissertation is as follows. In Chapter II we develop a method for calculating electrical conductivity based on the Kubo formula. The details of the calculational procedures are discussed. In Chapter III we test this method by applying it to cases which can be solved more or less exactly by alternative methods. In Chapter IV we calculate the d.c. conductivity in narrow-band materials and discuss the results we obtain. Chapter V is devoted to superionic conductors. A model for these materials is set up and their conductivity calculated. The effect on the conductivity due to the presence of two isotopes of the mobile ion is examined. In the last chapter our concluding remarks on our work on superionic conductors and narrow-band materials are presented.
CHAPTER II
THE MOMENT METHOD FOR CALCULATING ELECTRICAL CONDUCTIVITY

In this chapter we present the formalism and describe in detail the method used to calculate the high-temperature electrical conductivity in the Hubbard model. The role of quantum statistics arising from the interchange of particles is examined. We also present arguments to extend the high temperature results to lower temperatures.

A. Formalism

The Hubbard hamiltonian may be written

$$H = \sum_{i,j}^{\text{ site}} t_{ij} a_{i\sigma}^{+} a_{j\sigma} + U \sum_{i}^{\text{ site}} n_{i\uparrow} n_{i\downarrow}$$  \hspace{1cm} (2.1)

where $a_{i\sigma}^{+}$ ($a_{i\sigma}$) is the creation (destruction) operator for an electron with spin $\sigma$ in a Wannier state at site $i$, $n_{i\sigma} = a_{i\sigma}^{+} a_{i\sigma}$ is the number operator for site $i$, $t_{ij}$ is the transfer matrix element associated with the hopping of an electron from site $i$ to site $j$, and $U$ is the intra-atomic interaction between electrons. The transfer matrix element $t_{ij}$ is related to the band energy, $\varepsilon_{k\sigma}$, of a single electron with spin $\sigma$ and wave-vector $\mathbf{k}$ via

$$t_{ij} = \frac{1}{N} \sum_{\mathbf{k}} \varepsilon_{k\sigma} e^{i \mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)}$$ \hspace{1cm} (2.2)
where $N$ is the total number of lattice sites in the crystal and $\mathbf{R}_i$ is the position vector of the $i$'th site.

The first term of the Hubbard hamiltonian describes the band motion of the electrons, i.e., the hopping of the electrons from site to site. The second term represents the interaction between the electrons. Two electrons interact only when they are on the same site, and the interaction energy is $U$. Thus, the Hubbard model incorporates both the kinetics and the correlations of the electrons.

It is assumed that each lattice site can accommodate at most two electrons. The Pauli exclusion principle requires two electrons on the same site to have oppositely directed spins. A maximum of $2N$ electrons can be accommodated in the lattice.

The hopping of an electron onto a site that is already occupied by another electron (of opposite spin) is energetically unfavorable because the energy of the system is increased by an amount $U$. In other words, the band motion of the electrons is inhibited by electronic correlations and consequently localization of electrons is enhanced. However, this localization increases their kinetic energy, as is easily seen from the Heisenberg uncertainty principle. Bloch states have small kinetic energy but large potential energy, whereas localized states have small potential energy but large kinetic energy. Thus it is not at all obvious what the ground state of the Hubbard
hamiltonian would be in general.

We assume that the hopping of electrons takes place only between nearest-neighbor sites. Also, unless specified otherwise, the hopping matrix element will be assumed to isotropic. Thus

\[ t_{ij} = \begin{cases} 
  t & \text{if } i \text{ and } j \text{ are nearest-neighbors} \\
  0 & \text{otherwise} 
\end{cases} \]

In view of the fact that in most narrow-band materials the intra-atomic Coulomb energy is much greater than the bandwidth \((U \gg t)\), we consider the atomic limit, i.e., \(U\) is taken to be infinitely large. This implies, in the case of a band less than half full, i.e., the number of electrons is less than the number of lattice sites, that there will be no doubly occupied sites. A state with even one doubly occupied site has infinitely greater energy than one with no doubly occupied sites. Conduction can only take place by the hopping of electrons onto hole sites, whereby a "hole" we simply mean the absence of an electron. When the number of electrons is greater than the number of lattice sites, i.e., when the band is more than half-full, some sites will necessarily be doubly occupied even in the ground state of the system. Here the conduction will take place by the hopping of electrons from doubly occupied sites onto singly occupied sites. In this case, we may look upon doubly occupied sites as the current carriers.
By symmetry, a doubly occupied site has the same conductivity as a hole.

The number of holes (or doubly occupied sites) is conserved in the conduction process, since the excited states have infinitely greater energies than the ground state. In other words, we need not concern ourselves with those terms in the Hamiltonian (2.1) which connect configurations with different numbers of holes (or doubly occupied sites). We may then rewrite (2.1) as

\[ H = P \{ t \sum_{<i,j>} a_{i\sigma}^+ a_{j\sigma} \} P \]  

where \( P \) is the projection operator that projects the system-states onto a subspace with a given number of holes (or doubly occupied sites) of the entire Hilbert space. By \( <i,j> \) we mean that \( i \) and \( j \) are nearest-neighbors.

We assume that the electrons that are responsible for the electrical conductivity are also responsible for the magnetism of the material, as is the case in transition metal oxides, for example. Thus a singly occupied site will necessarily be "magnetic" whereas a doubly occupied site, as a consequence of the Pauli exclusion principle, will necessarily be "non-magnetic".

Our calculation of the d.c. conductivity proceeds from the Kubo formula, which is a very general result that is derived from linear-response theory. The Kubo formula expresses the conductivity in terms of the...
current-current correlation function:

\[
\sigma_{xx}(\omega) = \frac{1}{2\Omega} \lim_{\mu \to 0^+} \int_0^\infty d\tau \int_0^\beta d\lambda e^{i(\omega - \mu)\tau} \frac{\partial}{\partial \mu} \ln Z \left( e^{iH(\tau/\mu + i\lambda)/\mu} \right),
\]

(2.4)

where \( \sigma_{xx}(\omega) \) is the conductivity in the x-direction at frequency \( \omega \), \( H \) is the Hamiltonian, \( \Omega \) is the volume of the lattice, \( Z \) is the partition function of the system

\[
Z = \text{Tr} \left\{ e^{-\beta H} \right\}
\]

(2.5)

and \( J_x \) is the current operator in the x-direction:

\[
J_x = \frac{i\alpha t}{\hbar} \sum_{i\sigma} (a_{i+\sigma}^+ a_{i\sigma} - a_{i-\sigma}^+ a_{i\sigma})
\]

(2.6)

\( \alpha \) being the lattice parameter, \( e \) the electronic charge and \( i \pm x \) referring to the nearest neighbors of site \( i \) in the \( \pm x \) directions. The trace is a sum over all the states with a specified number of spin-up and spin-down electrons. Equation (2.6) is the difference in the currents produced by the hopping of electrons in the forward (i.e., \( +x \)) and backward (\( -x \)) directions and so represents the net forward current.

Let us denote the exact eigenstates and eigenvalues of \( H \) by \( |n> \) and \( \varepsilon_n \) respectively. Expressing the trace in (2.4) in this basis and introducing the complete set
between the two current operators in (2.4), we have

\[
\sigma_{xx}(\omega) = \frac{1}{2\Omega} \lim_{\mu \to 0^+} \int_0^\infty \, d\tau \, e^{(i\omega-\mu)\tau} \int_0^\beta d\lambda \times \sum_{m,n} e^{-\beta \epsilon_m} e^{\lambda (\epsilon_m - \epsilon_n)} e^{i(\epsilon_n - \epsilon_m)\tau/\hbar} |<m|J_x|n>|^2
\]

(2.7)

Now

\[
\int_0^\beta d\lambda \, e^{\lambda (\epsilon_m - \epsilon_n)} = e^{\beta (\epsilon_m - \epsilon_n)} \left( e^{\epsilon_m - \epsilon_n} - 1 \right)
\]

(2.8)

We then have, using (2.8)

\[
\sigma_{xx}(\omega) = \frac{1}{\Omega} \lim_{\mu \to 0^+} \sum_{m,n} \left( \frac{\rho_n - \rho_m}{\omega_{mn}} \right) |<m|J_x|n>|^2 \times \int_0^\infty e^{-\omega_{mn} + i\mu \tau} \, d\tau ,
\]

(2.9)

where

\[
\omega_{mn} = \frac{\epsilon_m - \epsilon_n}{\hbar}
\]

(2.10)

and
\[ \rho_m = e^{-\beta \varepsilon_m / Z} \]  

(2.11)

On performing the integral over \( \tau \) and using the identity

\[ \lim_{\mu \to 0^+} \frac{1}{x + i \mu} = P \left( \frac{1}{x} \right) - i \pi \delta(x), \]  

(2.12)

where \( P \) represents the principal part, we obtain the real part of the conductivity:

\[ \text{Re}[\sigma_{xx}(\omega)] = \frac{\pi}{\Omega} \sum_{m,n} \frac{\rho_n - \rho_m}{\omega_{mn}} |<m|J_x|n>|^2 \delta(\omega - \omega_{mn}) \]  

(2.13)

The \( \lambda \)'th moment, \( M_\lambda \), of the real part of the conductivity defined via

\[ M_\lambda = \int_{-\infty}^{+\infty} \text{Re}[\sigma_{xx}(\omega)] \omega^\lambda d\omega \]  

(2.14)

is given by

\[ M_\lambda = \frac{\pi}{\Omega} \sum_{m,n} \frac{\rho_n - \rho_m}{\omega_{mn}} |<m|J_x|n>|^2 \omega_{mn}^\lambda \]  

(2.15)

Expression (2.15) is exact. In the limit of high temperatures, we may retain only the term linear in \( \beta \):

\[ M_\lambda = \frac{\pi \beta}{\Omega} \sum_{m,n} \omega_{mn}^\lambda |<m|J_x|n>|^2 . \]  

(2.16)

Writing
\[
M_\ell = \frac{\pi \beta}{\Omega \mathcal{H}} \sum_{m,n} \sum_{k=0}^{\ell} (-1)^k \frac{\ell!}{k!(\ell-k)!} \langle m|H^{\ell-k}_x H^{k}_x|n\rangle <n|J_x|m> ,
\]

which may be cast in the representation-independent form

\[
M_\ell = \frac{\pi \beta}{\Omega \mathcal{H}} \sum_{k=0}^{\ell} (-1)^k \frac{\ell!}{k!(\ell-k)!} \text{Tr}(H^k_x H^{\ell-k}_x J_x^- J_x^-) \quad (2.19)
\]

We may write the current operator as

\[
J_x = \frac{i \text{det}}{\hbar} (J_x^+ - J_x^-) ,
\]

where

\[
J_x^+ = \sum_{i,\sigma} a_i^\dagger \sigma \mathcal{H}_i^\sigma a_i \sigma \quad (2.21)
\]

so that (2.19) takes the form

\[
M_\ell = \frac{2\pi \beta a^2 e^2 t^2}{\Omega \mathcal{H}^2} \sum_{k=0}^{\ell-1} (-1)^{k-1} \frac{\ell!}{k!(\ell-k)!} \times \text{Tr}(H^k_x H^{\ell-k}_x J_x^- J_x^- - H^k_x H^{\ell-k}_x J_x^+ J_x^+) \quad (2.22)
\]
Using the final expression (2.22) we evaluate the first few moments and obtain the conductivity by fitting a suitable line shape for $\sigma(\omega)$. We assume that the lattice is simple cubic, although the procedure can be generalized to other simple crystal structures. The hole concentration, denoted by $P$, is taken to be arbitrary. $P$ represents the probability that any site is occupied by a hole. When the band is more than half-full $P$ represents the probability that any site is doubly occupied. Let $C$ denote the concentration of randomly distributed spin-up electrons at singly occupied sites. As $C$ varies from 0 through 1/2 the magnetic order of the lattice changes from a completely ferromagnetic order to a completely random one. This facilitates the study of electrical conductivity as a function of the magnetic order of the system. In order to simulate a realistic situation we allow for the presence of randomly distributed impurities with an arbitrary concentration $Q$. It is assumed that an impurity prevents an electron or a hole from hopping onto its site, i.e., it effectively eliminates a lattice site from the crystal. The impurities are taken to be static.

B. Evaluation of Moments

The calculation of the moments, $M_\lambda$, centers around the evaluation of the trace that appears in Eq. (2.22). We use the path formulation introduced by Nagaoka\textsuperscript{95} and later used by Ohata and Kubo\textsuperscript{52} and Brinkman and Rice.\textsuperscript{55} The
state of the system is uniquely determined by specifying the positions of the holes and the electrons and the spins of the latter. We may represent the state-vector of the system by \( |i,j,...;a_i,a_j,...\rangle \), where \( i,j,... \) are the positions of the electrons and \( a_i \) denotes the spin of the electron at site \( i \), i.e., the \( a \)'s define the magnetic configuration of the system for that particular distribution of electrons and holes.

Consider, for example, the case of a single hole in the absence of impurities. The result of a \( H \) or a \( J_x \) operator acting on this hole state is to hop the hole onto a nearest-neighbor site. Thus the operator \( H_{x}^{k} J_x H_{x}^{\ell-k} J_x \) appearing in (2.19) can be thought of as taking the hole for an excursion of \((\ell+2)\) hops (or steps). As the hole traverses this path, it successively interchanges its position with nearest-neighbor electrons and consequently there is a possibility of the spin configuration of the system being altered. Clearly, if the trace in (2.19) is to be non-zero for a particular path of the hole, the final state of the system must be the same as its initial state. This is possible only if (i) the final position of the hole is the same as its initial position, i.e., the hole must return to its starting point, and (ii) the spin (or magnetic) configuration of the system after the hole traverses the path must be the same that before it made its excursion. These two requirements greatly restrict the
possible paths the hole can traverse. If, however, these
two conditions are satisfied by any path, the contribution
of this path to the $l'$th moment, $M_{l'}$, is proportional to
the binomial coefficient in (2.19).

To give a concrete example, let us consider an anti-
ferromagnetic system. Suppose the hole walks on a square
path as shown in Fig. 1(a). Since there are four steps,
this path could possibly contribute to the second moment,
$M_2$, of the conductivity. After the hole traverses the
square once, say in the counter-clockwise direction, the
positions of the three electrons are cyclically permuted,
giving the final spin configuration shown in Fig. 1(b).
Since the spin configuration is altered, this particular
path will not contribute to the second moment. After one
more revolution around the square, configuration 1(c) is
produced and after yet another revolution, i.e., after a
total of 12 steps, one obtains the spin configuration in
Fig. 1(d). Since the last spin configuration is the same
as the initial one, this path will contribute to the tenth
moment, $M_{10}$, of the conductivity. This is the essence of
the path formulation method of Nagaoka as applied to the
present problem.

It is not possible for a hole to take an odd number
of steps in a simple cubic lattice and return to its
starting point. Thus all the odd moments vanish. This is
also true for more complicated lattice structures, and
follows from the general symmetry requirement that the
conductivity must be an even function of the frequency. Before we proceed to the description of the evaluation of the moments in the general case, we consider the special case of a single hole in a ferromagnet without impurities. Since all the electrons have their spins aligned in this case, $H$ and $J_x$ commute; one arrives at the same final spin configuration irrespective of the order in which these operators act on the hole state. We may therefore write \( (2.19) \) in this case as

\[
M_{\ell} = \frac{\pi \beta}{\Omega H} \sum_{k=0}^{\ell} \frac{(-1)^{k \ell}}{k! (\ell-k)!} \text{Tr} \{ H^k J_x^2 \} \quad (2.23)
\]

so that

\[
M_{\ell} = 0 \quad \text{unless} \quad \ell = 0 \quad . \quad (2.24)
\]

Since all except the zeroth moment vanish in the case of a ferromagnet, it follows that the conductivity is represented by a delta-function spike at $\omega=0$. The d.c. conductivity is thus infinite. The physical description of this situation is that the hole is described by a Bloch wave without attenuation. It is capable of free propagation because there is no scattering from the electron spins, which are all aligned. This result is valid even for an arbitrary concentration of holes. The situation is altered when a few of the spins are reversed, for now there is a
possibility of the magnetic ordering being altered as a result of the hole-motion. Whenever a propagating hole encounters a reversed spin, it will tend to avoid it in order to preserve the spin configuration of the system, as explained earlier. Thus the spin-flip effectively "scatters" the hole and so the hole is no longer capable of free propagation. In other words, there is a resistance to the motion of the hole arising from spin-scattering. In the presence of impurities even a ferromagnet will have a finite hole conductivity; scattering from impurities always introduces a resistance.

We have calculated the zeroeth, second and fourth moments and have obtained the d.c. conductivity by fitting a suitable line shape to these moments. As mentioned earlier, we assume arbitrary concentrations of holes, spin-up electrons and impurities. Clearly, a path is "allowed" only if no impurities fall on it. In order to clarify the procedure, we give an example of an allowed path (diagram) for each of the three moments calculated and evaluate its contribution to the moment.

A path that contributes to the zeroeth moment, $M_0$, can have only two steps, both in the x-direction. This path, shown in Fig. 2(a), also happens to be the only allowed path for $M_0$. The circle denotes a hole and the cross an electron. We shall obtain a non-zero contribution to $M_0$ only if sites 1 and 2 are not both occupied by holes (or electrons). The probability that we shall have one
electron and one hole is $P(1-P)$. Impurities cannot be present at either site if the path is to be an allowed one, the probability of which is $(1-Q)^2$. Thus we get from (2.22)

$$M_0 = \frac{2\beta\pi a^2 e^2 t^2}{\Omega \mu^2} \text{Tr}\{j^+ j^+ - j^- j^-\}$$

i.e.,

$$M_0 = \frac{2\beta\pi a^2 e^2 t^2 N}{\Omega \mu^2} P(1-P)(1-Q)^2 \quad (2.25)$$

The factor $N$ arises out of the fact that the hole could have been located on any one of the $N$ lattice sites.

We see that the zeroeth moment is independent of the spin-configuration of the system. All higher order moments, however, explicitly depend on the magnetic ordering of the system -- except, of course, in the ferromagnetic case noted earlier.

The two diagrams of Fig. 2(b) are examples of paths that contribute to $M_2$. The first diagram is a "retraceable path", i.e., the hole hops to site 3 via site 2 and returns along the same path. Each electron is restored to its original position after the path is traversed and there is no interchange of electrons. As a result, irrespective of what the original magnetic configuration was, the spin order is restored. In other words, the contributions from such retraceable paths are always independent of the
magnetic ordering of the system. The contribution to the second moment from the particular path and electron-hole distribution as shown in the first diagram of Fig. 2(b) is

\[
\frac{2\beta \pi a^2 e^{-2t^4}}{\Omega^4} N P (1-P)^2 (1-Q)^3
\]

(2.26)

The square in Fig. 2(b) is another path that contributes to \( M_2 \). This path is traversed by the holes at sites 1 and 3 in the counter-clockwise direction, at the end of which the holes interchange places. Consequently, the electrons at sites 2 and 4 also exchange places. As explained earlier, the final spin configuration must be the same as the initial one if the path is to contribute to \( M_2 \). For this to happen, one requires the spins of both the electrons to be in the same direction. The probability that both the electrons have spin-up is \( C^2 \) and both spin-down \( (1-C)^2 \). Thus the probability that both the electrons have their spins in the same direction is \( [C^2+(1-C)^2] \).

The contribution of each diagram to the moments has further to be multiplied by a phase factor that depends on the number of electrons interchanged after that particular path has been traversed. This phase factor has its origin in the anti-commutation property of the Fermi operators, and the manner in which it arises is illustrated below.

Consider the square in Fig. 2(b) with the electron-hole distribution as shown. The initial state vector,
\[ |\psi_i\rangle, \text{ of this system may be written} \]

\[ |\psi_i\rangle = |2,\sigma_2;4,\sigma_4\rangle, \quad (2.27) \]

\(\sigma_2\) and \(\sigma_4\) being the spins of the electrons at sites 2 and 4 respectively. The final state vector, \(|\psi_f\rangle\), describing the system after the holes traverse the path can be obtained by operating on \(|\psi_i\rangle\) by a series of electron creation and destruction operators. For example,

\[ |\psi_f\rangle = (a_{2\sigma_2}^\dagger a_{3\sigma_4}^\dagger)(a_{4\sigma_4}^\dagger a_{1\sigma_2}^\dagger)(a_{3\sigma_4}^\dagger a_{4\sigma_4}^\dagger)(a_{1\sigma_2}^\dagger a_{2\sigma_2}^\dagger)|\psi_i\rangle, \quad (2.28) \]

where the Fermi operators obey the anticommutation rule

\[ \{a_{i\sigma_i}^\dagger, a_{j\sigma_j}^\dagger\} = \delta_{ij} \delta_{\sigma_i,\sigma_j} \]

By successive anti-commutation (2.28) can be cast in the form:

\[ |\psi_f\rangle = -(a_{4\sigma_2}^\dagger a_{4\sigma_4}^\dagger)(a_{2\sigma_4}^\dagger a_{2\sigma_2}^\dagger)(a_{3\sigma_4}^\dagger a_{3\sigma_4}^\dagger)(a_{1\sigma_2}^\dagger a_{1\sigma_2}^\dagger)|\psi_i\rangle \]

\[ = -|2,\sigma_2;4,\sigma_4\rangle, \quad (2.29) \]

Thus the final state is the same as the initial state, up to a phase factor, provided \(\sigma_2=\sigma_4\). A very important phase
factor (-1) is obtained when two electrons are interchanged.

In Fig. 2(b) had sites 2, 3 and 4 been occupied by electrons, then when the single hole at site 1 traverses the square, all the three electrons would be cyclically permuted. In this case, we would have

$$|\psi_i\rangle = |2, \sigma_2, 3, \sigma_3, 4, \sigma_4\rangle$$

(2.30)

and

$$|\psi_f\rangle = (a_{4\sigma_2}^+ a_{1\sigma_2}^-)(a_{3\sigma_4}^+ a_{4\sigma_4}^-)(a_{2\sigma_3}^+ a_{3\sigma_3}^-)(a_{1\sigma_2}^+ a_{2\sigma_2}^-)|\psi_i\rangle$$

(2.31)

which may be rewritten:

$$|\psi_f\rangle = + (a_{4\sigma_2}^+ a_{4\sigma_4}^-)(a_{3\sigma_4}^+ a_{3\sigma_3}^-)(a_{2\sigma_3}^+ a_{2\sigma_2}^-)(a_{1\sigma_2}^+ a_{1\sigma_2}^-)|\psi_i\rangle$$

$$= + |2, \sigma_3, 3, \sigma_4, 4, \sigma_2\rangle$$

(2.32)

The final state would be the same as the initial one provided $\sigma_2 = \sigma_3 = \sigma_4$. The phase factor for this case of three interchanged electrons would be +1. In general, the phase factor arising in this manner is given by

$$(-1)^{n_e-1}$$

(2.33)
where $n_e$ is the number of electrons interchanged after the path is traversed. This phase factor is entirely due to the Fermi nature of the electrons. Had the charge carriers been bosons, one would always get a phase factor of $+1$, irrespective of the number of bosons interchanged. This is so because Bose operators commute rather than anti-commute. We will have occasion to return to this point again.

Returning to our example in Fig. 2(b) and upon including the appropriate phase factor, we obtain the contribution of this diagram to the second moment as

$$-\frac{4\beta\pi a^2 e^2 t^4 N}{\Omega} p^2 (1-p)^2 (1-q)^4 \left[C^2 + (1-C)^2\right] \tag{2.34}$$

There are four linearly independent spin states possible for the system of two electrons in Fig. 2(b):

$$|2,\uparrow;4,\uparrow>, |2,\uparrow;4,\downarrow>, |2,\downarrow;4,\uparrow>, \text{ and } |2,\downarrow;4,\downarrow> \tag{2.35}$$

The first of these states gives a contribution $C^2$ to (2.34), the second contributes $(1-C)^2$ and the last two give no contribution. These contributions are, in fact, the expectation values of the quantum mechanical operator

$$\frac{1}{2} + 2 \hat{s}_2 \cdot \hat{s}_4 \tag{2.36}$$
in the four different states, \( \hat{S}_2 \) and \( \hat{S}_4 \) being the spin operators for the electrons on sites 2 and 4.

At low temperatures, even though the net magnetization of the lattice may be zero, there may be correlations between local spins that lie close together. In this case, the spin configuration of the two electrons will in general be linear combinations of the states (2.35). The factor \([C^2 + (1-C)^2]\) will then have to be replaced by

\[
\frac{1}{2} + 2\langle \hat{S}_2 \cdot \hat{S}_4 \rangle
\]  

(2.37)

A similar substitution has to be made for all other diagrams that give a spin-dependent contribution to the second and fourth moments. Near a second order phase transition, terms like \( \langle \hat{S}_2 \cdot \hat{S}_4 \rangle \) will vary as

\[
(1 - T_c/T)^\alpha,
\]

(2.38)

where \( T_c \) is the critical temperature. The critical exponent, \( \alpha \), which affects near-neighbor spin-spin correlations, will be reflected in the conductivity. This point was noted by Fisher and Langer for a simple model of conduction electrons in a magnetic system.

As a final example, we consider the path shown in Fig. 2(c), which contributes to the fourth moment. Depending on the order in which the electrons are hopped,
after the path is traversed it is possible to have either only two of the electrons or all three of them inter-
changed with respective probabilities \([C^2+(1-C)^2]\) and \([C^3+(1-C)^3]\). The phase factors associated with these processes are \(-1\) and \(+1\) respectively. The contribution of this path for the chosen electron-hole distribution is

\[
\frac{8B\pi a^2 e^2 t^6}{\Omega A^6} N P^2 (1-P)^3 (1-Q)^5 \{-4[C^2+(1-C)^2]+3[C^3+(1-C)^3]\}
\]

(2.39)

Since the hole concentration is arbitrary, we also have to consider the contributions from disconnected diagrams. Fig. 2(d) is an example of one such diagram which might contribute to \(M_4\). It turns out, however, that the contributions from disconnected diagrams to all the moments identically vanish (see Appendix B).

In expression (2.22) we have retained only the term linear in \(\beta\). In principle, expression (2.15), which is exact, may be expanded in a power series in \(\beta\) and the contributions of terms higher order in \(\beta\) may be obtained. However, the evaluation of the contribution of terms higher than linear order in \(\beta\) becomes increasingly difficult. It is already fairly tedious to evaluate the contribution to the fourth moment which is linear in \(\beta\). There are 300 geometrically distinct diagrams which
contribute to the fourth moment, and each diagram can have a variety of electron-hole distributions which must be appropriately averaged.

Using the zeroeth, second and fourth moments we have calculated the real part of the conductivity by fitting \( \text{Re}[\sigma_{xx}(\omega)] \) to a suitable line shape. For our simple model, \( \sigma(\omega) \) should be a smooth function of \( \omega \). Furthermore, we require that

(i) \( \text{Re}[\sigma_{xx}(\omega)] > 0 \) \hspace{1cm} (2.40a)

(ii) \( \text{Re}[\sigma_{xx}(\omega)] = \text{Re}[\sigma_{xx}(-\omega)] \) \hspace{1cm} (2.40b)

(iii) \( \lim_{\omega \to \infty} \text{Re}[\sigma_{xx}(\omega)] = 0 \) \hspace{1cm} (2.40c)

The quantity relevant for fitting line shapes is the ratio\textsuperscript{52,99}

\[
\gamma = \frac{M_0 M_4}{3M_2^2}
\] \hspace{1cm} (2.41)

The minimum value of this ratio is seen to be 1/3. The usual line shapes one uses are Lorentzians and Gaussians. The fourth moment of a Lorentzian diverges much more rapidly than its second moment, whereas for a Gaussian these two moments are of the same order. Consequently, for a Lorentzian line shape

\[
\gamma \gg 1
\] \hspace{1cm} (2.42)
and for a Gaussian

$$\gamma = 1$$ \hspace{1cm} (2.43)$$

For two separated Gaussians symmetrically placed about the origin,

$$\frac{1}{3} \leq \gamma \leq 1$$ \hspace{1cm} (2.44)$$

As $\gamma$ approaches the lower limit $1/3$, the ratio of the separation of the Gaussians to their width diverges. The lower limit for $\gamma$ is uniquely obtained from two $\delta$-function spikes symmetrically placed about the origin.

The line shape we choose is

$$\text{Re}[\sigma_{xx}(\omega)] = \frac{N_1}{\omega^2 + \omega_0^2} e^{-\left(\omega/\omega_1\right)^2} \text{ when } 1 < \gamma < \infty$$ \hspace{1cm} (2.45a)$$

and

$$\text{Re}[\sigma_{xx}(\omega)] = N_2 \left[ e^{-\left(\omega-a\right)^2 b} + e^{-\left(\omega+a\right)^2 b} \right] \text{ when } \frac{1}{3} \leq \gamma \leq 1 ,$$ \hspace{1cm} (2.45b)$$

where $N_1$, $N_2$, $\omega_0$, $\omega_1$, $a$, and $b$ are parameters that are adjusted to give agreement with the calculated moments.

We observe, in passing that (2.45a) simulates a Lorentzian
when \( \omega_1 \gg \omega_0 \) and a Gaussian when \( \omega_0 \gg \omega_1 \). The fitting of the line shape was done numerically. This gave us the high temperature d.c. conductivity.

We approximately obtain the low temperature d.c. conductivity, \( \text{Re}[\sigma_{\text{low}}(0)] \), from that at high temperatures as follows. (By "low temperatures" we mean temperatures small compared to the bandwidth but larger than temperatures at which additional ordering -- apart from the ordering we have assumed -- may be introduced.) For convenience we set \( \hbar = e = a = 1 \). The low temperature d.c. conductivity is related to the relaxation time, \( \tau \), and the effective mass, \( m^* \), of the charge carriers by the familiar result

\[
\text{Re}[\sigma_{\text{low}}(0)] = \frac{\tau}{m^*} \tag{2.46}
\]

The relaxation time is related to the diffusion constant, \( D \), via

\[
D \approx v_x^2 \tau \tag{2.47}
\]

where \( v_x^2 \) is the mean square velocity of the carriers in the \( x \)-direction. The diffusion constant is in turn obtainable from the high temperature d.c. conductivity, since
Using (2.46), (2.47) and (2.48) we get

\[
\text{Re}[\sigma_{\text{high}}(0)] = \beta D \tag{2.48}
\]

Now \( t \) is the energy associated with the hopping from site to site. The kinetic energy associated with the hopping is \(-t\), so that

\[
\frac{m^* v_x^2}{\beta m v_x} \sim t \tag{2.50}
\]

Combining (2.49) and (2.50), we get

\[
\text{Re}[\sigma_{\text{low}}(0)] = \frac{\text{Re}[\sigma_{\text{high}}(0)]}{K\beta t}, \tag{2.51}
\]

where \( K \) is a dimensionless constant of order unity that may be approximately estimated for different specific cases. The fitting of the conductivity to the line shape (2.45) always yields a high temperature conductivity which is linear in \( t \). The low temperature conductivity obtained by dividing the high temperature result by \( K\beta t \) will then be hopping independent. This peculiar result will be demonstrated more rigorously in the next chapter using two particular examples and the values of \( K \) obtained.

In summary, in this chapter we have developed a technique for calculating the electrical conductivity in
the Hubbard model. We find the zeroeth, second and fourth moments of the conductivity at high temperatures and fit an appropriate line shape. The moments are expressed in terms of the path formulation of Nagaoka. In general, the moments are seen to depend on the hole concentration, the impurity concentration and on the magnetic ordering of the system. We have shown that the evaluation of the moments must include a phase factor that depends on the number of electrons interchanged in the path whose contribution is being evaluated. This phase factor originates from the Fermi statistics obeyed by electrons. If the charge carriers were bosons no such phase factor would be involved, irrespective of the number of particles interchanged. We have also shown how the high temperature conductivity can be used to obtain the conductivity at lower temperatures.
CHAPTER III
TEST OF APPROXIMATIONS AND PRELIMINARY APPLICATIONS

Since the moment method is approximate, it is important to consider simple examples which can be solved more or less exactly by other methods. A comparison of results yields a partial test of our approximations and the range of their validity. In this chapter, we consider two such examples in detail; the simple problem of a single electron confined to two sites, and the anisotropic d.c. conductivity in a planar antiferromagnet.

A. Two-Site Problem

Our first example is merely meant to illustrate the technique described in Chapter II. We consider the simple case of single electron hopping between two sites. We first calculate the conductivity exactly and then demonstrate that the moment-method reproduces the exact result in this case. This simple case is generalizable and one can obtain the exact conductivity (even in the presence of impurities) for a one dimensional chain of arbitrary length. In one dimension, the electrons are not rearranged and so the conductivity is independent of the spin configuration; the resistance is entirely produced by impurities. One can then assume ferromagnetic order. A further simplification is introduced by the Pauli exclusion
principle which prohibits any two electrons from occupying the same site since all the electron spins are aligned. Thus the electrons are essentially non-interacting and we need only calculate the one-electron conductivity. However, since this example is merely meant to explicitly demonstrate the theory and the validity of the assumptions made, we restrict ourselves to a chain with only two sites.

The Hamiltonian, $H$, and the current operator, $J_x$, for this two-site problem may be written

$$H = t \sum_\sigma (a_{1\sigma}^+ a_{2\sigma} + a_{2\sigma}^+ a_{1\sigma})$$

(3.1)

and

$$J_x = i \frac{e \alpha t}{\hbar} \sum_\sigma (a_{2\sigma}^+ a_{1\sigma} - a_{1\sigma}^+ a_{2\sigma})$$

(3.2)

The two eigenstates of the Hamiltonian, assuming that the electron has spin up, are

$$|a\rangle = \frac{1}{\sqrt{2}} (a_{1\uparrow}^+ a_{2\uparrow}^+) |0\rangle$$

(3.3a)

and

$$|b\rangle = \frac{1}{\sqrt{2}} (a_{1\uparrow}^+ - a_{2\uparrow}^+) |0\rangle$$

(3.3b)

where $|0\rangle$ is the vacuum state. By operating on these states with the Hamiltonian (3.1), we find that their
respective eigenenergies are

\[ \varepsilon_a = +t; \quad \varepsilon_b = -t \]  

(3.4)

The matrix elements of the current operator are

\[ <a|J_x|b> = -<b|J_x|a> = i \frac{e_a t}{\hbar} \]  

(3.5a)

\[ <a|J_x|a> = <b|J_x|b> = 0 \]  

(3.5b)

Using (2.13), we obtain the exact conductivity to be

\[ \sigma(\omega) = \frac{\pi e^2 a^2 t^2}{\Omega \hbar^2} \frac{(\rho_b - \rho_a)}{\omega_{ab}} [\delta(\omega - \omega_{ab}) + \delta(\omega + \omega_{ab})] \]  

(3.6)

where

\[ \omega_{ab} = (\varepsilon_a - \varepsilon_b)/\hbar = 2t/\hbar \]  

(3.7)

Now, the partition function, \( Z \), is given by

\[ Z = 1 + e^{-\beta \varepsilon_a} + e^{-\beta \varepsilon_b} + e^{-\beta(\varepsilon_a + \varepsilon_b)} \]  

(3.8)

At high temperatures (\( \beta^{-1} \gg t \)) we have

\[ Z = 4 + \beta^2 t^2 \]  

(3.9)
Also,

\[ \rho_a = e^{-\beta t/Z} + (1-\beta t)/4 \quad (3.10a) \]

and

\[ \rho_b = e^{+\beta t/Z} + (1+\beta t)/4 \quad (3.10b) \]

Thus the conductivity as given by (3.6) becomes, at high temperatures,

\[ \sigma(\omega) = \frac{\pi \beta e^2 a^2 t^2}{4\Omega k^2} \left[ \delta(\omega - \frac{2t}{K}) + \delta(\omega + \frac{2t}{K}) \right] \quad (3.11) \]

We now calculate the high-temperature conductivity using the moment method. The zeroeth, second and fourth moments of the conductivity are trivially calculated for this case:

\[ M_0 = \frac{2\beta \pi a^2 e^2 t^2}{\Omega k^2} \rho(1-P)(1-Q)^2 \quad (3.12a) \]

\[ M_2 = \frac{4M_0 t^2}{k^2} \quad (3.12b) \]

\[ M_4 = \frac{16M_0 t^4}{k^4} \quad (3.12c) \]
The ratio, \( \gamma \), that determines the line-shape is

\[
\gamma = \frac{M_0M_4}{3M_2^2} = \frac{1}{3}
\]  

(3.13)

As pointed out earlier, this is the minimum value possible for \( \gamma \) and is uniquely obtained from a line shape that consists of two delta-function spikes placed symmetrically about the origin:

\[
\sigma(\omega) = N[\delta(\omega-\omega_0) + \delta(\omega+\omega_0)]
\]  

(3.14)

where \( N \) and \( \omega_0 \) are parameters to be determined. Requiring that the zeroeth moment of (3.14) be equal to the calculated value (3.12a) gives

\[
N = \frac{1}{2} M_0
\]  

(3.15)

Equating the second and fourth moments of (3.14) to the calculated values (3.12b) and (3.12c), respectively, we get

\[
\omega_0 = \frac{2t}{M}
\]  

(3.16)

In the absence of impurities, \( Q=0 \). Further, since there is only one electron between the two sites, we have \( P=1/2 \). Hence, the high temperature conductivity as given by the moment method is
\[
\sigma_{\text{high}}(\omega) = \frac{\pi \beta \alpha e^{2} t^{2}}{4 \Omega M} [\delta(\omega - \frac{2t}{M}) + \delta(\omega + \frac{2t}{M})] \quad (3.17)
\]

which is in exact agreement with (3.11).

We now calculate the low temperature conductivity exactly. At low temperatures, we may replace \( \rho_a \) and \( \rho_b \) by the Fermi-Dirac distribution functions:

\[
\rho_a = \frac{1}{e^{-\beta \epsilon_a} + 1} \quad (3.18a)
\]

and

\[
\rho_b = \frac{1}{e^{-\beta \epsilon_b} + 1} \quad (3.18b)
\]

The Fermi-Dirac distribution function is essentially a step-function at low temperatures, so that

\[
\rho_b = 1 \quad \rho_a = 0 \quad (3.19)
\]

Using (2.13) we obtain the low-temperature conductivity to be

\[
\sigma_{\text{low}}(\omega) = \frac{\pi e^{2} \alpha^{2} t}{2 \Omega M} [\delta(\omega - \frac{2t}{M}) + \delta(\omega + \frac{2t}{M})] \quad (3.20)
\]

From results (3.17) and (3.20) we see that

\[
\sigma_{\text{low}}(\omega) = \frac{\sigma_{\text{high}}(\omega)}{K \beta t} \quad (3.21)
\]
with \( K = 1/2 \). This verifies our claim that the high temperature result can be used to obtain the low temperature conductivity.

**B. Planar Antiferromagnet**

The next example we consider is that of a planar antiferromagnet; a simple cubic lattice with electrons on the same plane being ferromagnetically aligned, but spin directions on alternate planes being opposite. In this particular example, only one hole is assumed to be present and impurities are assumed absent.

If the hole were restricted to a single ferromagnetic plane, say the x-y plane, then the d.c. conductivity in the x or y directions would be infinite since both impurity- and spin-scattering would be absent. However, allowing the hole to hop off this plane, i.e., in the z direction, makes the conductivity finite even in a ferromagnetic plane, as we shall see. We assume that the hopping is anisotropic and that

\[
\begin{align*}
    t_z &< t_x, t_y \\
    \text{(3.22)}
\end{align*}
\]

where \( t_x \), \( t_y \) and \( t_z \) are the hopping matrix elements in the x, y and z directions respectively.

We write the Hamiltonian, \( H \),
\[ H = H_0 + H_z \quad (3.23) \]

where \( H_0 \) describes the motion of the hole in the \( x-y \) plane and \( H_z \) that perpendicular to it. Since \( t_z < t_x, t_y \), \( H_z \) can be treated as a perturbation on \( H_0 \). The zeroth order Hamiltonian, \( H_0 \), can be written explicitly as

\[
H_0 = P \left\{ \Sigma_{i,j,\sigma} t_x (a_{i}^{\dagger} a_{i+j \sigma} + a_{i-x \sigma}^{\dagger} a_{i+j \sigma}) + t_y (a_{i+j \sigma}^{\dagger} a_{i+j \sigma}^{\dagger} + a_{i-y \sigma} a_{i+j \sigma}^{\dagger}) \right\} P \quad (3.24)
\]

where, in this case, \( P \) is the projection operator that projects the system-states onto the single-hole subspace of the entire Hilbert space.

Let \( |n_x,n_y;p> \) denote the state of the system when the hole is on site \((n_x,n_y)\) of the \( p'th \) plane parallel to the \( x-y \) plane. The Bloch state of wave-vector \((q_x,q_y)\), describing the motion of the hole in this plane may be written

\[
|q_x,q_y;p> = \frac{1}{\sqrt{N}} \sum_{n_x,n_y} e^{i(q_x a_{n_x} + q_y a_{n_y})} |n_x,n_y;p> ,
\]

(3.25)

where \( N \) is the number of lattice sites on the plane.

Operating \( H_0 \) on the Bloch state \( |q_x,q_y;p> \), we find that
\[ H_0 |q_x, q_y; p> = \varepsilon(q_x, q_y) |q_x, q_y; p> \quad (3.26) \]

where

\[ \varepsilon(q_x, q_y) = 2[t_x \cos(q_x a) + t_y \cos(q_y a)] \quad (3.27) \]

is the eigen-energy of \( H_0 \) associated with the eigenfunction \( |q_x, q_y; p> \).

The moments, \( M_\ell^{(0)} \), of the conductivity that are of zero order in \( t_z \) are obtained from (2.19) by setting \( H=H_0 \). On expressing the trace in (2.19) in the basis of the eigenfunctions (3.25) of \( H_0 \) and noting that

\[ J_x |q_x, q_y; p> = \frac{2e\alpha t_x}{\hbar} \sin(q_x a) |q_x, q_y; p> \quad , \quad (3.28) \]

we get

\[ M_\ell^{(0)} = \frac{4\beta e^2 \alpha t_x^2}{\Omega \hbar^2} \sum_{q_x, q_y, p} \varepsilon(q_x, q_y) \sin^2(q_x a) \]
\[ \times \sum_{k=0}^\ell \frac{(-1)^{k \ell \ell !}}{k ! (\ell-k) !} \quad (3.29) \]

so that

\[ M_\ell^{(0)} = 0 \quad \text{unless} \quad \ell = 0 \quad (3.30) \]

As noted before, this result merely says that the
conductivity $\text{Re}\{\sigma_{xx}(\omega)\}$ when the hole is restricted to the x-y plane is a delta-function in $\omega$, i.e., the d.c. conductivity is infinite.

Allowing the hole to hop off the x-y plane clearly leaves the zeroeth moment linear in $\beta$ unaltered, since the only path that contributes to this moment is one with two hops, both of which are in the x direction. However, the inclusion of $H_z$ does alter the higher moments. The lowest order correction to these higher moments is second order in $t_z$, since the hole requires an even number of hops perpendicular to the x-y plane in order to return to its original position. There are several terms of order $t_z^2$ in the trace of (2.19), an example of which is

$$
\text{Tr}\{H_{z}^{k-1} H_{x}^{j_{x}} H_{z}^{\ell-k-1} H_{x}^{j_{x}}\}
$$

$$
= \frac{4a^2e^2t_x^2}{\hbar^2} \sum_{q_x,q_y,p} \varepsilon^{k-1}(q_x,q_y)\varepsilon^{\ell-k-1}(q_x',q_y')\sin(q_x)\sin(q_x')
$$

$$
\times |<q_x,q_y;p|H_z|q_x',q_y';p'>|^2
$$

expressed in the basis of the Bloch states (3.25). The important physics of the situation is contained in the quantity

$$
W = \sum_{p'} \left|<q_x,q_y;p|H_z|q_x',q_y';p'>\right|^2
$$

(3.32)
since this factor determines the effect of including \( H_z \) up to second order. Now since \( H_z \) merely hops the hole in the \( z \)-direction without translating it in the \( x-y \) plane, we must have \( p' = p + 1 \) and it follows that

\[
W = 2t_z^2 \quad (3.33)
\]

Calculation of the moments up to order \( t_z^2 \) using expression (2.19) involves the computation of certain tedious integrals -- a procedure that is not very illuminating physically. Instead we proceed by drawing a complete equivalence, up to second order in \( t_z \), between the present problem of a hole scattering off the spins in a planar antiferromagnet with that of a hole scattering off spinless impurities in a single plane. We then calculate the zero frequency conductivity to order \( t_z^2 \) using the Born approximation. Comparing the result of the Born approximation with that of the moment method, we again find good agreement if the high temperature conductivity obtained from the moment method is divided by \( K \beta t_x \) to obtain the low temperature result. The constant \( K \) in this case is \((1/16)\sqrt{14/\pi}\).

We envisage a random distribution of spinless impurities in a single plane. Let \( A_{ij}^{(\alpha)} \) denote the probability of finding an impurity at site \((i,j)\) in a particular distribution, \( \alpha \), of impurities. The sum over all possible distributions gives us the probability \( C \) of
finding an impurity at any site:

\[ \sum_{\alpha} A^{(\alpha)}_{ij} = C \]  

(3.34)

We assume that each impurity is a point scatterer, so that
the potential, \( V \), seen by the hole is of the form

\[ V = V_0 \sum_{i,j,\alpha} A^{(\alpha)}_{ij} a_j^\dagger a_i \]  

(3.35)

where \( V_0 \) is a parameter that is to be determined. If \( V \)
is small, the basic physics is determined by the quantity

\[ W' \equiv |<q_x',q_y'|V|q_x,q_y>|^2 \]  

(3.36)

Using (3.34) and (3.35), we find

\[ W' = V_0^2 c^2 \delta_{q_x',q_x} \delta_{q_y',q_y} + (C-C_0^2)V_0^2 \]  

(3.37)

The diagonal term in the above relation may be ignored
for it can be eliminated by merely adding a constant \(-V_0C\)
to the potential \( V \) in (3.35). The scattering of a hole
off spinless impurity scatterers with potential \( V \) would be
entirely equivalent to the original problem of hole-
scattering in a planar antiferromagnet provided the
squared matrix elements \( W \) and \( W' \) are identical. Thus the
equivalence is guaranteed, up to second order in \( t_z \), if
we require
\[ C(1-C)\psi^2_o = 2t^2_z \quad (3.36) \]

which for low impurity concentration may be written

\[ C\psi^2_o = 2t^2_z \quad (3.37) \]

The hole conductivity may now be calculated using the scattering formalism. Since we have assumed that \( t_z < t_x, t_y \), it follows that \( V_o \) is small compared to the kinetic energy of the hole and so the Born approximation may be used. The scattering amplitude, \( f(k, \theta) \), in the Born approximation (in two dimensions) is given by the formula

\[ f(k, k') = \frac{m}{2\hbar^2 \sqrt{2\pi k}} \int \frac{e^{i(k' - k) \cdot \mathbf{r}}}{V(\mathbf{r}) \, d^2r} \quad (3.38) \]

where \( V(\mathbf{r}) \) is the scattering potential, \( \mathbf{k} \) and \( \mathbf{k}' \) are the incoming and scattered wave-vectors, respectively, and \( m \) is the mass of the scattered particle. In our case of point scatterers with potential (3.35), the scattering amplitude becomes

\[ f(k, \theta) = \frac{V_o m^* a^2}{2\hbar^2 \sqrt{2\pi k}} \quad (3.39) \]

where \( \theta \) is the angle between \( \mathbf{k} \) and \( \mathbf{k}' \) and \( m^* \) the effective mass of the hole. The conductivity in the presence of impurities is given by
\[ \sigma = \frac{ne^2\tau}{\tau} \quad \text{(3.40)} \]

where \( n \) is the number of charge carriers per unit volume, and where \( \tau \) is the relaxation time obtained from\(^{100}\)

\[ \frac{1}{\tau} = \frac{c^2}{a^2} \int_{-\pi}^{+\pi} \langle v_k \xi(k,\theta) \rangle (1 - \cos \theta) d\theta \quad \text{(3.41)} \]

Here \( \xi(k,\theta) \) is the differential cross-section, \( v_k \) is the hole-velocity at wave-vector \( k \) and \( \langle \cdots \rangle \) denotes the thermal average.

Setting \( v_k = \hbar k/m^* \) and using (3.41) we get

\[ \frac{1}{\tau} = \frac{v^2 c^2 m^* a^2}{8\pi m^3 \hbar^3} \int_{-\pi}^{+\pi} (1 - \cos \theta) d\theta \]

i.e.,

\[ \frac{1}{\tau} = \frac{m^* t^2 a^2}{2\hbar^3} \quad \text{(3.42)} \]

where we have used (3.37). Thus, the conductivity, \( \sigma^{(B)} \), in the Born approximation as given by (3.40) is

\[ \sigma^{(B)} = \frac{2e^2 \hbar^3}{\Omega a^2 m^* t^2 z} \quad \text{(3.43)} \]

Let us assume that the hopping of the hole is isotropic in the plane, i.e., \( t_x = t_y \). At low temperatures, the energy
of the hole will be close to the minimum of the band represented by (3.27). Since the hopping integral, $t$, for holes is negative, the band minimum occurs at zero wave-vector. On expanding (3.27) around the band-minimum, we get the effective mass of the hole as

$$m^* = \frac{\hbar^2}{2at_x}$$  \hspace{1cm} (3.44)

The low temperature hole-conductivity in the presence of impurity scattering may then be written in the Born approximation as

$$\sigma_{\text{low}} (B) = 8 \frac{a^2 e^2}{\hbar^2} \left( \frac{t_x}{t_z} \right)^2$$  \hspace{1cm} (3.45)

We have obtained the low temperature conductivity of a hole in a planar antiferromagnet using the scattering formalism. We now proceed to calculate the high temperature hole conductivity using the moment method. For the planar antiferromagnet, the zeroeth, second and fourth moments in the high temperature domain ($\beta^{-1} >> t$) up to second order in $t_z$ are

$$M_0 = \frac{2\beta \pi a^2 e^2 t_z^2 N}{\hbar^2}$$  \hspace{1cm} (3.46a)

$$M_2 = \frac{4t_z^2}{\hbar^2} M_0$$  \hspace{1cm} (3.46b)
\[ M_4 = \frac{28t_x^2t_z^2}{\mu^4} M_0 \]  

(3.46c)

Since \( t_z \ll t_x \), we have

\[ \gamma = \frac{M_0^2 M_4}{3M_2^2} \gg 1 \]  

(3.47)

so that the line shape is a Lorentzian. Fitting this line shape to the moments gives

\[ \text{Re}[\sigma_{\text{high}}(0)] = \frac{1}{2} \sqrt{\frac{14}{\pi}} \frac{\beta a^2 e^2}{\gamma \mu} \frac{t_x^3}{t_z^2} \]  

(3.48)

From results (3.45) and (3.48), we see that

\[ \text{Re}[\sigma_{\text{low}}(0)] = \frac{\text{Re}[\sigma_{\text{high}}(0)]}{K \beta t_x} \]  

(3.49)

with

\[ K = \frac{1}{16} \sqrt{\frac{14}{\pi}} \]  

(3.50)

The d.c. conductivities \( \text{Re}[\sigma|| (0)] \) and \( \text{Re}[\sigma\perp (0)] \), parallel and perpendicular to the ferromagnetic planes of a planar antiferromagnet can be calculated in the moment method even when \( t_z \) is not small. For isotropic hopping, i.e., \( t_x = t_y = t_z = t \), the moments of the conductivity in directions parallel and perpendicular to the ferromagnetic planes are
\[ M_{0//} = \frac{2\beta \pi a^2 e^2 t^2}{\Omega \hbar^2} N \quad M_{0\perp} = M_{0//} \]  

\[ M_{2//} = \frac{4t^2}{\hbar^2} M_0 \quad M_{2\perp} = \frac{8t^2}{\hbar^2} M_0 \]  

\[ M_{4//} = \frac{64t^4}{\hbar^4} M_0 \quad M_{4\perp} = \frac{192t^4}{\hbar^4} M_0 \]  

In this case \( \gamma = 1 \). On using a Gaussian fit, we obtain

\[ \frac{\text{Re}[\sigma// (0)]}{\text{Re}[\sigma\perp (0)]} = \sqrt{2} \]  

The anisotropy in the d.c. conductivities is entirely due to the magnetic ordering of the conduction electrons. This qualitatively explains the anisotropic conductivity of nickel sulfide,\textsuperscript{101,102} in which the nickel planes form a planar antiferromagnet. Brinkman and Rice\textsuperscript{103} have also investigated the anisotropy in the conductivity of a planar antiferromagnet. They found similar results for a hexagonal structure more appropriate for NiS and V\textsubscript{2}O\textsubscript{3}.

Result (3.52) differs from what one would obtain from band theory. The conductivity as given by band theory is infinite since the relaxation times of electrons in Bloch states are essentially infinite. On introducing planar antiferromagnetism into the system, we find that the velocities of the electrons (or holes) perpendicular
to the ferromagnetic plane vanish in the large interaction limit, giving rise to zero conductivity in this direction. Thus, according to band theory, the ratio of the d.c. conductivities along and perpendicular to the ferromagnetic planes of a planar antiferromagnet diverges in the limit of strong electron-electron interaction.

To summarize, in this chapter, we have tested the validity of the moment method by applying it to two examples which we have solved by alternative methods. The first example, which was meant purely for illustrative purposes, was that of a single electron confined to two lattice sites. The moment method was shown to reproduce the exact high temperature conductivity in this case. It was explicitly demonstrated that the low temperature conductivity can be obtained from the high temperature result. Our second example was that of hole-conductivity in a planar antiferromagnet, a model appropriate to NiS and V$_2$O$_3$. We showed how the spin scattering arising from its magnetic order produces an anisotropic conductivity, even if the hopping matrix element is taken to be isotropic.
CHAPTER IV

THE RANDOM-SPIN HUBBARD LATTICE

Having adequately tested the accuracy of the moment method in the previous chapter, we now apply it to the isotropic three-dimensional Hubbard lattice. We calculate the conductivity of the system for arbitrary electron and impurity concentrations and for arbitrary magnetization. There is no "test case" for this system and we can only trust that the moment method will give reasonable results, as it did for the examples in Chapter III.

After summing literally hundreds of diagrams for the three-dimensional lattice with isotropic hopping, we obtain the zeroeth, second and fourth moments of the conductivity. The contributions arising from the various diagrams are shown in detail in Appendix A. The final expressions we obtain for the moments are:

\[ M_0 = \frac{2\beta \pi a^2 e^2 t^2 N}{\Omega \mu^2} \]  

\[ M_2 = \frac{M_0 t^2}{\mu^2} \left\{ 4+4(1-Q)-8(1-P)^2(1-Q)^2[C^3+(1-C)^3] \right\} \]

\[ - 16P(1-P)(1-Q)^2[C^2+(1-C)^2]-8P^2(1-Q)^2 \]  

(4.1a)

(4.1b)
\[ M_4 = \frac{M_0 t^4}{h^4} \left\{ 16 + 120 (1-P)(1-Q) + 40 (1-P)^2 (1-Q)^2 - 96 (1-P)^2 (1-Q)^2 [C^3 + (1-C)^3] - 144 (1-P)^3 (1-Q)^3 [C^3 + (1-C)^3] + 64 (1-P)^4 (1-Q)^4 [C^5 + (1-C)^5] + 120 P (1-Q) + 240 P (1-P) (1-Q)^2 - 352 P (1-P) (1-Q)^2 [C^2 + (1-C)^2] - 288 P (1-P)^2 (1-Q)^2 [C^2 + (1-C)^2] - 144 P (1-P)^2 (1-Q)^2 [C^2 + (1-C)^2] + 256 P (1-P)(1-Q)^4 [C^4 + (1-C)^4] - 56 P^2 (1-Q)^2 - 144 P^2 (1-P)(1-Q)^3 - 288 P^2 (1-P)(1-Q)^3 [C^2 + (1-C)^2] + 384 P^2 (1-P)^2 (1-Q)^4 [C^3 + (1-C)^3] - 144 P^3 (1-Q)^3 + 256 P^3 (1-P)(1-Q)^4 [C^2 + (1-C)^2] + 64 P^4 (1-Q)^4 \right\} \] (4.1c)

By fitting the line shape (2.45) to these moments, we have obtained the electrical conductivity.

There are two mechanisms that contribute to the resistivity of the material: (i) scattering arising from spin disorder, and (ii) scattering from impurities.

When the system is a saturated ferromagnet, i.e., when \( C = 0 \), the resistivity arises entirely from impurity scattering. The results we obtain for the real part of the d.c. conductivity of a saturated ferromagnet with various impurity concentrations is shown as a function of
the number of electrons per atom in Fig. 3. The nearly parabolic nature of the curves suggests that to within 10% 

$$\text{Re}[\sigma_{xx}(0)] \approx P(1-P)g(Q); \quad C = 0$$

where \( g(Q) \) is a function only of \( Q \). It appears that the impurity scattering depends on the number of holes and on the number of electrons present.

The presence of impurities in our model essentially removes lattice sites from the crystal. If the d.c. conductivity is to be non-zero, then clearly there must be a finite probability that the remaining lattice sites fall into infinite clusters. For clearly, if the lattice sites available to the conduction electrons all fall into disconnected and localized clusters, hopping of electrons cannot take place and the d.c. conductivity would vanish. The maximum impurity concentration for which this probability is non-zero is called the percolation limit. For a simple cubic lattice the percolation limit is \( Q = 0.68 \). For impurity concentrations greater than this value percolation theory demands that the d.c. conductivity vanish. The resistivity of a saturated ferromagnet when \( P = 0.5 \) is shown as a function of the impurity concentration in Fig. 4. The resistivity of the system beyond the percolation limit is seen to be very large.

In the absence of impurities, the resistivity is due to magnetic scattering. The real part of the d.c.
conductivity as a function of the electron concentration when $Q=0$ is shown as the top curve in Fig. 5. To within about 10% the plot is linear and may be described by the approximate relation

$$\text{Re}[\sigma_{xx}(0)] = Pf(C) ; \quad Q = 0$$

(4.3)

where $f(C)$ is a function only of $C$. We note that the magnetic scattering appears to depend only on the number of holes or doubly occupied sites present. This suggests that one can view the charge carriers in this model as being "non-magnetic" particles (holes or doubly occupied sites). Even when there are only a few "magnetic" particles they can be viewed as scatterers rather than as charge carriers.

The conductivity in the absence of impurities is non-zero even when the number of electrons goes to zero -- an unphysical result. To obtain realistic results we need to allow for the presence of impurities, as is seen from Fig. 5.

We evaluate $f(C)$ by calculating the conductivity analytically in the limit $P \rightarrow 1$ and $Q=0$. In this limit, we retain only terms up to second order in $(1-P)$ in the moments:

$$M_0 = \frac{2 \beta \pi a^2 e^2 t^2 N}{\Omega^2} \; P(1-P)$$

(4.4a)
\[ M_2 = 16 \frac{M_0 t^2}{h^2} [1-C^2-(1-C)^2]P(1-P) \]  

\[ M_4 = 64 \frac{M_0 t^4}{h^4} \{3[1-C^2-(1-C)^2]P(1-P) \] 
\[ + 7[1-C^2-(1-C)^2]P^2(1-P) \} \] 
\[ - 4[1-C^2-(1-C)^2]P^3(1-P) \]  

(4.4b)  

(4.4c)  

In the limit \( P \rightarrow 1 \), we see that \( \gamma \gg 1 \) so that the appropriate line shape is a Lorentzian. On fitting this line shape to the conductivity we find that

\[ f(C) = \frac{1}{AC(1-C)} \]  

(4.5)  

where \( A \) is a constant. For a saturated ferromagnet, i.e., for \( C=0 \) or \( 1 \), we see that the conductivity is infinite, as noted earlier.

Since magnetic and impurity scatterings are quite strong it is not obvious how the total conductivity would behave when both these processes are operative. We find, however, that to a very good accuracy (within 3\%), for a fixed hole concentration the resistivities due to the magnetic and impurity scatterings simply add:

\[ \rho(C,Q,P) = \rho(C,O,P) + \rho(O,Q,P) \]  

(4.6)
where $\rho(C,Q,P)$ is the resistivity of the system when the concentration of spin-up electrons is $C$, the impurity concentration is $Q$ and the hole concentration is $P$. Relation (4.6) is a generalized form of Matthiessen's rule. The fractional variation from this rule is shown in Fig. 6.

In the limit $Q \to 0$ and $C \to 0$, when to lowest order the number of carriers and scatterers are the same in impurity and magnetic scattering, we find that

$$\frac{1}{C} \rho(C,0,P) > \frac{1}{Q} \rho(0,Q,P) \quad (4.7)$$

This is a rather surprising result because one might expect the removal of a lattice site, which is effectively what an impurity does, would affect the resistivity more adversely than flipping a spin. It seems, however, that a spin-flip scatters more efficiently than a static impurity.

Combining results (4.2), (4.3), (4.5) and (4.6) we obtain an approximate expression of the resistivity for the large interaction limit of the random-spin Hubbard lattice:

$$\rho(C,Q,P) = A \frac{C(1-C)}{P} + \frac{h(Q)}{P(1-P)} \quad (4.8)$$

where $h(Q) = 1/g(Q)$.

The high temperature conductivity in our model is always proportional to $\beta t$. We have seen, by means of two examples, that result (2.51) is valid to a very good
approximation, i.e., the low temperature conductivity can be obtained from the high temperature result simply by dividing the latter by a constant times $\beta t$. We thus obtain the peculiar result that the low temperature conductivity is independent of the hopping matrix element $t$. The order of magnitude of this conductivity is given by

$$\sigma \approx \frac{e^2}{h \lambda}$$  \hspace{1cm} (4.9)$$

where $\lambda$ is the mean inter-electron (or inter-hole) separation. Result (4.9) (for $\lambda \approx 10^{-8}$ cm) corresponds to a conductivity of about $10^4$ (ohm-cm)$^{-1}$, which is one or two orders of magnitude smaller than the conductivities of pure metals at room temperature.

In general, we suggest that for systems in which electron-electron interactions are strong a conductivity on the order of $10^4$ (ohm-cm)$^{-1}$ should be an upper bound for the conductivity at temperatures above the magnetic ordering temperatures of these systems. Most of the transition metal oxides and materials that undergo metal-insulator transitions\textsuperscript{105} have conductivities less than $10^4$ (ohm-cm)$^{-1}$. Mott\textsuperscript{106} has obtained a similar result for the "minimum metallic conductivity" for non-interacting electrons in a random potential. It is probably not surprising that the conductivity of strongly interacting electrons is qualitatively similar to that of non-interacting electrons in a strongly scattering potential.
In this chapter, we have reported and discussed the results we obtained for the electrical conductivity in the three-dimensional Hubbard lattice. The results suggest that the charge carriers in this model are "non-magnetic" particles, i.e., holes or doubly occupied sites. The conductivity of a ferromagnet was seen to be infinite in the absence of impurities. For those cases where a meaningful comparison can be made, it was shown that the resistivity produced by spin misalignment from ferromagnetic order is greater than that produced by impurities. The d.c. conductivity was seen to rapidly approach zero for large impurity concentrations, which is consistent with the exact result of percolation theory. We have also shown that to a very good accuracy, a generalized Matthiessen's rule is valid: the resistivities due to impurity and spin scatterings are additive. Finally, from our results we have estimated an upper bound of \( -10^4 \) (ohm-cm\(^{-1}\)) on the conductivities of narrow-band materials.
CHAPTER V

MODEL OF SUPERIONIC CONDUCTION
AND ISOTOPE EFFECT IN SUPERIONIC CONDUCTIVITY

In this chapter we set up a model for superionic conductors and apply the moment method developed and tested in earlier chapters to calculate the d.c. conductivity in these materials. We calculate the mobilities of two different isotopes of the conducting ion and show that a significant difference arises due to the different spin statistics of the isotopes. Hence, superionic conductivity in our model leads to isotopic separation. Based on the results we present, we remark about the diffusion constants in superionic conductors and the breakdown of the Nernst-Einstein relation.

A. The Model

We have seen in the Introduction that superionic conductivity is due to the motion of ions (usually positive) through a relatively rigid network of anions. The cations can be viewed as hopping from lattice site to lattice site. The number of sites available to the cations are larger than the number of cations present.

Our model of a superionic conductor consists of a set of ions which are free to perform nearest-neighbor hops on a simple cubic lattice. Although this model may be too
naive to explain all the experimental data, it is a logical starting point. We assume that the lattice contains randomly distributed impurities. It is taken that an impurity merely prevents a cation from hopping onto its site. Let \( Q \) denote the probability that any site contains an impurity. We include impurities in our model primarily to show that the quantum mechanical effects we obtain are not characteristic only of ideal systems.

We assume that all cation sites are surrounded by the same number of anions. Consequently, the energy of a localized cation arising from its interaction with the anions is site-independent, and so can be ignored. The interaction between two cations at different sites is likely to be strongly screened by the surrounding positive charge. We therefore take two cations on different sites to be essentially non-interacting. Clearly, it will not be feasible to accommodate two cations on the same lattice site because of their considerable size. Moreover, the large Coulomb energy that would result from a doubly occupied site would make such a situation energetically very unfavorable. Therefore, the motions of the ions would be strongly correlated in a manner so as to avoid the occurrence of doubly occupied sites. Hopping can take place only if not every available cation site is occupied. The ratio of the number of cations to the number of available sites is denoted by \( n \), and \( 0 < n < 1 \).
Only ions with filled electron shells are considered. The quantum state of a single cation is completely determined in this model by specifying the lattice position and the spin quantum numbers of the nucleus. Let $I$ denote its total nuclear spin quantum number and $m$ its $z$-component ($-I \leq m \leq I$). The average time for which a nucleus retains the same $z$-component of its total spin -- the nuclear relaxation time -- has not been measured for ions in superionic conductors. We expect that it is much larger than the average time taken by an ion to hop from one site to another. In alkali metals, for example, the nuclear relaxation time ($\sim 10^{-2} - 10^{-6}$ sec) is several orders of magnitude larger than the hopping time ($\sim 10^{-12} - 10^{-14}$ sec). This insures that the spin quantum numbers of the nucleus of an ion remain unchanged while it is hopping. We may then write the Hamiltonian of our model superionic conductor as

$$H = P \{ t \sum_{<i,j>} \sum_{m=-I}^{I} C_{i,m}^\dagger C_{j,m} \} P \tag{5.1}$$

where $C_{i,m}^\dagger (C_{i,m})$ creates (annihilates) an ion at site "i" with the $z$-component of the nuclear spin equal to $m$, $<i,j>$ means that "i" and "j" are nearest-neighbor sites, $t$ is the nearest-neighbor hopping matrix element, and $P$ projects the system-states onto the subspace of the Hilbert space with no doubly occupied lattice sites.
Note that our Hamiltonian is isomorphic with the strong interaction limit of the Hubbard model when $I=1/2$.\textsuperscript{77} We can therefore calculate the electrical conductivity in superionic conductors using the moment method developed in Chapter II and applied in Chapters III and IV. Because of the considerable size of the cations and the large polarizability of the anions of superionic conductors, one would expect that it would be important to include ionic-polarons in our model. Coll and Beni\textsuperscript{109} have worked out the conductivity of a Hubbard chain with electron-phonon coupling included. They have shown that the conductivity can be written as a sum of two terms. The first term has a form identical to that of the Hubbard model, with a renormalized hopping matrix element and electron-electron interaction. This term arises from the band motion of the polarons. The second term, arising from the random hopping of the polarons, is of a more complicated nature, involving the emission and absorption of phonons. We ignore this latter term. As a result, a transformation to polaron coordinates simply yields a renormalized Hubbard Hamiltonian.

As shown in Chapter II, the $\ell$'th moment, $M_\ell$, of the conductivity is given in the limit of high temperatures ($\beta^{-1} \gg t$) by

$$M_\ell = \frac{\beta \pi}{\Omega \xi} \sum_{n=0}^{\ell} (-1)^n \frac{\ell!}{n!(\ell-n)!} \text{Tr}\left\{ H_0^\ell J_x H_0^{\ell-n} J_x \right\}, \quad (5.2)$$
where the current operator, \( J_x \), in the case of a superionic conductor may be written

\[
J_x = \frac{i\epsilon a t}{\hbar} \sum_{i,m} \{ C_{i,m}^{+} C_{i-1m} - C_{i,m}^{+} C_{i+1m} \} \rho_x ,
\]  

(5.3)

"i+1" denoting the nearest neighbor of site "i" in the +x direction.

We obtain the ionic conductivity in our model superionic conductor by calculating the zeroeth, second and fourth moments and fitting the line shape (2.45), as in the case of electronic conductivity in narrow band materials.

The calculation of the moments proceeds almost exactly as in the case of electrons in narrow-band materials, which was described in detail in Chapter II. The electron spin is here replaced by the nuclear spin of the ion. The expression for the \( \ell' \)th moment of \( \sigma(\omega) \) involves the evaluation of the contribution of paths with \( \ell' + 2 \) hops, each of which moves an ion from one site to an adjacent site. A given path will contribute to the moment only if the nuclear spin configuration of the ions after the path is traversed is the same as that before. For otherwise, the trace in expression (5.2) would vanish. Clearly, the nuclear spins of the ions will be randomly oriented. The \( z \)-component of the nuclear spin, \( I \), can have any one of \((2I+1)\) values, with probability \( 1/(2I+1) \). The probability that the nuclei of \( K \) ions will all have the same \( z \)-component
is \((2I+1)^{1-K}\), which gives the probability that a cyclic permutation of \(K\) ions will contribute to the trace in (5.2).

As we explained in Chapter II, there is a phase factor that must be taken into account when evaluating the contribution of a given path to the moments. This phase factor is always +1 for bosons. For fermions, this phase factor is -1 when an even number of ions are interchanged and +1 when an odd number are interchanged. As has been pointed out earlier, this phase factor has its origin in the different quantum statistics obeyed by fermions and bosons. In the present case, the phase factor is determined entirely by the nuclear spin of the ions because we have assumed the electrons in these ions to form closed shells.

The moments of the conductivity of our model superionic conductor can be directly obtained from those of electrons in narrow-bands by making the replacements:

\[ P \rightarrow (1-n) \quad (5.4a) \]

\[ [C^K+(1-C)^K] \rightarrow (2I+1)^{1-K} \quad (5.4b) \]

On making these substitutions and taking care to include the appropriate phase factors, we get for the moments of the conductivity in our model superionic conductor:
\[ M_0 = \frac{2\beta \pi a^2 e^2 t^2}{\Omega \mu^2} n(1-n)(1-Q)^2 , \quad (5.5a) \]

\[ M_2 = \frac{4M_0 t^2}{\mu^2} \{2-Q-2(1-n)^2(1-Q)^2+2n(1-Q)^2 \]
\[ [2(-1)^2I(1-n)(2I+1)^{-1}-n(2I+1)^{-2}] \} \quad (5.5b) \]

\[ M_4 = \frac{8M_0 t^4}{\mu^4} \{17-15Q+(1-Q)^2[-7+44n-32n^2] \]
\[ -18(1-n)^2(1-Q)^3+8(1-n)^4(1-Q)^4 \]
\[ -4(-1)^2I(2I+1)^{-1}n(1-n)(1-Q)^2[-20+9Q+8(1-n)^2(1-Q)^2] \]
\[ +6(2I+1)^{-2}n^2(1-Q)^2[-5+3Q+8(1-n)^2(1-Q)^2] \]
\[ -8(-1)^2I(2I+1)^{-3}n^4(1-Q)^4 \} , \quad (5.5c) \]

where \( N \) is the total number of lattice sites in the crystal. By fitting an appropriate line shape to the moments we obtain the conductivity. The result in units of \( e^2 a^2 \delta t / \mu \) is shown as a function of \( n \) in Fig. 7 for several values of the nuclear spin, \( I \), and \( Q=0.1 \). Note that even though the different isotopes are described by essentially identical Hamiltonians, the conductivities may differ by as much as a factor of two.
B. Isotope Separation

We now allow for the presence of two cation isotopes and compare their mobilities. For simplicity, we consider the case of an abundant isotope A and a rare isotope B. In the presence of an external electric field, $E$, the currents $J_A$ and $J_B$ of the A and B ions, respectively, are given in general by

$$J_A = (\sigma_{AA} + \sigma_{AB})E$$  \hspace{1cm} (5.6a) $$J_B = (\sigma_{BB} + \sigma_{BA})E$$  \hspace{1cm} (5.6b)

Here $\sigma_{AA}$ and $\sigma_{BB}$ represent the conductivities of ions of one type when the field is applied to the ions of the same type. $\sigma_{AB}$ and $\sigma_{BA}$ represent the "drag" conductivities in which currents of one type of ion are produced by the electric field acting on the second type of ion.

Let $n_A$ and $n_B$ represent the concentrations of the A and B ions respectively. Since A is the abundant isotope, we may take $n_B << n_A$ and $n_A \approx n$, where $n$ is the total concentration of mobile ions. The ratio of the mobilities, $\mu_B$ and $\mu_A$, of the two isotopes are given by

$$\frac{\mu_B}{\mu_A} = \frac{J_B/n_B}{J_A/n_A} = \frac{n(\sigma_{BB} + \sigma_{BA})}{n_B \sigma_{AA}}$$  \hspace{1cm} (5.7)
where we have used the fact that \( \sigma_{AA} \gg \sigma_{BB}, \sigma_{BA} \) and \( \sigma_{AB} \).

The conductivities \( \sigma_{AA}, \sigma_{BB} \) and \( \sigma_{BA} \) are obtained by a straightforward generalization of the Kubo formula. For example, the d.c. drag conductivity \( \sigma_{BA} \) is given by

\[
\sigma_{BA} = \frac{1}{2\Omega} \int_{-\infty}^{0} d\tau \int_{0}^{\beta} d\lambda \text{ Tr}\{e^{-\beta H} J_B \ e^{iH(\tau/\Omega+\lambda)} \} A e^{-iH(\tau/\Omega+\lambda)}
\]

(5.8)

where \( J_A \) and \( J_B \) are current operators corresponding to \( A \) and \( B \) ions, respectively. The conductivity, \( \sigma_{AA} \), of the majority isotope \( A \) remains unchanged to lowest order on addition of the rare isotope \( B \). Therefore the same moments obtained above in expressions (5.5) may be used to calculate \( \sigma_{AA} \). The conductivity \( (\sigma_{BB}+\sigma_{BA}) \) is also calculated using the moment method. The only change is that those hopping paths which interchange ions of type \( A \) with those of type \( B \) will not contribute to the trace in (5.2). Since \( n_B \ll n \), in the calculation of the moments of \( (\sigma_{BB}+\sigma_{BA}) \) we include cases in which there is only one \( B \) ion per path, the rest of the sites on the path being either vacant or occupied by \( A \) ions. Paths with more than one \( B \) ion are ignored because they involve quadratic and higher order terms in \( n_B \). The contributions of the various paths to the moments are shown in detail in Appendix A. The resulting moments for \( (\sigma_{BB}+\sigma_{BA}) \) are
\[ M_0 = \frac{2\pi a^2 e^2 t^2 N}{\Omega a^2} n_B (1-n) (1-Q)^2 \]  
\[ M_2 = \frac{4 M_0 t^2}{M^2} \{ 2-Q-2(1-n)^2 (1-Q)^2 \} \]  
\[ M_4 = \frac{8 M_0 t^4}{M^4} \{ 17-15Q+(1-Q)^2 [-7+44n-32n^2]-18(1-n)^2 (1-Q)^3 \} \]

Using these moments to fit line shapes, we obtain the results for \( u_B/u_A \) as a function of Q shown in Fig. 8 for the case \( n=0.2 \). The curves are labelled by the nuclear spin of isotope A. In the limit of small concentrations the results are independent of the nuclear spin of the B ions; interchange of B ions cannot occur because only one B ion is present in every path that contributes to \( \sigma_{BB}+\sigma_{BA} \). Our results show a striking difference in isotope mobilities even when the impurity scattering is quite strong. Thus the isotope-spin dependent conductivity in our model could lead to isotope separation.
We must, of course, exercise caution in extrapolating the model results to the real world. Experimentally, we would not expect anywhere nearly as strong an isotope effect as we have obtained here. One reason for this is that we have picked an ion concentration (n=0.2) which accentuates the isotope effect. More importantly, we have ignored many interactions in this model. Roughly speaking, the d.c. conductivity decreases as scattering mechanisms increase the width of \( \sigma(\omega) \). The scattering that would result from the interactions we have neglected would dilute but not eliminate the isotope effect.

A particularly simple interaction we can deal with is the case of nearest-neighbor interaction between cations. Suppose this interaction energy is \( \tilde{U} \). As a cation hops from one site to another, the number of nearest cation-neighbors may change. The cation energy, as a result, can change by an integral multiple of \( \tilde{U} \), say \( m\tilde{U} \). The cation can be made to participate in the conduction process if it is provided this much energy by incident photons of frequency \( m\tilde{U}/\hbar \). Thus the frequency-dependent conductivity will show peaks separated by \( \Delta\omega = \tilde{U}/\hbar \). This intuitively obvious result can also be arrived at in the high temperature regime \( (k_B T > > \tilde{U} > > t) \) using the moment method. Inclusion of nearest-neighbor cation interactions would alter the d.c. conductivity but would not eliminate the isotope effect.
We have seen in Chapter IV that the high temperature d.c. conductivity obtained from the moment method is of the form

\[ \sigma = \frac{K \alpha^2 e^2}{\Omega \mu} \beta t , \]  

(5.10)

where \( K \) is a dimensionless constant. The transfer matrix element \( t \) will, of course, be much smaller for ions in a superionic conductor than for electrons in narrow-band materials. We have assumed \( t \) to be independent of temperature. In reality, however, one would expect \( t \) to be strongly temperature-dependent in superionic conductors, where the ion hopping is thermally activated. The temperature dependence of \( t \) may be assumed to have the plausible form:

\[ t = t_o e^{-\Delta/k_B T} , \]  

(5.11)

where \( t_o \) is a constant independent of temperature and, as before, \( \Delta \) is the activation energy. Using (5.10) and (5.11) we get the high temperature d.c. conductivity of a superionic conductor to be

\[ \sigma(T) = \frac{K \alpha^2 e^2}{\Omega \mu} \frac{t_o}{k_B T} e^{-\Delta/k_B T} \]  

(5.12)

which is of the Arrhenium form (1.1).
The system is said to be in the low temperature regime when \( k_B T \ll t \). Since the hopping matrix element \( t \) decreases exponentially with temperature, the above inequality will never be satisfied. In other words, our model superionic conductor will never be in the "low temperature regime" no matter how low the absolute temperature may be. Consequently, the result (5.12) will be valid for all temperatures i.e., the conductivity in our model will always be of the Arrhenium type -- as observed experimentally.

Using some of the results presented in this chapter, Kimball has very recently explained the deviation from the Nernst-Einstein relation (1.2) which is observed in some superionic conductors. The diffusion constant, \( D \), of these materials is measured using what is known as the tracer diffusion technique. A small percentage of a radioactive isotope of the mobile ion is maintained in the superionic conductor. Thus the material has a majority isotope, A, and a minority (radioactive) isotope, B. The diffusion of the radioactive isotope is easily detected and the diffusion constant \( D \) subsequently obtained. The electrical conductivity of the material is largely determined by the conductivity per ion of the majority isotope. Kimball has shown that the tracer diffusion constant, however, depends only on the conductivity per ion of the minority (radioactive) isotope. It is found that \( \sigma_{AA}/n_A \)
and $\sigma_{BB}/n_B$ differ significantly, due to strong correlations between the ions. As a result, the tracer diffusion constant measured experimentally differs from what one would obtain from the Nernst-Einstein relation. The successful explanation of the failure of the Nernst-Einstein relation also justifies our basic assumption that the ionic motions in a superionic conductor are strongly correlated.

In summary, in this chapter, we set up a model for superionic conductors, in which the motion of the ions are strongly correlated. The d.c. conductivity was calculated using the moment method and was shown to be of the Arrhenius form (1.1). Quantum statistics was shown to play an important role in superionic conduction. The conductivities of different isotopes of the mobile ion were shown to be significantly different. This difference could, in principle, lead to isotope separation.
CHAPTER VI
SUMMARY AND CONCLUSION

We have presented in this dissertation a calculation of the electrical conductivity in superionic conductors and in narrow-band materials. The Hamiltonian of our model superionic conductor was seen to be isomorphic, in a special case, to the strong-interaction Hubbard Hamiltonian, which is very often used to study narrow-band materials. Our calculation of the d.c. conductivities in superionic conductors and narrow-band materials thus proceeded on similar lines.

Our method for calculating the conductivity consisted of fitting an appropriate line shape to the frequency-dependent conductivity. The fitting of the line shape was done with the help of the exactly calculated zeroeth, second and fourth moments of the conductivity. The moments were evaluated using Nagaoka's path formulation. To keep the calculation general, we had assumed arbitrary concentrations of current-carriers and impurities and also, in the case of narrow-band materials, an arbitrary magnetization. The moment method is strictly valid only for high temperatures (\( \beta^{-1} \gg t \)), but we have demonstrated that we can obtain the low temperature conductivity from the high temperature results.
The first non-trivial result we have obtained is the hole-conductivity in a planar antiferromagnet, a model appropriate to materials like NiS and V$_2$O$_3$. We have shown that the spin-scattering arising from the magnetic ordering of a planar antiferromagnet produces an anisotropic conductivity similar to that observed in these materials.

In the absence of impurities, the d.c. conductivity in the random-spin Hubbard lattice was seen to be proportional to the number of holes or doubly occupied sites present. The impurity-limited conductivity was seen to be approximately proportional to the product of the concentration of electrons and holes (or doubly occupied sites). The conductivity in a ferromagnet without impurities was shown to be infinite because both spin and impurity scatterings are absent.

For large impurity concentrations, the d.c. conductivity was found to vanish quite rapidly. This is consistent with the exact result of percolation theory which says that the d.c. conductivity should vanish in a simple cubic lattice when there are about 68% impurities. To an excellent accuracy we have also shown that the resistivities arising from spin and impurity scatterings are additive, establishing a generalized Matthiessen's rule.
We have estimated an upper bound of $-10^4 \text{ (ohm-cm)}^{-1}$ on the conductivities of narrow-band materials. This estimate is in agreement with most of the available experimental data on such materials.

To obtain the electrical conductivity in superionic conductors, we have set up a model for such materials in which the ionic motions are strongly correlated. The moment method was again applied to obtain the conductivity as a function of the ion and impurity concentrations. The conductivity in superionic conductors was shown to be of the Arrhenius form, in agreement with experiment.

The dependence of the conductivity on the nuclear spin of the mobile ions in superionic conductors was also obtained. Quantum statistics was shown to play an important role; the conduction process introduces the possibility of interchanging indistinguishable ions. In particular, the effect of the presence of two isotopes of the mobile ion was investigated. A significant difference was seen in the conductivities of the two isotopes, arising from correlated motions of the ions. The difference in the conductivities was seen to be large enough to produce isotope separation.
REFERENCES

36. A. D. Le Claire in Ref. 5, p. 51.
37. M. O'Keeffe in Ref. 5, p. 233.
43. J. C. Wang, M. Gaffari and Sang-il Choi, private communication.


These papers have extensive lists of references on the subjects.
106. N. F. Mott, Phil. Mag. 26, 1015 (1972).


FIGURE CAPTIONS

Fig. 1 Hole-walk on a square path in an antiferromagnet. (a) initial configuration (b) after one revolution (b) after two revolutions (c) after three revolutions.

Fig. 2 Diagrams (a), (b) and (c) are examples of paths that contribute to the zeroeth, second and fourth moments respectively. (d) is an allowed disconnected diagram that could contribute to the fourth moment.

Fig. 3 The real part of the d.c. conductivity $\tilde{\sigma}$ for a saturated ferromagnet as a function of the number of electrons per atom for various impurity concentration. For high temperatures $\sigma = \frac{\delta t e^2 a^2}{h} \tilde{\sigma}$, but for low temperatures $\sigma \approx \frac{e^2 a^2}{h} \tilde{\sigma}$. The same notation applies for all subsequent figures.

Fig. 4 The resistivity of a saturated ferromagnet as a function of impurity concentration when the probability of a hole on a lattice site ($P$) is 0.5.

Fig. 5 The d.c. conductivity for various impurity concentrations as a function of the number of electrons per atom for randomly oriented spins.
The fractional variation \( \frac{\Delta \rho}{\rho} \) from Mattheissen's rule plotted as a function of the impurity concentration, where \( \Delta \rho = \rho(C,Q,P) - \rho(C,0,P) - \rho(0,Q,P) \).

The d.c. conductivity of the model superionic conductor is shown as a function of the mobile ion concentration for various values of nuclear spin, I. Since \( Q=0.1 \), one atom in 10 is removed at random from the lattice.

The ratio of the rare isotope mobility to the abundant isotope mobility tends to unity as \( Q \) increases because the resistivity becomes impurity dominated. The ratio is independent of the spin of the rare isotope nucleus, and I is the spin of the abundant isotope nucleus.
Figure 1
Figure 2

\[ \text{O = HOLE} \quad \text{X = ELECTRON} \]
Figure 3
Figure 4

Resistivity ($\rho$) vs Impurity Concentration

- $C = 0.0$
- $P = 0.5$

Percolation Limit
Figure 5
Figure 7
Figure 8
APPENDIX A

We now present the contribution to the moments from every possible path, with various distributions of holes (vacancies) and electrons (ions). The cross (x) in the diagrams below represents the electron (ion) that makes the first hop, and the circle (0) denotes the hole (vacancy) site onto which this electron (ion) hops. A double line on any diagram means that that part of the path has been traversed twice. A given path can have different numbers of electrons (ions) and holes (vacancies). We have entered the contribution for each case separately. The contributions written down are the values of the quantity

\[ \sum_{k=0}^{\lambda} \frac{(-1)^k \lambda!}{k!(\lambda-k)!} \text{Tr}[H^k J_x H^{\lambda-k} J_x] \]

(ignoring factors of e,\hbar,\alpha,\tau) for each path and for a given number of electrons (ions) or holes (vacancies). The probabilities associated with the paths have been suppressed.

We also enter a "symmetry factor" for each diagram. By symmetry factor we mean the number of geometrically different paths of the same type which give the same contribution to the moments as the one shown.

We present only the contributions to the moments of \( \sigma_A \) and \( (\sigma_{BB} + \sigma_{BA}) \), where A and B denote the abundant and rare...
isotopes, respectively, of the mobile ion. When the contributions to $\sigma_A$ and $(\sigma_{BB}+\sigma_{BA})$ are the same only one entry is made under the column "Contribution". When the contributions are different, separate entries are made. The first entry is the contribution of the path to $\sigma_A$ and the second entry that to $(\sigma_{BB}+\sigma_{BA})$.

The quantity $\phi$ represents the phase factor explained in the text. $\phi$ is -1 if an even number of fermions are interchanged and +1 otherwise.

The contributions to the moments of the conductivity in narrow-band materials can be obtained from the values entered for $\sigma_A$ simply by setting $\phi = -1$ wherever it occurs.

As has been explained in the text, in the calculation of the moments of $(\sigma_{BB}+\sigma_{BA})$ we have used the fact that concentration of the B ions is very small compared to that of the A ions. Consequently, we have assumed that one and only one B ion is present in each path contributing to $(\sigma_{BB}+\sigma_{BA})$ and it is this ion that makes the first hop.

There is only one path that contributes to the zeroeth moment:

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O---------------x
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- Number of Particles Interchanged: 3
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- Symmetry Factor: 4

Path 2:
- Number of Holes: 2
- Number of Particles Interchanged: 2
- Contribution to $\sigma_A (\sigma_{BB} + \sigma_{BA})$: −4ϕ
- Symmetry Factor: 4

Path 3:
- Number of Holes: 3
- Number of Particles Interchanged: 3
- Contribution to $\sigma_A (\sigma_{BB} + \sigma_{BA})$: +2
- Symmetry Factor: 4

Path 4:
- Number of Holes: 4
- Number of Particles Interchanged: 0
- Contribution to $\sigma_A (\sigma_{BB} + \sigma_{BA})$: +2
- Symmetry Factor: 4
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APPENDIX B

We now show that the contributions to the moments of the conductivity arising from disconnected diagrams identically vanish. Consider two such diagrams A and B as shown below.

Let $n$ denote the total number of steps in the two diagrams. Such disconnected diagrams would arise in the calculation of moments of order $\geq (n-2)$. Let $m$ denote the number of steps in diagram B, that in diagram A is therefore $(n-m)$. Suppose the positions of the hops corresponding to the two $J_x$ operators in the trace of (2.19) are arbitrarily fixed as shown in the figure above. Let $\ell$ denote the number of steps between the two $J_x$-hops, ignoring hops from diagram B. Clearly all these $\ell$ steps will belong to diagram A. In general, the number of steps between the $J_x$-hops can be $(\ell+k)$, where $k$ denotes the number of steps belonging to diagram B ($k=0,1...,m$). The number of steps after the second $J_x$-hop is $(n-\ell-k-2)$. 

145
The number of ways, \( N_1(k) \), in which we can have \((\ell+k)\) steps between the two \(J_x\)-hops is clearly given by

\[
N_1(k) = \frac{(\ell+k)!}{k!\ell!}
\]

Similarly, the number of ways, \( N_2(k) \), in which we can have \((n-\lambda-k-2)\) steps after the second \(J_x\)-hop is

\[
N_2(k) = \frac{(n-\lambda-k-2)!}{(m-k)!\Gamma(n-\lambda-m-2)}
\]

The total number of ways in which we can have \((\ell+k)\) steps intervening between the two \(J_x\)-hops is \(N_1(k)N_2(k)\).

Associated with each way, there is a contribution to the \((n-2)\)'th moment given by

\[
(-1)^{\ell+k} \frac{(n-2)!}{(\ell+k)!\Gamma(n-\lambda-k-2)} \equiv C(k)
\]

The net contribution of the two disconnected diagrams A and B to the \((n-2)\)'th moment, when the positions of the \(J_x\)-hops are arbitrarily fixed, is given by

\[
\sum_{k=0}^{\infty} C(k)N_1(k)N_2(k)
\]

\[
= (-1)^\ell \frac{(n-2)!}{\ell!(n-\lambda-m-2)!} \sum_{k=0}^{m} (-1)^k \frac{1}{k!(m-k)!}
\]

\[
= 0
\]
Since nothing specific has been assumed about the disconnected diagrams A and B, it follows that the contribution to the moments from any pair of disconnected diagrams vanishes. If we had three disconnected diagrams, say, A, B and C, we can consider A and B as one diagram, A', by arbitrarily fixing the order of the hops in these two diagrams. By proceeding as demonstrated above we can show that the contributions from A' and C identically vanish. In this manner, we can extend the proof for an arbitrary number of disconnected diagrams. Thus we have the general theorem that the contributions to the moments of the conductivity from disconnected diagrams identically vanish.
VITA

Mukesh Eswaran was born on September 24, 1950 in Deolali, India. He graduated from St. Aloysius' High School, Jabalpur, India in 1966. He obtained his B. S. degree from Jabalpur University, India in 1969 and his M. S. degree (Physics) from the Indian Institute of Technology, Kanpur, India in 1971. He is presently a candidate for the Doctor of Philosophy degree in physics at Louisiana State University.
EXAMINATION AND THESIS REPORT

Candidate: Mukesh ESWARAN

Major Field: Physics

Title of Thesis: Electrical Conductivity in Superionic Conductors and Narrow-band Materials

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:

July 8, 1975