THEORY OF MAGNETISM AND METAL-NONMETAL TRANSITION

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CERTIFICATE

Certified that the thesis entitled ' THEORY OF MAGNETISM AND METAL-NONMETAL TRANSITION' which is being submitted by Shri Ram Kishore in fulfilment for the award of the Degree of Doctor of Philosophy in Physics of University of Roorkee is a record of his own work carried out by him under my supervision and guidance. The matter embodied in this thesis has not been submitted for the award of any other Degree.

This is further to certify that he has worked for a period equivalent to 24 months full time research for preparing his thesis for Ph.D. Degree at the University.

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RESUME

The unique feature of the transition metals is the presence of somewhat tightly bound electrons in d-bands and more mobile electrons in the s band. The magnetism of the transition metals is presumably associated with the d bands. However the electrons in the s band are magnetically polarised due to the magnetism associated with the d electrons. Therefore for the discussion of the magnetic properties of the transition metals the s and d bands should be considered simultaneously. At this early stage of the theory, it is excusable if we ignore the fivefold degeneracy of the d-bands. Accordingly we limit our study to a single nondegenerate d band described by the tight binding form and a nearly free electron like s band.

Anderson's theory of dilute alloys of the transition metals is able to explain the occurrence of the localized magnetic moment on transition metal impurities dissolved in a nonmagnetic metal. In Anderson's model, the band states of the host metal are treated as independent quasi-particles. The impurity is introduced as an extra-localized orbital which interacts with the band states by a hybrid matrix element. All two-body Coulomb interactions are neglected except the Coulomb interaction between the opposite spin electrons on the localized orbital. As an extension of this model, a transition metal can be imagined as a system having a localized d orbital at each lattice site. However, this is an approximate picture of a transition metal, in the sense that there would be no direct

interaction between d electrons on the different sites-only an indirect coupling via the conduction electrons. It is well known that a considerable fraction of the width of the 3d band in transition metals arises from the overlap of the 3d wavefunction on neighboring lattice sites. We assume here that the d electrons form a band and they interact among themselves only via the Coulomb interaction between opposite spin electrons at the same lattice site. This is the Hubbard model for a single nondegenerate narrow energy band. The effect of the s band is taken into account by adopting the one-particle interaction between s and d electrons given by Anderson. Using the Green's function technique, the self consistent ferromagnetic solutions of this model are obtained within the Hartree-Fock approximation. An approximate solution of the correlation problem is obtained. The ferromagnetic solutions for which the correlation effects are taken into account are compared with those obtained in the Hartree-Fock approximation. The model is also used to investigate the role of the s-d interaction in metal-nonmetal transitions. It is possible to understand the difficulty of observing the pressure-induced nonmetal-metal transition.

The Hubbard Hamiltonian, which is certainly a gross oversimplification for real systems, has been extended by including the interatomic Coulomb interactions. An approximate solution of the correlation problem for this model is obtained and the conditions for ferromagnetism are discussed.

The dynamical susceptibility for a system of electrons in a narrow energy band has been studied. The Hamiltonian of the system consists of single particle energies of electrons in the absence of interactions, the intraatomic Coulomb interaction and interatomic Coulomb and exchange interactions. An approximate expression for the susceptibility is derived by using the random phase approximation. Instability of the paramagnetic state against the ferro and the antiferromagnetic states is discussed. An expression for the dynamical susceptibil ty is derived for a system with strong intraatomic interaction. In this case the conditions for the paramagnetic instability against the ferro and antiferromagnetic state, and the spin-flip excitations are discussed.

The Hamiltonian, used to study the dynamical susceptibilit has been used to investigate the phenomenon of metal-nonmetal transitions in the ferro and antiferromagnetic systems having one electron per atom. In the ferromagnetic system there exist two phase transitions at two different critical temperatures: T_M at which a ferromagnetic nonmetal changes into a ferromagnetic metal, and T_C at which system becomes a paramagnetic metal. T_C is always higher than T_M. In an antiferromagnetic system two phase transitions, as found in ferromagnetic system, do not occur. In ferromagnetic system at absolute zero a first order phase transition, where a ferromagnetic nonmetal changes into a paramagnetic metal, occurs at some particular values of interaction parameters. In antiferromagnetic system no phase transition is possible at absolute zero.

In appendices the Hubbard model has been solved using improved decoupling approximations for the higher order Green's functions. The results agree with the exact results known in some limiting cases. It is found that within the Hartree-Fock approximation, the Hubbard model for a single nondegenerate band gives the exchange spliting of the d band in nickel in close agreement with the value derived from the detailed energy band calculations. An expression for the electronic spin polarization $p(\vec{r})$ due to s-d exchange interaction between the conduction electrons and the localized impurity of spin 1/2 in a dilute magnetic alloy is obtained. For large distances $p(\vec{r})$ is found to exhibit exponentially damped behavior.

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1. Shear Viscosity of Insulating Solids, Phys. Letters, 25A, 201 (1967).
2. Electrical Conductivity of Metals, Physica Status Solidi 26, 133 (1968).
3. On Transverse Electrical Conductivity of Metals, Physica Status Solidi, 28, 695 (1968).
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7. Electron Correlation in Ferromagnetism, Phys. Rev., 186, 484 (1969).
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CHAPTER I

INTRODUCTION

I. THEORETICAL CONCEPTS IN MAGNETISM

A. Itinerant versus Localized-Spin Models

For over forty years the occurence of ferromagnetism or antiferromagnetism in transition metals have been a subject of much speculation. Broadly speaking there have been two schools of thought about this problem and all others may be considered as variations on these two themes. The Heisenberg[1] model is based on the assumption that the electrons are localized on atoms and the interatomic exchange effects can be treated by introducing an interaction $-2 J_{ij} \vec{S}_i \cdot \vec{S}_j$ between the electrons localized on the sites i and j. Here J_{ij} is an exchange integral, $\vec{S}_i$ and $\vec{S}_j$ are spin operators corresponding to the electrons at the sites i and j. The itinerant electron model, on the other hand, developed by Bloch,[2] Stoner[3] and Slater,[4] is based on the competition between the kinetic energy of the electrons in a band and electron exchange in the Hartree-Fock approximation. The literature on the itinerant electron model has been reviewed by Mott,[5] Herring,[6] and Beeby.[7]

Experimental facts suggest that neither of these models is correct in its naive form.[6] Itinerant electron model explains the d band specific heat, nonintegral magneton numbers, the low entropy of the antiferromagnetic transition in chromium and the absence of magnetic disorder scattering of neutrons above its Neel point. On the other hand experimental evidences from the critical scattering of neutrons, entropies of ferromagnetic transitions, spin waves and the behavior of ferromagnetic moments on alloying favor the localized picture. In the light of modern refinements of the theories such arguments are not quite significant. For example when correlation effects are included in the itinerant electron theory it provides natural places for spin waves, critical fluctuations and other phenomena once considered explicable only on the localized model. The localized model, in turn, has been generalized not only in the direction of allowing conduction electrons to mediate the exchange coupling (indirect exchange), but also in that of allowing the magnetic electrons to participate in conduction. Thus each model has acquired some of the principal features of the other. However a clear residue of evidence remains in favor of an itinerant model for iron group metals and a localized model for rare earths. For iron group, moreover, galvanomagnetic data and other evidences suggest that the d like electrons are quite mobile and hence the former belief[8-11] that the d electrons constitute a low mobility group clearly separable from conduction electrons, must now be discarded.

We restrict our study to the theory of magnetism in transition metals and therefore we shall not discuss the Heisenberg model which is particularly suited to the case of insulators. For a review of exchange in insulators one may refer to Anderson.[12] In the next three subsections a summary of the literature on the ferromagnetism, collective excitations and spin density waves based on the itinerant electron model will be given.

B. Ferromagnetism

In 1938 Wigner[13] refining his earlier calculations[14] of the correlation energy of a free electron gas, argued convincingly that, in contrast to Bloch's Hartree-Fock result, such a gas would probably not be ferromagnetic at any density. The physical principle involved is that the Coulomb repulsion of electrons of antiparallel spin will always keep them reasonably well apart. Thus the electrostatic energy of a nonferromagnetic state, which has more antiparallel pairs than a ferromagnetic state, will not be as positive in an exact wave function as in a determinantal one, for which antiparallel electrons are spatially uncorrelated. After Wigner's work several authors[15-23] concentrated their attention on this problem of electron correlation in free electron gas. Apart from the intrinsic interest of this problem, the free electron gas serves as a model for the conduction bands of metals and alloys.

When the electrons involved are not free, but merely migrate among the rather compact d shells of the various atoms of transition metals, the overestimate of the energy of the nonmagnetic state relative to the ferromagnetic state ought to be even greater. One can of course argue that the narrow width of the d bands reduces the kinetic energy relative to the exchange energy, thus favoring ferromagnetism. But this effect by itself is of essentially the same nature as decreasing the density of a free electron gas, and if one grants that a correlated electron gas is not ferromagnetic at any density, then it is not obvious that a correlated assembly of itinerant electrons in narrow bands can be ferromagnetic.

The responses that were made to the challenge posed by the problem of correlation may be grouped into those which undertook to graft correlation correction onto existing theories of the Hartree-Fock type, and those which made an entirely new start based on the many electron states of individual atoms. Papers of the former group were usually rather general and did not undertake quantitative estimates of correlation for real metals. Typical of this group is the work of Lidiard[24] who pointed out the need for a more adequate treatment of correlation in the Stoner model, and suggested that use of a screened Coulomb potential might take account of some of the principal correlation effects. A subsequent discussion by Wohlfarth[25] of the role of correlation in the Stoner model was also limited in aim. In the same period Slater[26] advocated a configuration interaction treatment with the band model as a starting point.

The other approach to correlation actually started some years before Wigner's work. The foundation was laid by Slater[27] who proposed a model of a metal as an array of atoms, some neutral with a Heisenberg type coupling of their spins and some in the form of positive or negative ions. This model was greatly extended by Schubin and Vonsovski.[28] Although it seems never to have been put into a form suitable for practical quantitative calculation, it is appealing in that it keeps electrons with antiparallel spins reasonably well apart, and yet allows electrical conduction, nonintegral magneton number etc. Independently Wolf[29] proposed a model based on neutral many electron atoms in ground and excited states, the later having a different magnetic moment from the former and the excitations on neighboring atoms being coupled.

An extreme form of this model was discussed in 1941 by Hurwitz[30] but it appeared in literature in 1953 when Van Vleck[31] published an elaboration of it. In its original form, which he called the 'minimum polarity' model, the d electrons of a metal like nickel were envisioned as distributed among atoms in states closely resembling d^{10} and d^{9} states of the free atom, the relative numbers being chosen to give agreement with the empirical number of d holes. The holes (d^{9} configuration) were envisaged as free to migrate through the lattice, subject to having to avoid one another. Van Vleck generalized the model by showing that these d holes could lower their energy appreciably by migrating more freely and occasionally occurring in pairs on the same atom giving this atom a d^{8} configuration. Since a d^{8} and a d^{10} configuration together have a much higher energy than two d^{9}'s, this occurrence should be moderately infrequent. However the cost in energy should be somewhat reduced by the screening effect of the 4s - 4p electrons. In a rough calculations, beset by many difficulties and uncertaintities, he argued that the participation of d^8 configuration with their Hund's rule coupling of the two d holes, might well be sufficient to explain the ferromagnetism of nickel.

It is clear that models such as that of Hurwitz and Van Vleck are properly described as correlated itinerant models rather than belonging to the localized family. Considerable further insight into the properties of such highly correlated narrow-band models has been provided by some recent theories. These theories are much more mathematical in nature and based on field theoretical techniques.

In the language of field theory the general Hamiltonian for a system of electrons in a solid can be written as

$$H = \sum_{\sigma} \int \psi_{\sigma}^{\dagger}(\vec{r}) \left[-\nabla^2/2m + V_c(\vec{r}) \right] \psi_{\sigma}(\vec{r})\, d^3r$$

$$+ \frac{1}{2} \sum_{\sigma\sigma'} \int \int \psi_{\sigma}^{\dagger}(\vec{r})\, \psi_{\sigma'}^{\dagger}(\vec{r}')\, V(\vec{r}-\vec{r})\, \psi_{\sigma'}(\vec{r}')\, \psi_{\sigma}(\vec{r})\, d^3r\, d^3r' \tag{1.1}$$

Here and hereafter we assume that $\hbar = 1$. $-\nabla^2/2m$ is the kinetic energy operator for the electrons and $V_c(\vec{r})$ represents the periodic potential which an electron experience due to the presence of positively charged ions. $V(\vec{r}-\vec{r})$ is the Coulomb potential between two electrons. $\psi_{\sigma}^{\dagger}(\vec{r})$ and $\psi_{\sigma}(\vec{r})$ are the creation and the annihilation field operators at the space point $\vec{r}$ corresponding to spin σ. They satisfy the usual anticommutation rules for fermions at equal times viz.

$$\begin{aligned} [\psi_{\sigma}(\vec{r}), \psi^{\dagger}_{\sigma'}(\vec{r}')]_{+} &= \delta_{\sigma\sigma'}\delta(\vec{r}-\vec{r}') \\ [\psi_{\sigma}(\vec{r}), \psi_{\sigma'}(\vec{r}')]_{+} &= [\psi^{\dagger}_{\sigma}(\vec{r}), \psi^{\dagger}_{\sigma'}(\vec{r}')]_{+} = 0 \end{aligned} \tag{1.2}$$

where $$[A,B]_{+} = AB + BA. \tag{1.3}$$

It is very difficult to develop any theory of electron correlation in narrow energy bands by taking into account the whole Hamiltonian (1.1). Therefore it is preferable to develop a theory with a Hamiltonian which exhibits the most important features of the system under investigation and at the same time simple enough to treat mathematically. An approximate Hamiltonian for narrow energy bands can be obtained by representing the Hamiltonian (1.1) in the Wannier representation. In Wannier representation the field operators $\psi_{\sigma}(\vec{r})$ and $\psi^{\dagger}_{\sigma}(\vec{r})$ are expressed as

$$\begin{aligned} \psi_{\sigma}(\vec{r}) &= \sum_{in} a_{in\sigma}\, \phi_{in}(\vec{r}) \\ \psi^{\dagger}_{\sigma}(\vec{r}) &= \sum_{in} a^{\dagger}_{in\sigma}\, \phi^{*}_{in}(\vec{r}) \end{aligned} \tag{1.4}$$

where $a_{in\sigma}$ and $a^{\dagger}_{in\sigma}$ are the annihilation and creation operators for an electron of spin σ in the band n at the lattice site i. These operators satisfy the anticommutation rules

$$[a_{in\sigma}, a_{jn'\sigma'}^{\dagger}]_+ = \delta_{ij}\,\delta_{nn'}\,\delta_{\sigma\sigma'}$$
$$[a_{in\sigma}, a_{jn'\sigma'}]_+ = [a_{in\sigma}^{\dagger}, a_{jn'\sigma'}^{\dagger}]_+ = 0 \qquad (1.5)$$

$\phi_{in}(\vec{r})$ is the Wannier function for the band n localized at the lattice site i. When the values of $\psi_{\sigma}(\vec{r})$ and $\psi_{\sigma}^{\dagger}(\vec{r})$ from Eq.(1.4) are substituted in Eq.(1.1), the Hamiltonian (1.1) in Wannier representation takes the form

$$H = \sum_{\substack{ij\sigma \\ n_1n_2}} T_{ij}^{n_1n_2}\, a_{in_1\sigma}^{\dagger}\, a_{jn_2\sigma} + \frac{1}{2} \sum_{\substack{ijk\ell \\ n_1n_2n_3n_4 \\ \sigma\sigma}} V_{ijk\ell}^{n_1n_2n_3n_4} \times$$
$$a_{in_1\sigma}^{\dagger}\, a_{jn_2\sigma'}^{\dagger}\, a_{kn_3\sigma'}\, a_{\ell n_4\sigma} \qquad (1.6)$$

where $$T_{ij}^{n_1n_2} = \int \phi_{in_1}^{*}(\vec{r})\left[-\frac{\nabla^2}{2m} + V_c(\vec{r})\right] \phi_{jn_2}(\vec{r})\, d^3r, \qquad (1.7)$$

$$V_{ijk\ell}^{n_1n_2n_3n_4} = \int \phi_{in_1}^{*}(\vec{r})\, \phi_{jn_2}^{*}(\vec{r}\,')\, V(\vec{r} - \vec{r})\, \phi_{kn_3}(\vec{r}\,')\, \phi_{\ell n_4}(\vec{r})\, d^3r d^3r \qquad (1.8)$$

The Hamiltonian (1.6) serves as a basis to obtain the approximate Hamiltonian exhibiting the most important features of the system. A very popular model for the study of electron correlation in narrow energy bands is the one band Hamiltonian

$$H = \sum_{ij\sigma} T_{ij}\, a_{i\sigma}^{\dagger}\, a_{j\sigma} + \frac{I}{2} \sum_{i\sigma} n_{i\sigma}\, n_{i\,-\sigma} \qquad (1.9)$$

where $I = V_{iiii}$ is the intraatomic Coulomb interaction and $n_{i\sigma} = a_{i\sigma}^{\dagger}\; a_{i\sigma}$. Since we are considering only one band, the band indices are dropped out. This Hamiltonian is obtainedd on the assumption that interaction between electrons are of very short range so that inter-atomic interactions can be neglected in comparison to the intraatomic interaction.

The Hubbard model (Hamiltonian (1.9)) invites the attention of the theorists because of its simplicity and richness. If we could completely understand the physical predictions of this model, we would be helped in analysing the models which correspond to the real situation. Once we have decided to analyse a model, however, it is required of us to make no distorting approximations. Little real progress can result from an uncertain treatment of a simplified model. In search of the exact solution of the Hubbard model several investigators[32-47] have concentrated their attention on the study of this model using different approaches and approximations. A review of the early approaches, of correlated wave function by Gutzwiller,[32] of two-body scattering operator by Kanamori,[33] and of one particle Green's function by Hubbard,[34] is given by Herring.[6] Later on these approaches have been used by many authors[35-42] using different approximations.

Recently Harris and Lange[43] have devised a method of analysing the Hubbard model. Their technique illuminates several properties of the spectral weight and density of state functions for the electrons which are unambiguously real within this model and not manifestations of an approximation scheme. Their results therefore shed considerable light on the model, the extent to which the model is sound and give information about the real narrow energy-band systems with which it is associated. Their results can also be used to check particular aspects of approximation schemes to see if the relationship they derive are found to be true for such approximate solutions. Pratt and Caron[44] suggested a cluster type treatment analogous to the Oguchi[48] treatment of ferromagnetism. Esterling and Lange[45] applied a degenerate mass operator perturbation theory to investigate the Hamiltonian (1.9). In spite of all these developments, it is not possible to solve the Hubbard model exactly in three dimension. However it has been shown that in one dimension it is exactly soluble.[49]

The Hubbard model is too simple to represent the real situation in the transition metals. To deal with the reality one must consider the degeneracy of the d band, the interatomic interactions, and the presence of the s band. The problem of degeneracy in d band has been discussed by Gutzwiller,[32] Kanamori,[33] ~~and~~ Hubbard[34], and Roth[37] for the short range Hamiltonian (1.9) which does not include the interatomic interactions. Effect of interatomic interactions has been discussed by many authors.[50-53] The presence of s band has been considered by Smith[54] and Kishore and Joshi[55] by taking into account the effect of hybridization of s and d bands on the Hubbard model.

C. Collective Excitations

A very important step in the evolution of itinerant electron theories of magnetism was the recognition that in a correlated wave function individual-particle and collective type of elementary excitations may co-exist. It is experimentall found that the spontaneous magnetization decreases with increasing temperature T as $T^{3/2}$ at low temperatures.[56] Theoretically, Bloch[57] has first shown that there exists a collective motion of spins in a ferromagnet, so called 'spin waves,' and the excitation of spin waves decreases the magnetisation as $T^{3/2}$ in the Heisenberg model. The absence of spin waves on an itinerant model was thought to be a serious drawback of the itinerant theory until it was shown by Slater[58] in 1937 that spin waves arise quite naturally out of a treatment of correlation effects in an itinerant electron model and one gets practically identical formulas starting from either the itinerant or localized picture. This view was later amplified by Herring and Kittel[59] and by Herring.[60]

The calculations of spin wave energies in a narrow energy band have been made by several authors.[23,37-39, 50,61-63] Most of these calculations are performed within the random phase approximation, Sakurai,[39] Roth,[37] Nagaoka[38], and Morris[63] have gone beyond the random phase approximation to include the correlation effects on the spin wave energies. The study of spin waves has not been confined only to the one band Hamiltonian. Spin waves in multiple band model have been discussed by Mattis,[64] Thompson[65], and Yamada and Shimizu.[66] In multiple band model the spin wave spectra consist of one acoustical intra-band branch, some optical intra-band branches and other branches due to interband transitions which are called interband spin waves.

It follows from the general considerations that in single band model for ferromagnetic metals when the wavelength of a spin wave is long, its energy ω must be related to the wave number q by $\omega = Dq^2$ in which D is a constant. Experiments have adequately confirmed the validity of this expression[67] and values of D have been determined in numerous cases. Edwards[68] has recently given an exact expression for this quantity. This expression cannot be evaluated in the general case. Calculations of D for some particular models have been reported.[69,70]

It is well known that there is another collective motion due to the density fluctuation of electrons in metals, which is called plasma oscillation or a plasmon.[71] This plasmon is experimentally found by inelastic scattering of electrons not only for alkali metals but also for ferromagnetic transition metals.[71] The plasmons in an electron gas ~~first~~ were first studied theoretically by Bohm and Pines.[72,73] The dispersion relations of plasmon in a ferromagnetic electron gas have recently been studied by Yamada.[74] So far no attempt has been made to study the plasmons in narrow energy bands.

D. Spin Density Waves

Ever since the original paper by Overhauser[75] suggesting the existence of spin density waves in free electron gas there has been much debate on their stability in real metals. The foundation of this concept was laid down by Slater in 1951. Spin density waves (SDW) are defined as the states of uniform, or nearly uniform, electron density but nonuniform density of spin magnetization. The uniform states: nonmagnetic and ferromagnetic can be considered as special cases of the simple SDW states (where the electron density is uniform). Specifically the ferromagnetic state can be regarded as a SDW of wave vector $\vec{q} = 0$. The nonmagnetic state, on the other hand, can be regarded as a simple SDW with any arbitrary wave vector $\vec{q}$ and amplitude zero. Several calculations[40,77-84] of SDW states for various simplified models have been performed. The results of these calculations have demonstrated the existence of stable finite amplitude SDW's under proper conditions.

II. METAL-NONMETAL TRANSITIONS

We differentiate between metals and nonmetals customarily in terms of a model of noninteracting electrons.[85] However this model does not always prove satisfactory[86] and in some situations it may become necessary to consider the Coulomb interaction between the electrons. Wigner[87] in 1938 specifically introduced the electron-electron interaction into the problem and suggested that at low density a free electron gas should crystallize in a nonconducting state. In 1949 a simple model was introduced by Mott[88] for the metal-nonmetal transition. He considered a lattice of hydrogen atoms arranged in a regular lattice. With only one electron per atom, two 1s states available for them, such a system constitute a half filled band, according to band theory. Thus it should be a metal. It is physically clear, however, that for large values of the lattice constant we have a system of independent hydrogen atoms and this should be an insulator.

To explain this Mott imagined the system as a lattice of electrons and holes. The holes are all atomic states not occupied by electrons. If an electron wants to leave its atom, or rather its hole, it feels an attractive potential. For a large lattice constant this is a Coulomb attraction which can keep the electron and the hole bound. Also the overlap of wavefunctions from one atom to the next is small, so the electron and the hole are not much inclined to move. As the lattice constant diminishes, the Coulomb attraction becomes screened and also the atomic wavefunctions overlap more. So the electron hole attraction is diminished while their motion is enhanced. Eventually a bound state cannot be maintained and the material becomes a metal.

A more quantitative discussion of the transition proposed by Mott has been given by Kohn[89] and Hubbard.[34] Kohn has considered a crystalline array of monovalent atoms spaced a distance apart and showed that for large enough values of the lattice constant such an array is a nonconducting. Hubbard has analysed the one band Hamiltonian (1.9). He has shown that for vanishingly small bandwidth (atomic limit), the band is split into two sub bands, separated by an energy gap of order I. Thus, for the case of one electron per atom, the lower band is completely filled and the upper band is empty at absolute zero. As the ratio of bandwidth to I is increased, the gap decreases until a critical value is reached, at which point the two bands overlap and hence the system changes from a nonmetal to metal. Since the gap decreases slowly to zero, conductivity will increase gradually as we pass through the critical ratio, unless a first order transition occurs. This is not a violent transition as Mott predicted. Later on Kemeny,[90] Kemeny and Caron[91], and Pratt and Caron[92] showed the possibility of Mott transition in the Hamiltonian (1.9). Recently Langer et al.[93] have shown the existence of two phase transitions in Hubbard model. They considered an antiferromagnetic system and showed that at a temperature T_N the system becomes magnetically disordered and at a high temperature T_M the atoms loose all vestige of localized moments and nonmetal-metal transition occurs.

It is not of course the case that all metal-nonmetal transitions are due to electron-electron interaction and inexplicable in the model of noninteracting electrons. Naturally a change of crystal structure may lead to a band gap, and it has been suggested that this is what happens in the vanadium oxide.[94,95] Also a metal-nonmetal transition can occur at a Neel point, as predicted by Slater[76] and observed in NiS.[96] Then of course in the Wilson model of noninteracting electrons any divalent metal will become a nonmetal if the lattice constant is increased above a critical value. There is another kind of transition which can be described in the model of noninteracting electrons, and which Mott[97] has termed as the 'Anderson transition.' Anderson[98] in 1958 considered an array of hydrogen atoms far enough apart for the tight binding approximation to be applicable and for the band width J to depend on the interaction between nearest neighbors only. He supposed that a potential energy V_n was applied at each atom n, with a random spread V_0. He showed that when V_0/J exceeded a critical value, a transition from a metallic to a nonmetallic state occurred. Also there is an excitonic insulator theory of metal-nonmetal transition described in a number of papers.[99-101] The entire subject of this theory is reviewed and the latest work is presented in the article by Halperin and Rice.[102]

III. PRESENT WORK

Many problems in theoretical physics are attacked by considering models with mathematical descriptions which are usefully simpler than those of real systems. Of cource, the model is usually not exactly soluble and consequently approximations must be employed. Thus we often find ourselves with approximate solutions to a model problem. When we want to know how to make connection with experiment two levels of questions arise. First, how well do the approximate solutions reflect the exact properties of the model, and then second, of course, how well does the model reflect the properties of real system?

The present work directs itself for the most part at the second type of question. The Hamiltonian (1.9) is an oversimplification if applications to real materials are contemplated. It does, however, furnish a situation in which many approximation schemes which may be applied to actual metals can be tested by comparison with exact results for the model. In addition, it is possible to extend the model either by including other bands, or by extending the range of the electron interaction to include nearest neighbor lattice sites.

In Chapter II we extend the Hubbard Hamiltonian by taking into account the presence of s band through the hybridization of s and d bands. The self-consistent ferromagnetic solutions are obtained within the Hartree-Fock approximation as well as in an approximation which takes into account the correlation effects. The ferromagnetic solutions for which the correlation effects are taken into account are compared with those in the Hartree-Fock approximation.

In Chapter III the effect of electron correlation on the ferromagnetism of a transition metal is investigated by taking a model Hamiltonian which includes the interatomic Coulomb interactions,in addition to intraatomic interaction in the Hubbard model. An approximate solution of the correlation problem for this model is obtained and the conditions for ferromagnetism for this solution are discussed.

In Chapter IV we study the dynamical susceptibility for a system of electrons in a narrow energy band. The Hamiltonian of the system consists of single particle energies of electrons in the absence of interactions, the intraatomic Coulomb interaction and interatomic Coulomb and exchange interactions. An approximate expression for the susceptibility is derived by using the random phase approximation. The instability of the paramagnetic state against the ferro and the antiferromagnetic states is discussed. We also study the dynamical susceptibility for a system of electrons with strong intraatomic interaction where the validity of the random phase approximation is dubious. In this case in addition to the conditions for the paramagnetic instability against the ferro and the antiferromagnetic states we have also discussed the spin flip excitations.

In Chapter V we study the metal-nonmetal transitions on the basis of the Hamiltonians used in Chapters II and IV. The existence of two phase transitions in ferromagnetic systems and the difficulty of observing pressure induced nonmetal-metal transitions are discussed.

In appendix A magnetic solutions of Hubbard model are obtained using an improved decoupling scheme for higher order Green's functions. Solutions are found to agree with the exact results in limiting cases. In appendix B exchange splitting of the d band in nickel is discussed within the Hartree-Fock approximation. In appendix C an expression for electronic spin polarization due to s-d exchange interaction between the conduction electrons and the localized impurity of spin 1/2 in a dilute magnetic alloy is obtained. For large distances it is found to exhibit the exponentially damped behavior.

IV. A GREEN's FUNCTION TECHNIQUE

In the succeeding chapters our method of calculations will be based upon the Green's function technique described by Zubarev.[103] In order to establish the notation, the principal definitions and basic equations of this technique are briefly reviewed in this section.

Following Zubarev[103] the double time temperature dependent retarded (+) and advanced (-) Green's functions involving two operators A and B are defined by

$$<<A(t),\ B(t')>>^{(\pm)} = \mp i\ \Theta(t-t')\ <[A(t),\ B(t')]_\eta> \qquad (1.10)$$

where

$[A,B]_\eta = AB + \eta BA;\ \eta = 1$ (whichever is more convenient). The time dependence of operators is defined by

$$A(t) = e^{iH't}\, A\, e^{-iH't}$$

where $$H = H - \mu N_p, \qquad (1.11)$$

μ is the chemical potential and N_p is the operator for the total number of particles. θ (t) is the unit step function, unity for positive t and zero for negative t. The angular brackets <....> denote a grand canonical ensemble average defined by

$$< 0 > = \frac{\mathrm{Tr}\ e^{-\beta H'} 0}{\mathrm{Tr}\ e^{-\beta H'}} \quad ,$$

where $\beta = 1/k_BT$, k_B is the Boltzmann's constant and T is the absolute temperature.

The Green's functions are the functions of $(t-t')$. This can easily be seen by writing down the time dependence of the operators and using the cyclic property of the operators under the Tr sign. Then one can define the Fourier transform of the Green's functions with respect to real ω

$$<<A,B>>_{\omega}^{(\pm)} = \frac{1}{2\pi}\int_{-\infty}^{\infty} <<A(t), B(t')>>^{(\pm)} e^{i\omega(t-t')} d(t-t') \tag{1.12}$$

In the case of the retarded (+) function the integral (1.12) converges also for complex ω provided Im $\omega>0$, so $<<A,B>>_{\omega}^{(+)}$ can be defined and is a regular function of ω in the upper half of the complex ω-plane. Similarly $<<A,B>>_{\omega}^{(-)}$ is a regular function in the lower half of the complex ω-plane. One may now define

$$\begin{aligned} <<A,B>>_{\omega} &= <<A,B>>_{\omega}^{(+)} \qquad \text{if Im } \omega > 0 \\ &= <<A,B>>_{\omega}^{(-)} \qquad \text{if Im } \omega < 0 \end{aligned}$$

which will be a function regular throughout the whole complex ω-plane except on the real axis. By differentiating the equation (1.10) with respect to t and then taking the Fourier transform (1.12), it can be shown that $<<A,B>>_{\omega}$ satisfies

$$\omega \langle\langle A,B \rangle\rangle_{\omega} = \frac{1}{2\pi} \langle [A,B]_{\eta} \rangle + \langle\langle [A,H']_{-}, B \rangle\rangle_{\omega} \qquad (1.13)$$

The correlation function $\langle B(t')\, A(t) \rangle$ can be obtained from the spectral theorem,[103]

$$\langle B(t')A(t) \rangle = i \lim_{\epsilon \to 0^{+}} \int_{-\infty}^{\infty} \frac{\langle\langle A,B \rangle\rangle_{\omega+i\epsilon} - \langle\langle A,B \rangle\rangle_{\omega-i\epsilon}}{e^{\beta\omega} + \eta}\, e^{-i\omega(t-t')} d\omega \qquad (1.14)$$

Equations (1.13) and (1.14) together form the essential basis of calculations with these Green's functions.

CHAPTER II

FERROMAGNETISM. I. HYBRIDIZATION OF s AND d BANDS

I. INTRODUCTION

Anderson's theory[104-5] of dilute alloys of the transition metals is able to explain the occurrence of the localized magnetic moment on transition metal impurities dissolved in nonmagnetic metals. In Anderson's model the band states of the host metal are treated as independent quasi-particles. The impurity is introduced as an extra localized orbital, which is mixed with the band states by a hybrid matrix element. All two body Coulomb interactions are neglected except the Coulomb interaction between the opposite spin electrons on the localized orbital. As an extension of this model a transition metal can be imagined as a system having a localized d orbital at each lattice site. Recently such a model has been analysed by Smith.[54] However, this is an approximate picture of a transition metal, in the sense that there would be no direct interaction between the d electrons on different sites, only an indirect coupling via the conduction electrons. It is well known that a considerable fraction of the width of the 3d band in transition metals arises from the overlap of the 3d wave functions on neighbouring lattice sites.[106]

Here we assume that the d electrons form a band and they interact among themselves only via the Coulomb interaction between opposite spin electrons at the same lattice site. The effect of the s band is taken into account by adopting the

the ith lattice site specified by lattice vector $\vec{R}_i$. I is the Coulomb interaction between electrons of opposite spin at the same lattice site. $n_{\vec{k}\sigma}$ and $n_{i\sigma}$ are, respectively, the number operators for the s electron of wave vector $\vec{k}$ and spin σ and the d electron of spin σ at the lattice site i. N is the total number of atoms in the system. $V_{\vec{k}d}$ is the hybrid matrix element defined by

$$V_{\vec{k}d} = \int d^3r \, \phi_d^*(\vec{r}) \, H_o(\vec{r}) \, \psi_k(\vec{r}) \qquad (2.3)$$

where $H_o(\vec{r})$ is the one particle Hamiltonian for an electron in the presence of the periodic lattice. $\phi_d(\vec{r})$ is an atomic d orbital and $\psi_{\vec{k}}(\vec{r})$ is a Bloch wave function for the conduction band.

In our analysis we work with Green's functions of the form

$$G^{\sigma}_{\mu\nu}(\omega) = \langle\langle a_{\mu\sigma} \, , \, a_{\nu\sigma}^{\dagger} \rangle\rangle_{\omega} \quad (\eta = + 1), \qquad (2.4)$$

where μ and ν are either the conduction band $\vec{k}$ states or d states on particular lattice sites. Thus we shall have here four different types of Green's functions in all. With the help of the commutators

$$[a_{i\sigma} \, , \, H]_- = \sum_j T_{ij} \, a_{j\sigma} + I \, n_{i-\sigma} \, a_{i\sigma} + \sum_k V_{\vec{k}d}^{*} \, e^{-i\vec{k}.\vec{R}_i} \, a_{\vec{k}\sigma} \qquad (2.5)$$

$$[a_{\vec{k}\sigma} \, , \, H]_- = \epsilon_{\vec{k}} \, a_{\vec{k}\sigma} + \sum_i V_{\vec{k}d} \, e^{i\vec{k}.\vec{R}_i} \, a_{i\sigma} \qquad (2.6)$$

$$[n_{i\sigma}\,,\,H]_- = \sum_j T_{ij}\,(\,a_{i\sigma}^{\dagger}\,a_{j\sigma} - a_{j\sigma}^{\dagger}\,a_{i\sigma}\,) - \sum_{\vec{k}} V_{\vec{k}d}\,e^{i\vec{k}.\vec{R}_i}\,a_{\vec{k}\sigma}^{\dagger}\,a_{i\sigma} + \sum_{\vec{k}} V_{\vec{k}d}^{*}\,e^{-i\vec{k}.\vec{R}_i}\,a_{\vec{k}\sigma}\,a_{i\sigma}^{\dagger}\,, \tag{2.7}$$

the equations of motion (Eq.1.13) for the Green's functions can be written as

$$(\omega+\mu-\epsilon_{\vec{k}})\;G^{\sigma}_{\vec{k}\vec{k}'}(\omega) = \frac{\delta_{\vec{k}\vec{k}'}}{2\pi} + \sum_i V_{\vec{k}d}\,e^{i\vec{k}.\vec{R}_i}\,G^{\sigma}_{i\vec{k}'}(\omega) \tag{2.8}$$

$$(\omega+\mu-\epsilon_{\vec{k}})\;G^{\sigma}_{\vec{k}j}(\omega) = \sum_i V_{\vec{k}d}\,e^{i\vec{k}.\vec{R}_i}\;G^{\sigma}_{ij}\;(\omega) \tag{2.9}$$

$$(\omega+\mu)\;G^{\sigma}_{ij}(\omega) = \frac{\delta_{ij}}{2\pi} + \sum_{\ell} T_{i\ell}\,G^{\sigma}_{\ell j}\;(\omega) + I \ll n_{i-\sigma}\,a_{i\sigma}\,, a_{j\sigma}^{\dagger}\gg_{\omega} + \sum_{\vec{k}} V^{*}_{\vec{k}d}\;e^{-i\vec{k}.\vec{R}_i}\;G^{\sigma}_{\vec{k}j}\;(\omega) \tag{2.10}$$

$$(\omega+\mu)\;G^{\sigma}_{i\vec{k}'}(\omega) = \sum_j T_{ij}\,G^{\sigma}_{j\vec{k}'}\;(\omega) + I \ll n_{i-\sigma}\,a_{i\sigma}\,,\,a_{\vec{k}'\sigma}^{\dagger}\gg \omega + \sum_{\vec{k}} V^{*}_{\vec{k}d}\;e^{-i\vec{k}.\vec{R}_i}\,G^{\sigma}_{\vec{k}\,\vec{k}'}\;(\omega) \tag{2.11}$$

We are mainly interested in finding out the Green's functions $G^{\sigma}_{\vec{k}\,\vec{k}}(\omega)$ and $G^{\sigma}_{d\vec{k}}(\omega)$. The later is defined by

$$G^{\sigma}_{ij}\;(\omega) = \frac{1}{N}\sum_{k} G^{\sigma}_{d\vec{k}}(\omega)\;e^{i\vec{k}.(\vec{R}_i-\vec{R}_j)} \tag{2.12}$$

These Green's functions are needed to evaluate the average number $\langle n_{s\sigma} \rangle$ of s electrons and $\langle n_{d\sigma} \rangle$ of d electrons per atom for spin σ. By taking the limit $t \to t'$ in Eq.(1.14) we get $\langle n_{s\sigma} \rangle$ and $\langle n_{d\sigma} \rangle$ as

$$\langle n_{s\sigma} \rangle = \frac{1}{N} \sum_{k} \langle a^{\dagger}_{k\sigma} a_{k\sigma} \rangle$$

$$= \int_{-\infty}^{\infty} \rho_s^{\sigma}(\omega) \left(e^{\beta\omega} + 1 \right)^{-1} d\omega, \qquad (2.13)$$

$$\langle n_{d\sigma} \rangle = \frac{1}{N} \sum_{i} \langle a^{\dagger}_{i\sigma} a_{i\sigma} \rangle$$

$$= \int_{-\infty}^{\infty} \rho_d^{\sigma}(\omega) \left(e^{\beta\omega} + 1 \right)^{-1} d\omega, \qquad (2.14)$$

where

$$\rho_s^{\sigma}(\omega) = \frac{i}{N} \lim_{\epsilon \to 0^+} \sum_{k} \left[G^{\sigma}_{\vec{k}\vec{k}}(\omega + i\epsilon) - G^{\sigma}_{\vec{k}\vec{k}}(\omega - i\epsilon) \right], \qquad (2.15)$$

$$\rho_d^{\sigma}(\omega) = \frac{i}{N} \lim_{\epsilon \to 0^+} \sum_{k} \left[G^{\sigma}_{d\vec{k}}(\omega + i\epsilon) - G^{\sigma}_{d\vec{k}}(\omega - i\epsilon) \right] \qquad (2.16)$$

are the density of states per atom for s and d electrons corresponding to spin σ. The total average number of electrons per atom for spin σ is given by

$$\langle n_{\sigma} \rangle = \langle n_{s\sigma} \rangle + \langle n_{d\sigma} \rangle \qquad (2.17)$$

III. HARTREE-FOCK THEORY

For the sake of comparison with the results of the one particle interaction between s and d electrons given by Anderson. In Sec. II we write the Hamiltonian for such a model in the second quantized form. In our analysis we use the Green's function method discussed by Zubarev.[103] In sec. III the self-consistent ferromagnetic solutions are obtained within the Hartree-Fock approximation for the zero and finite widths of the d band. In Sec. IV an approximate theory for the electron correlation is developed. The self-consistent ferromagnetic solutions for both the zero and the finite band widths of d band are obtained. In Sec.V the main results are summarised.

II. BASIC THEORY

We consider a system consisting of s and d electrons, described by the Hamiltonian

$$H = \sum_{\vec{k}\sigma} \epsilon_{\vec{k}}\, n_{\vec{k}\sigma} + \sum_{ij\sigma} T_{ij}\, a_{i\sigma}^{\dagger}\, a_{j\sigma} + I \sum_{i} n_{i\sigma}\, n_{i-\sigma}$$

$$+ \sum_{\vec{k}i\sigma} \left(V_{\vec{k}d}\, e^{i\vec{k}.\vec{R}_i}\, a_{\vec{k}\sigma}^{\dagger}\, a_{i\sigma} + V_{\vec{k}d}^{*}\, e^{-i\vec{k}.\vec{R}_i}\, a_{i\sigma}^{\dagger}\, a_{\vec{k}\sigma} \right),$$

where
$$T_{ij} = \frac{1}{N} \sum_{\vec{k}} \epsilon_{d\vec{k}}\, e^{i\vec{k}.(\vec{R}_i - \vec{R}_j)}\ , \qquad (2.2)$$

$\epsilon_{\vec{k}}$ and $\epsilon_{d\vec{k}}$ are the energies of s and d band electrons of wave vector $\vec{k}$, $a_{\vec{k}\sigma}^{\dagger}$, $a_{\vec{k}\sigma}$ are the creation and annihilation operators of the s electron of wave vector $\vec{k}$ and spin σ. $a_{i\sigma}^{\dagger}$, $a_{i\sigma}$ are the same for the d electrons of spin σ at theory to be developed in the next section for the correlation effects, it would be useful to investigate the problem in the Hartree-Fock approximation. Actually, we shall not make an exhaustive study of all possible Hartree-Fock solutions, but will restrict ourselves to particularly simple solutions which may represent paramagnetic or ferromagnetic states but not more complicated spin arrangements. The same restriction applies to the scope of the correlation theory developed in the next section.

In terms of the Green's functions, the Hartree-Fock approximation corresponds to the assumption that

$$\langle\langle n_{i-\sigma} a_{i\sigma} , a^{\dagger}_{\mu\sigma} \rangle\rangle_{\omega} \simeq \langle n_{i-\sigma} \rangle \langle\langle a_{i\sigma} , a^{\dagger}_{\mu\sigma} \rangle\rangle_{\omega} , \qquad (2.18)$$

where index μ is either j or k. We restrict ourselves to the class of solutions for which $\langle n_{i-\sigma} \rangle$ is independent of the lattice site i,

$$\langle n_{i\sigma} \rangle = \langle n_{d\sigma} \rangle \quad \text{for all } i. \qquad (2.19)$$

When we incorporate the assumptions (2.18) and (2.19) in Eqs. (2.10) and (2.11), Eqs. (2.8) - (2.11) assume a closed form. Solutions of these Eqs. for $G^{\sigma}_{\vec{k}\vec{k}}(\omega)$ and $G^{\sigma}_{d\vec{k}}(\omega)$ give

$$G^{\sigma}_{\vec{k}\vec{k}}(\omega) = \frac{\omega - E_{d\vec{k}} - I\langle n_{d-\sigma} \rangle}{\omega - E_{\vec{k}}} \, G^{\sigma}_{d\vec{k}}(\omega) \qquad (2.20)$$

and

$$G^{\sigma}_{d\vec{k}}(\omega) = \frac{1/2\pi}{\omega - E_{d\vec{k}} - I\langle n_{d-\sigma} \rangle - \dfrac{N|V_{\vec{k}d}|^2}{\omega - E_{\vec{k}}}} , \qquad (2.21)$$

where $E_{\vec{k}} = \epsilon_{\vec{k}} - \mu$ and $E_{d\vec{k}} = \epsilon_{d\vec{k}} - \mu$.

By substituting the values of $G^{\sigma}_{\vec{k}\vec{k}}(\omega)$ and $G^{\sigma}_{d\vec{k}}(\omega)$ from Eqs.(2.20) and (2.21) in Eqs.(2.15) and (2.16), we obtain the density of states per atom of s and d electrons corresponding to spin σ

$$\rho^{\sigma}_{s}(\omega) = \frac{1}{N} \sum_{\vec{k}} \left[A^{+}_{s\vec{k}\sigma} \, \delta\,(\omega - \omega^{+}_{\vec{k}\sigma}) + A^{-}_{s\vec{k}\sigma} \, \delta(\omega - \omega^{-}_{\vec{k}\sigma}) \right] \quad (2.22)$$

$$\rho^{\sigma}_{d}(\omega) = \frac{1}{N} \sum_{\vec{k}} \left[A^{+}_{d\vec{k}\sigma} \, \delta\,(\omega - \omega^{+}_{\vec{k}\sigma}) + A^{-}_{d\vec{k}\sigma} \delta\,(\omega - \omega^{-}_{\vec{k}\sigma}) \right] \quad (2.23)$$

where

$$\omega^{p}_{\vec{k}\sigma} = \frac{1}{2} \left[E_{\vec{k}} + E_{d\vec{k}} + I \langle n_{d-\sigma} \rangle + p \left\{ (E_{d\vec{k}} \, E_{\vec{k}} + I \langle n_{d-\sigma} \rangle)^{2} + 4N |V_{\vec{k}d}|^{2} \right\}^{1/2} \right] \quad (2.24)$$

$$A^{p}_{s\vec{k}\sigma} = p \, \frac{\omega^{p}_{\vec{k}\sigma} - E_{d\vec{k}} - I \langle n_{d-\sigma} \rangle}{\omega^{+}_{\vec{k}\sigma} - \omega^{-}_{\vec{k}\sigma}} \, , \quad (2.25$$

$$A^{p}_{dk\sigma} = p \, \frac{\omega^{p}_{\vec{k}\sigma} - E_{\vec{k}}}{\omega^{+}_{\vec{k}\sigma} - \omega^{-}_{\vec{k}\sigma}} \, . \quad (2.26)$$

Here p is either (+) or (-).

The expressions (2.22) and (2.23) for the density of states per atom of s and d electrons corresponding to spin σ show that s and d bands are admixed into two new bands with dispersion laws $\omega = \omega^{+}_{\vec{k}\sigma}$ and $\omega = \omega^{-}_{\vec{k}\sigma}$. For an unpertuurbed d band, $\epsilon_{d\vec{k}}$ of zero width, the new bands are always separated by an energy gap. In this case the lower band always lies below $T_o - \mu + I \langle n_{d-\sigma} \rangle$ while the upper band always lies above this energy. Here T_o is the mean energy of the d band $\epsilon_{d\vec{k}}$ (i.e. $T_o = \frac{1}{N} \sum_{\vec{k}} \epsilon_{d\vec{k}}$). As the width of the band $\epsilon_{d\vec{k}}$ increases, the gap between the two bands decreases and finally they overlap each other. From Eqs. (22.5) and (2.26) it is clear that $A^{-}_{s\vec{k}\sigma} + A^{-}_{d\vec{k}\sigma} = A^{+}_{s\vec{k}\sigma} + A^{+}_{d\vec{k}\sigma} = 1$. This shows that for both the new bands the density of states per atom for each spin is always equal to one. Therefore if there are two electrons per atom in the two bands together, then for the zero width of the d band, system always behaves as an insulator. As we increase the d band width, an insulator to metal transition occurs at some critical d band width. In Chapter V we shall discuss this type of transition in detail.

A. Zero Bandwidth

In the limit of the zero band-width, $\epsilon_{d\vec{k}} = T_o$ for all $\vec{k}$. It is easy to show from Eq.(2.24) that

$$\omega^{-}_{\vec{k}\sigma} < E_{\vec{k}} < \omega^{+}_{\vec{k}\sigma} \quad ,$$

and
$$\omega^{-}_{\vec{k}\sigma} < (E_{d\vec{k}} + I\langle n_{d-\sigma}\rangle) < \omega^{+}_{\vec{k}\sigma} \quad ,$$

so that $A^{p}_{s\vec{k}\sigma}$ and $A^{p}_{d\vec{k}\sigma}$ are positive. Then by replacing

$\epsilon_{d\vec{k}}$ by T_o in Eqs. (2.22) and (2.23), we get

$$\rho_s^{\sigma}(\omega) = \frac{1}{N} \sum_{\vec{k}} | \omega + \mu - T_o - I\langle n_{d-\sigma}\rangle | \delta\{(\omega - \omega_{\vec{k}\sigma}^{+})(\omega - \omega_{\vec{k}\sigma}^{-})\} , \quad (2.27)$$

$$\rho_d^{\sigma}(\omega) = \frac{1}{N} \sum_{\vec{k}} | \omega + \mu - \epsilon_{\vec{k}} | \delta\{(\omega - \omega_{\vec{k}\sigma}^{+})(\omega - \omega_{\vec{k}\sigma}^{-})\} . \quad (2.28)$$

For the sake of simplicity we assume that the hybrid matrix element $V_{\vec{k}d}$ is independent of $\vec{k}$. Then these Eqs. can be expressed in terms of the density of states for the s band

$$N(\omega) = \frac{1}{N} \sum_{\vec{k}} \delta(\omega - \epsilon_{\vec{k}}), \quad (2.29)$$

which is normalized to unity since $\vec{k}$ is limited to the first Brillouin zone and the higher plane wave bands will be neglected. In terms of $N(\omega)$ Eqs. (2.27) and (2.28) can be written as

$$\rho_s^{\sigma}(\omega) = N\{f_{\sigma}(\omega + \mu)\} , \quad (2.30)$$

$$\rho_d^{\sigma}(\omega) = \left| \frac{\omega + \mu - f_{\sigma}(\omega + \mu)}{\omega + \mu - T_o - I\langle n_{d-\sigma}\rangle} \right| N\{f_{\sigma}(\omega + \mu)\} , \quad (2.31)$$

where

$$f_{\sigma}(\omega) = \omega - \frac{|V|^2}{\omega - T_o - I\langle n_{d-\sigma}\rangle} , \quad (2.32)$$

$$|v|^2 \quad = N \, |V_{\vec{k}d}|^2 \quad . \tag{2.33}$$

Finally the average numbers of s and d electrons per atom for spin σ at absolute zero are given by

$$\langle n_{s\sigma}\rangle = \int_{-\infty}^{\mu} N \left\{ f_{\sigma} \, (\omega) \right\} d\omega \tag{2.34}$$

$$\text{and} \quad \langle n_{d\sigma}\rangle = \int_{-\infty}^{\mu} \left| \frac{\omega - f_{\sigma}(\omega)}{\omega - T_0 - I\langle n_{d-\sigma}\rangle} \right| N \left\{ f_{\sigma}(\omega) \right\} d\omega . \tag{2.35}$$

These Eqs. give the total average number of electrons per atom for spin σ at absolute zero.

$$\langle n_{\sigma}\rangle = \langle n_{s\sigma}\rangle + \langle n_{d\sigma}\rangle$$

$$= \int_{-\infty}^{\mu} \left\{ 1 + \left| \frac{\omega - f_{\sigma}(\omega)}{\omega - T_0 - I \, \langle n_{d-\sigma}\rangle} \right| \right\} N \left\{ f_{\sigma}(\omega) \right\} d\omega \, . \tag{2.36}$$

With the Fermi level as a variable parameter Eq.(2.35) for $\langle n_{d\sigma}\rangle$ must be solved self-consistently. Then Eq.(2.36) can be used to fix the Fermi level from the total number of electrons per atom $n = (\langle n+\rangle + \langle n-\rangle)$ which is assumed given. The ferromagnetic solutions are possible only when $\langle n_{d\sigma}\rangle \neq \langle n_{d-\sigma}$ Solutions of the integrals (2.35) and (2.36) depend on the form of the density of states $N(\omega)$. For simplicity we consider the square density of states defined by

$$N(\omega) = \frac{1}{\alpha} \quad \text{if } 0<\omega < \alpha$$
$$= 0 \quad \text{otherwise} \tag{2.37}$$

where α is the width of the s band. For the square density of states we have

$$N\left\{f_{\sigma}(\omega)\right\} = \frac{1}{\alpha}\left[\sum_{p=\pm}\left\{\theta(\omega - \omega_{1\sigma}^{p}) - \theta(\omega - \omega_{2\sigma}^{p})\right\}\right], \tag{2.38}$$

where

$$\omega_{1\sigma}^{p} = \frac{1}{2}\left[T_0 + I<n_{d-\sigma}> + p\sqrt{\left\{(T_0 + I<n_{d-\sigma}>)^2 + 4|v|^2\right\}}\right],$$

$$\omega_{2\sigma}^{p} = \frac{1}{2}\left[\alpha+T_0+I<n_{d-\sigma}> + p\sqrt{\left\{(T_0 + I<n_{d-\sigma}>-\alpha)^2 + 4|v|^2\right\}}\right]$$

Now we substitute the values of $f_{\sigma}(\omega)$ and $N\left\{f_{\sigma}(\omega)\right\}$ from Eqs. (2.32) and (2.38) in Eqs.(2.35) and (2.36) and get

$$<n_{d\sigma}> = \int_{-\infty}^{\mu} \frac{|v|^2 \sum_{p=\pm}\left\{\theta(\omega - \omega_{1\sigma}^{p}) - \theta(\omega-\omega_{2\sigma}^{p})\right\}}{\alpha(\omega - T_0 - I<n_{d-\sigma}>)^2}\, d\omega, \tag{2.39}$$

$$<n_{\sigma}> = \int_{-\infty}^{\mu} \frac{1}{\alpha}\left\{1 + \frac{|v|^2}{(\omega - T_0 - I<n_{d-\sigma}>)^2}\right\}$$

$$\times \sum_{p=\pm}\left\{\theta(\omega - \omega_{1\sigma}^{p}) - \theta(\omega - \omega_{2\sigma}^{p})\right\} d\omega \quad . \tag{2.40}$$

Integrals (2.39) and (2.40) are easy to evaluate. Limits of integrations are controlled by 0 functions.

Now by taking μ as a variable parameter we solve Eq.(2.39) self-consistently for some perticular choice of parameter I, α and T_0 to obtain $\langle n_{d\sigma} \rangle$ and $\langle n_{d-\sigma} \rangle$. Then Eq.(2.40) is used to fix the value of μ for the integral values (n = 1,2,3) of the total number of electrons in both the bands together. We do not consider n = 4 because in this case both the bands are completely filled and hence there is no possibility of ferromagnetism. In Fig.(2.1) we have plotted $Q = \mu/T_0$ vs $Z = T_0/\alpha$ for three values 0.1, 0.2 and 1.0 of $S = v/T_0$ for a particular value of $P = I/T_0 = 2.0$. The range of existence of the ferromagnetic solutions between the values of Z from 0 to 1 is shown in Table 2.1. The value of Q corresponding to a particular value of Z can be read from Fig.2.1. To show explicitely the magnetic solutions we have plotted $\langle n_{d+} \rangle$ and $\langle n_{d-} \rangle$ in Fig.2.2. Results of our calculations show that the range of the ferromagnetic solutions decreases as the hybridization of s and d bands increases i.e. the hybridization of s and d bands decreases the tendency towards ferromagnetism. To have an idea about the variation of the ferromagnetic solutions with respect to the strength of interatomic interaction, we have plotted, Q vs Z in Fig.2.3 for three different values of P, 0.5, 1.0 and 2.0 for a particular value of S = 0.1. The range of ferromagnetic solutions is shown in Table 2.2. It is found that the increase of intraatomic interaction is favorable to ferromagnetism.

B. Finite Band Width

We shall assume that the form of the d band is the same as that of the s band. We represent it by the expression

$$\epsilon_{d\vec{k}} = A\,\epsilon_{\vec{k}} + T_o - A\alpha/2 \,, \tag{2.41}$$

where A is some positive constant less than unity i.e. it is assumed that the width of d band is smaller than that of the s band. A = 0 corresponds to the zero band width. This choice is made because the density of states $\rho_s^{\sigma}(\omega)$ and $\rho_d^{\sigma}(\omega)$ given by Eqs.(2.22) and (2.23) can then be expressed in terms of the density of states of the s band N (ω). Substituting the expression (2.41) for $\epsilon_{d\vec{k}}$ in Eqs.(2.22) and (2.23) and using the approximation (2.33), we get

$$\rho_s^{\sigma}(\omega) = \frac{1}{N}\sum_{\vec{k}} \left| \frac{\omega + \mu - A\epsilon_{\vec{k}} - T_o + A\alpha/2 - I\langle n_{d-\sigma}\rangle}{A} \right| \times \delta\left\{ \left(g_{\sigma}^{+}(\omega+\mu) - \epsilon_{\vec{k}}\right)\left(g_{\sigma}^{-}(\omega+\mu) - \epsilon_{\vec{k}}\right)\right\} , \tag{2.42}$$

$$\rho_d^{\sigma}(\omega) = \frac{1}{N}\sum_{\vec{k}} \left| \frac{\omega + \mu - \epsilon_{\vec{k}}}{A} \right| \delta\left\{ \left(g_{\sigma}^{+}(\omega+\mu) - \epsilon_{\vec{k}}\right)\left(g_{\sigma}^{-}(\omega+\mu) - \epsilon_{\vec{k}}\right)\right\} , \tag{2.43}$$

where

$$g^{p}_{\sigma}(\omega) = \frac{1}{2A}\Big[(A+1)\,\omega - T_o + A\alpha/2 - I\,\langle n_{d-\sigma}\rangle$$

$$+ p\sqrt{\left\{(1-A)\,\omega - T_o + A\alpha/2 - I\langle n_{d-\sigma}\rangle^{2} + 4A|v|^{2}\right\}}\Big] .$$

(2.44)

Eqs.(2.42) and (2.43) can be written in terms of the density of states $N(\omega)$:

$$\rho^{\sigma}_{s}(\omega) = \frac{1}{A}\sum_{p=\pm}\left|\frac{\omega+\mu - T_o + A\alpha/2 - I\langle n_{d-\sigma}\rangle - A\,g^{p}_{\sigma}(\omega+\mu)}{g^{+}_{\sigma}(\omega+\mu) - g^{-}_{\sigma}(\omega+\mu)}\right|$$

$$\times N\left\{g^{p}_{\sigma}(\omega+\mu)\right\} , \qquad (2.45)$$

$${}^{\sigma}_{d}(\omega) = \frac{1}{A}\sum_{p=\pm}\left|\frac{\omega+\mu - g^{p}_{\sigma}(\omega+\mu)}{g^{+}_{\sigma}(\omega+\mu) - g^{-}_{\sigma}(\omega+\mu)}\right| N\left\{g^{p}_{\sigma}(\omega+\mu)\right\} .$$

(2.46)

For the square density of states for the unperturbed s aband, $N\left\{g^{p}_{\sigma}(\omega+\mu)\right\}$ is given by

$$N\left\{g^{p}_{\sigma}(\omega+\mu)\right\} = \frac{1}{\alpha}\left[\theta\,(\omega+\mu-\omega^{-p}_{1\sigma}) - \theta\,(\omega+\mu-\omega^{-p}_{2\sigma})\right] ,$$

(2.47)

where $\omega^{p}_{1\sigma} = \frac{1}{2}\left[T_o - A\alpha/2 + I\,\langle n_{d-\sigma}\rangle + p\sqrt{\left\{(T_o - A\alpha/2 + I\langle n_{d-\sigma}\rangle)^{2} + 4|v|^{2}\right\}}\right]$

(2.48)

and

$$\omega_{2\sigma}^{p} = \frac{1}{2}\Big[\Big(\frac{A}{2} + 1\Big)\alpha + T_o + I\langle n_{d-\sigma}\rangle + p\sqrt{\Big\{\Big(\Big(\frac{A}{2} - 1\Big)\alpha + T_o + I\langle n_{d-\sigma}\rangle\Big)^2 + 4|v|^2\Big\}}\Big], \tag{2.49}$$

By substituting the values of $g_{\sigma}^{p}\ (\omega+\mu)$ and $N\{\ g_{\sigma}^{p}(\omega+\mu)\}$ from Eqs. (2.44) and (2.47) in Eqs. (2.45) and (2.46) we get at absolute zero

$$\langle n_{s\sigma}\rangle = \int_{-\infty}^{\mu} \frac{1}{2\alpha} \sum_{p=\pm}\Big[1 - p\,\frac{(1-A)\omega - T_o + \frac{A\alpha}{2} - I\langle n_{d-\sigma}\rangle}{\sqrt{\{((1-A)\omega - T_o + \frac{A\alpha}{2} - I\langle n_{d-\sigma}\rangle)^2 + 4A|v|^2\}}}\Big]$$

$$X\ [\theta(\omega-\omega_{1\sigma}^{-p}) - \theta(\omega-\omega_{2\sigma}^{-p})], \tag{2.50}$$

$$\langle n_{d\sigma}\rangle = \int_{-\infty}^{\mu} \frac{1}{2A\alpha} \sum_{p=\pm}\Big[1 + p\,\frac{(1-A)\omega - T_o + \frac{A\alpha}{2} - I\langle n_{d\sigma}\rangle}{\sqrt{\{((1-A)\omega - T_o + \frac{A\alpha}{2} - I\langle n_{d-\sigma}\rangle)^2 + 4A|v|^2\}}}\Big]$$

$$X\ [\theta(\omega-\omega_{1\sigma}^{-p}) - \theta(\omega-\omega_{2\sigma}^{-p})]\,d\omega. \tag{2.51}$$

As in the case of the zero bandwidth, by taking μ as a variable parameter $\langle n_{d\sigma}\rangle$ and $\langle n_{d-\sigma}\rangle$ are obtained self-consistently from Eq.(2.51). Then Eq.(2.17) and (2.50) are used to fix the Fermi level for an integral number of electrons. In Fig.2.4 Q vs Z curves are shown for three values 0.1, 0.2 and 0.4 of A. Values of P and S are taken equal to 2.0 and 0.1 respectively. Table 2.3 indicates that the range of the ferromagnetic solutions diminishes as the d band width increases. This shows that the localization of the d electrons favors the existence of ferromagnetism.

IV. CORRELATION THEORY

In this section we discuss the effect of correlation by considering the equation of motion of the higher order Green's function $<<n_{i\sigma} a_{i\sigma}, a^{\dagger}_{\mu\sigma}>>_{\omega}$ where ___ is either j or $\vec{k}$. The equation of motion for this Green's function is given by

$$\omega<<n_{i-\sigma} a_{i\sigma}, a^{\dagger}_{\mu\sigma}>>_{\omega} = \frac{<n_{i-\sigma}>\delta_{i\mu}}{2\pi} + \sum_{\ell} T_{i\ell}<<n_{i-\sigma} a_{\ell\sigma}, a^{\dagger}_{\mu\sigma}>>$$

$$+I<<n_{i-\sigma} a_{i\sigma}, a^{\dagger}_{\mu\sigma}>>\omega$$

$$+\sum_{\vec{k}} V^{*}_{\vec{k}d}\, e^{-i\vec{k}.\vec{R}i}<<n_{i-\sigma} a_{\vec{k}\sigma}, a^{\dagger}_{\mu\sigma}>>_{\omega}$$

$$+\sum_{\ell} T_{i\ell}<<(a^{\dagger}_{i-\sigma} a_{\ell-\sigma} - a^{\dagger}_{\ell-\sigma} a_{i-\sigma}) a_{i\sigma}, a^{\dagger}_{\mu\sigma}$$

$$-\sum_{\vec{k}} V_{\vec{k}d} e^{i\vec{k}.\vec{R}i} <<a^{\dagger}_{\vec{k}-\sigma} a_{i-\sigma} a_{i\sigma}, a^{\dagger}_{\mu\sigma}>>_{\omega}$$

$$+\sum_{\vec{k}} V^{*}_{\vec{k}d}\, e^{-i\vec{k}.\vec{R}i}<<a_{k-\sigma} a^{\dagger}_{i-\sigma} a_{i\sigma}, a^{\dagger}_{\mu\sigma}>>_{\omega}$$

(2.52)

We assume that the correlations between electrons at different lattice sites and the correlations between s and d electrons are very small as compared to the correlations between electrons at the same lattice site. In this approximation we can decouple the Green's functions on the right band side of Eq.(2.52) by replacing the operators at the same lattice site by their average values as follows

$$\begin{aligned}
&\langle\langle n_{i\sigma} a_{\ell\sigma} , a^{\dagger}_{\mu\sigma} \rangle\rangle_{\omega} \simeq \langle n_{d-\sigma} \rangle \langle\langle a_{\ell\sigma} , a^{\dagger}_{\mu\sigma} \rangle\rangle_{\omega} , \text{ if } i \neq \ell \\
&\langle\langle a^{\dagger}_{i-\sigma} a_{\ell-\sigma} a_{i\sigma} , a^{\dagger}_{\mu\sigma} \rangle\rangle_{\omega} \simeq -\langle a^{\dagger}_{i-\sigma} a_{i\sigma} \rangle \langle\langle a_{\ell-\sigma} , a^{\dagger}_{\mu\sigma} \rangle\rangle_{\omega} , \text{ if } i \neq \ell \\
&\langle\langle a^{\dagger}_{\ell-\sigma} a_{i-\sigma} a_{i\sigma} , a^{\dagger}_{\mu\sigma} \rangle\rangle_{\omega} \simeq \langle a_{i-\sigma} a_{i\sigma} \rangle \langle\langle a^{\dagger}_{\ell-\sigma} a^{\dagger}_{\mu\sigma} \rangle\rangle_{\omega} , \text{ if } i \neq \ell \\
&\langle\langle n_{i-\sigma} a_{\vec{k}\sigma} , a^{\dagger}_{\mu\sigma} \rangle\rangle_{\omega} \simeq \langle n_{d-\sigma} \rangle \langle\langle a_{\vec{k}\sigma} , a^{\dagger}_{\mu\sigma} \rangle\rangle_{\omega} , \\
&\langle\langle a^{\dagger}_{k-\sigma} a_{i-\sigma} a_{i\sigma} , a^{\dagger}_{\mu\sigma} \rangle\rangle_{\omega} \simeq \langle a_{i-\sigma} a_{i\sigma} \rangle \langle\langle a^{\dagger}_{\vec{k}-\sigma} , a^{\dagger}_{\mu\sigma} \rangle\rangle_{\omega} , \\
&\langle\langle a_{k-\sigma} a^{\dagger}_{i-\sigma} a_{i\sigma} , a_{\mu\sigma} \rangle\rangle_{\omega} \simeq \langle a^{\dagger}_{i-\sigma} A_{i\sigma} \rangle \langle\langle a_{k-\sigma} , a^{\dagger}_{\mu\sigma} \rangle\rangle_{\omega} .
\end{aligned} \qquad (2.53)$$

We also assume that

$$\langle a^{\dagger}_{i-\sigma} a_{i\sigma} \rangle = \langle a_{i-\sigma} a_{i\sigma} \rangle = 0 \, . \qquad (2.54)$$

Under these approximations Eq.(2.52) becomes

$$(\omega+\mu - T_o - I\ ) \langle\langle n_{i-\sigma}\, a_{i\sigma}\, ,\, a^{\dagger}_{\mu\sigma} \rangle\rangle_{\omega}$$

$$= \frac{\langle n_{d-\sigma}\rangle \delta_{i\mu}}{2\pi} + \langle n_{d-\sigma}\rangle \sum_{\ell\neq i} T_{i\ell}\, G^{\sigma}_{\ell\mu}(\omega)$$

$$+ \langle n_{d-\sigma}\rangle \sum_{\vec{k}} V^{*}_{\vec{k}d}\; e^{-i\vec{k}\cdot\vec{R}i}\; G^{\sigma}_{\vec{k}\mu}(\omega)\ . \qquad (2.55)$$

When we substitute the values of the Green's functions $\langle\langle n_{i-\sigma}\, a_{i\sigma}\ ,\ a^{\dagger}_{\mu\sigma} \rangle\rangle_{\omega}$ from Eq.(2.55) in Eqs.(2.10) and (2.11), Eqs.(2.8) - (2.11) acquire a closed form. By solving these Eqs. for $G^{\sigma}_{\vec{k}\vec{k}}(\omega)$ and $G^{\sigma}_{d\vec{k}}(\omega)$ we get

$$G^{\sigma}_{\vec{k}\vec{k}}(\omega) = \frac{\dfrac{(\omega+\mu-T_o)(\omega+\quad -T_o-I)}{\omega+\mu-T_o\ -I(1-\langle n_{d-\sigma}\rangle)} - (\epsilon_{d\vec{k}} - T_o)}{\omega+\mu-\epsilon_{\vec{k}}}\, G^{\sigma}_{d\vec{k}}(\omega) \ ,$$

(2.56)

$$G^{\sigma}_{d\vec{k}}(\omega) = \frac{1/2\pi}{\dfrac{(\omega+\mu-T_o)(\omega+\quad -T_o-I)}{\omega+\mu-T_o-I(1-\langle n_{d-\sigma}\rangle)} - (\epsilon_{d\vec{k}} - T_o) - \dfrac{N|V_{\vec{k}d}|^2}{\omega+\mu-\epsilon_k}}\ .$$

(2.57)

These Green's functions have the same singularities which are simple poles. There are three quasi-particle bands which arise from the s band crossing and hybridizing with the two pseudo-d-bands given by the roots of the equation.

$$(\omega+\mu-T_o)(\omega+\mu-T_o-I)-(\epsilon_{d\vec{k}}-T_o)(\omega+\mu-T_o-I(1-\langle n_{d-\sigma}\rangle))=0 \tag{2.58}$$

In general the roots of the cubic equation which determines the poles of the Green's function, are not all real. However we can avoid this situation by taking the limit I → ∞. In this limit the upper band given by Eq.(2.58) is pushed out to infinity and we have only two bands to consider. When I → ∞ the Green's functions $G^{\sigma}_{\vec{k}\vec{k}}(\omega)$ and $G^{\sigma}_{d\vec{k}}(\omega)$ are given by

$$G^{\sigma}_{\vec{k}\vec{k}}(\omega)=\frac{\dfrac{\omega+\mu-T_o}{1-\langle n_{d-\sigma}\rangle}-(\epsilon_{d\vec{k}}-T_o)}{\omega+\mu-\epsilon_{\vec{k}}}\,G^{\sigma}_{d\vec{k}}(\omega), \tag{2.59}$$

$$G^{\sigma}_{d\vec{k}}(\omega)=\frac{1/2\pi}{\dfrac{\omega+\mu-T_o}{1-\langle n_{d-\sigma}\rangle}-(\epsilon_{d\vec{k}}-T_o)-\dfrac{N(V_{\vec{k}d})^2}{\omega+\mu-\epsilon_{\epsilon\vec{k}}}} \tag{2.60}$$

By substituting the values of $G^{\sigma}_{\vec{k}\vec{k}}(\omega)$ and $G^{\sigma}_{d\vec{k}}(\omega)$ from Eqs.(2.59) and (2.60) in Eqs.(2.15) and (2.16), we obtain

$$\rho^{\sigma}_{s}(\omega)=\frac{1}{N}\Sigma\left[B^{+}_{s\vec{k}\sigma}\delta(\omega-\tilde{\omega}^{+}_{\vec{k}\sigma})+B^{-}_{s\vec{k}\sigma}\delta(\omega-\tilde{\omega}^{-}_{\vec{k}\sigma})\right], \tag{2.61}$$

the number of states per atom for each spin in the lower band is not equal to 1. Therefore a system having two electrons per atom will behave as a metal instead of an insulator. However for some particular choice of parameters I, v, T_o and α it may behave as an insulator. The number of states per atom for each spin in both the bands together is equal to $B^{+}_{s\vec{k}\sigma} + B^{-}_{s\vec{k}\sigma} + B^{+}_{d\vec{k}\sigma} + B^{-}_{d\vec{k}\sigma} = 2-\langle n_{d-\sigma}\rangle$ instead of 2 as in the Hartree-Fock approximation. This is due to the fact that the upper band given by Eq.(2.58) has been pushed out to infinity.

A. Zero Bandwidth

In the zero-bandwidth case Eqs.(2.61) and (2.62) take the form

$$\rho_s^{\sigma}(\omega) = N\left\{f_{\sigma}^{c}(\omega+\mu)\right\} \qquad (2.66)$$

$$\rho_d^{\sigma}(\omega) = (1-\langle n_{d-\sigma}\rangle)\left|\frac{\omega+\mu-f_{\sigma}^{c}(\omega+\mu)}{\omega+\mu-T_o}\right| N\left\{f_{\sigma}^{c}(\omega+\mu)\right\} \qquad (2.67)$$

where
$$f_{\sigma}^{c}(\omega) = \omega - \frac{|v|^2(1-\langle n_{d-\sigma}\rangle)}{\omega - T_o} \qquad (2.68)$$

Eqs.(2.66) and (2.67) give the average number of s and d electrons per atom for spin σ as

$$\langle n_{s\sigma}\rangle = \int_{-\infty}^{\mu} N\left\{f_{\sigma}^{c}(\omega)\right\} d\omega \qquad (2.69)$$

$$\langle n_{d\sigma}\rangle = (1-\langle n_{d-\sigma}\rangle)^2 \int_{-\infty}^{\mu} \frac{|v|^2}{(\omega-T_o)^2} N(f_{\sigma}^{c}(\omega)) d\omega \qquad (2.70)$$

Above equations are used to obtain the ferromagnetic solutions for square density of states. In Fig.2.5 Q-versus-Z curves are plotted for three different values of S, 0.1, 0.3, 1.0. Here and in the next subsection we do not consider the case n = 3 because in this case both s and d bands are completely filled. It is found that ferromagnetic solutions are possible only for n = 1.0, S = 1.0 and Z from 0.01 to 0.12. This shows that the square density of states is less favourable to ferromagnetism than the parabolic density of states studied by smith who found that for n = 1, ferromagnetic solutions are possible for S = 1.0 and also for S = 0.3. Thus the ferromagnetic solutions are influenced by the shape of the density of states. In Fig.2.6 the self consistent magnetic solutions are shown.

B. Finite Bandwidth

To consider the effect of the width of the d band on the ferromagnetic solutions, we take the d band given by Eq.(2.41). The density of states $\rho_s^{\sigma}(\omega)$ and $\rho_d^{\sigma}(\omega)$ are given by

$$\rho_s^{\sigma}(\omega) = \frac{1}{N} \sum_{\vec{k}} \left| \omega + \mu - T_o - A(1 - \langle n_{d-\sigma} \rangle)(\epsilon_{\vec{k}} - \alpha/2) \right| \times \delta \left\{ (\omega - \tilde{\omega}_{\vec{k}\sigma}^{+})(\omega - \tilde{\omega}_{\vec{k}\sigma}^{-}) \right\} \qquad (2.71)$$

$$\rho_d^{\sigma}(\omega) = \frac{1}{N} \sum_{\vec{k}} (1 - \langle n_{d-\sigma} \rangle) \left| \omega + \mu - \epsilon_{\vec{k}} \right| \delta \left\{ (\omega - \omega_{\vec{k}\sigma}^{+})(\omega - \omega_{\vec{k}\sigma}^{-}) \right\} \qquad (2.72)$$

If we assume that $A(1-\langle n_{d-\sigma}\rangle) \neq 0$, these equations can be rewritten as

$$\rho_s^{\sigma}(\omega) = \frac{1}{A(1-\langle n_{d-\sigma}\rangle} \sum_{p=\pm} \frac{\omega+\mu-T_o+\frac{A(1-\langle n_{d-\sigma}\rangle}{2}(\alpha-2g_{\sigma}^{p}(\omega+\mu)}{g_{\sigma}^{+}(\omega+\mu)-g_{\sigma}^{-}(\omega+\mu)}$$

$$\times N\{g_{\sigma}^{p}(\omega+\mu)\} \qquad (2.73)$$

$$\rho_d^{\sigma}(\omega) = \frac{1}{A}\sum_{p=\pm}\left|\frac{\omega+\mu-g_{\sigma}^{p}(\omega+\mu)}{g_{\sigma}^{+}(\omega+\mu)-g_{\sigma}^{-}(\omega+\mu)}\right| N\{g_{\sigma}^{p}(\omega+\mu)\} \qquad (2.74)$$

where

$$g_{\sigma}^{p}(\omega) = \frac{1}{2A(1-\langle n_{d-\sigma}\rangle)}\Big[\omega-T_o+(1-\langle n_{d-\sigma}\rangle)(A\omega+\frac{A\alpha}{2})$$

$$+ p\sqrt{[\omega-T_o-(\omega-\alpha/2)A(1-\langle n_{d-\sigma}\rangle)]^2+4|v|^2(1-\langle n_{d-\sigma}\rangle)^2}$$

$$(2.75)$$

From Eqs.(2.73) and (2.74) we obtain $\langle n_{s\sigma}\rangle$ and $\langle n_{d\sigma}\rangle$ at absolute zero.

$$\langle n_{s\sigma}\rangle = \frac{1}{A(1-\langle n_{d-\sigma}\rangle)}\int_{-\infty}^{\mu}\sum_{p=\pm}\left|\frac{\omega-T_o+\frac{A(1-\langle n_{d-\sigma}\rangle}{2}(\alpha-2g_{\sigma}^{p}(\omega)}{g_{\sigma}^{+}(\omega)-g_{\sigma}^{-}(\omega)}\right|$$

$$\times N\{g_{\sigma}^{p}(\omega)\}\, d\omega \qquad (2.76)$$

$$\rho_d^{\sigma}(\omega) = \frac{1}{N}\sum_{\vec{k}} \left[B^{+}_{d\vec{k}\sigma}\,\delta(\omega-\tilde{\omega}^{+}_{\vec{k}\sigma}) + B^{-}_{d\vec{k}\sigma}\,\delta(\omega-\tilde{\omega}^{-}_{\vec{k}\sigma})\right] . \qquad (2.62)$$

where

$$\tilde{\omega}^{p}_{\vec{k}\sigma} = -\mu + \frac{1}{2}\Big[\epsilon_{\vec{k}} + T_o + (\epsilon_{d\vec{k}} - T_o)\,(1-\langle n_{d-\sigma}\rangle)$$
$$+p\sqrt{\left\{T_o+(\epsilon_{d\vec{k}}-T_o)(1-\langle n_{d\sigma}\rangle)-\epsilon_{\vec{k}}\right\}^2+4N|V_{\vec{k}d}|^2(1-\langle n_{d-\sigma}\rangle)}\Big]$$
$$(2.63)$$

$$B^{p}_{s\vec{k}\sigma} = p\,\frac{\tilde{\omega}^{p}_{\vec{k}\sigma} + \mu - T_o - (\epsilon_{d\vec{k}} - T_o)(1-\langle n_{d-\sigma}\rangle)}{\tilde{\omega}^{+}_{\vec{k}\sigma} - \tilde{\omega}^{-}_{\vec{k}\sigma}} \qquad (2.64)$$

$$B^{p}_{d\vec{k}\sigma} = p(1-\langle n_{d-\sigma}\rangle)\,\frac{\tilde{\omega}^{p}_{\vec{k}\sigma} + \mu - \epsilon_{\vec{k}}}{\tilde{\omega}^{+}_{\vec{k}\sigma} - \tilde{\omega}^{-}_{\vec{k}\sigma}} \qquad (2.65)$$

Eqs.(2.61) and (2.62) show that both s and d bands are split into two bands with dispersion laws $\omega = \tilde{\omega}^{+}_{\vec{k}\sigma}$ and $\omega = \tilde{\omega}^{-}_{\vec{k}\sigma}$. The general form of these bands comes out to be similar to that in the Hartree-Fock approximation. Here again for zero width of the d band, the two bands are always separated by an energy gap. But in this case the two bands are separated by an asymptote at $T_o - \mu$ instead of $T_o - \mu + I\langle n_{d-\sigma}\rangle$ in the Hartree-Fock approximation.

Again the band gap decreases as the d-band width increases and finally they overlap each other. In this case, in general,

$$\langle n_{d\sigma} \rangle = \frac{1}{A} \int_{-\infty}^{\mu} \sum_{p=\pm} \left| \frac{\omega - g^{p}_{\sigma}(\omega)}{g^{+}_{\sigma}(\omega) - g^{-}_{\sigma}(\omega)} \right| N \left\{ g^{p}_{\sigma}(\omega) \right\} d\omega \quad (2.77)$$

Equations (2.76) and (2.77) are analysed to get the magnetic solutions. For the zero width of the d-band the case of parabolic density of states was analysed by Smith and square density of states by us in the last section. We consider here both the square and the parabolic density of states, to get on idea of the change of the magnetic solutions with d band width. In Figs. 2.7 and 2.8 the plots of Q versus Z are given for the square and parabolic density of states respectively. We have taken A = 0.1, 0.2 and 0.4 and S = 1.0. A search for magnetic solutions shows that the ferromagnetic solutions are not possible for any of these curves.

VI. CONCLUSIONS

The results of the correlation theory for ferromagnetic solutions are in marked disagreement with those of Hartree-Fock theory. In Hartree-Fock theory, as the strength of s-d hybridization increases, the tendency towards ferromagnetism decreases, while reverse is true for the correlation theory. In the Hartree-Fock theory the ferromagnetic solutions are possible for n = 1,2,3 while according to correlation theory ferromagnetic solutions are possible only for n = 1. In both the theories the tendency towards ferromagnetism decreases as the band width increases. Our conclusions that ferromagnetism is possible for square density of states* disagrees with the Hubbard's theory which predicts that for this type of density of states ferromagnetism is not possible. Furthermore in correlation theory tendency towards ferromagnetism increases as the hybridization between the s and d bands increases. This shows the importance of s-d hybridization in the correlation theory of ferromagnetism. In the Hartree-Fock theory the strength of the intraatomic interaction favors ferromagnetism.

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* Here we have taken the form of the d band same as that of s band, therefore the form of the density of states should be the same for both the bands. Since square density of states is taken for s band, we shall have square density of state for d band also.

Table 2.1: Range of Z for ferromagnetic solutions for zero width of the d band

P	S	n	Z
2.0	0.1	1.0	0.01 - 0.45
		2.0	0.05 - 0.95
		3.0	0.4 - 1.0
	0.3	1.0	0.01 - 0.35
		2.0	0.05 - 0.65
		3.0	0.2 - 1.0
	1.0	1.0	0.01 - 0.2
		2.0	0.01 - 0.1
		3.0	0.4 - 1.0

Table 2.2: Range of Z for ferromagnetic solutions for zero width of the d band.

S	P	n	Z
0.1	0.5	1.0	0.01 - 0.35
		2.0	0.1 - 0.85
		3.0	0.4 - 1.0
	1.0	1.0	0.01 - 0.45
		2.0	0.05 - 0.95
		3.0	0.4 - 1.0
	2.0	1.0	0.01 - 0.45
		2.0	0.05 - 0.95
		3.0	0.04 - 1.0

Table 2.3: Range of Z for ferromagnetic solutions for the finite width of the d band

P	S	A	n	Z
2.0	0.1	0.1	1.0	0.05 - 0.4
			2.0	0.11 - 1.0
			3.0	0.26 - 1.0
		0.2	1.0	0.1 - 0.4
			2.0	0.16 - 1.0
			3.0	0.26 - 1.0
		0.4	1.0	0.15 - 0.4
			2.0	0.26 - 1.0
			3.0	0.31 - 1.0

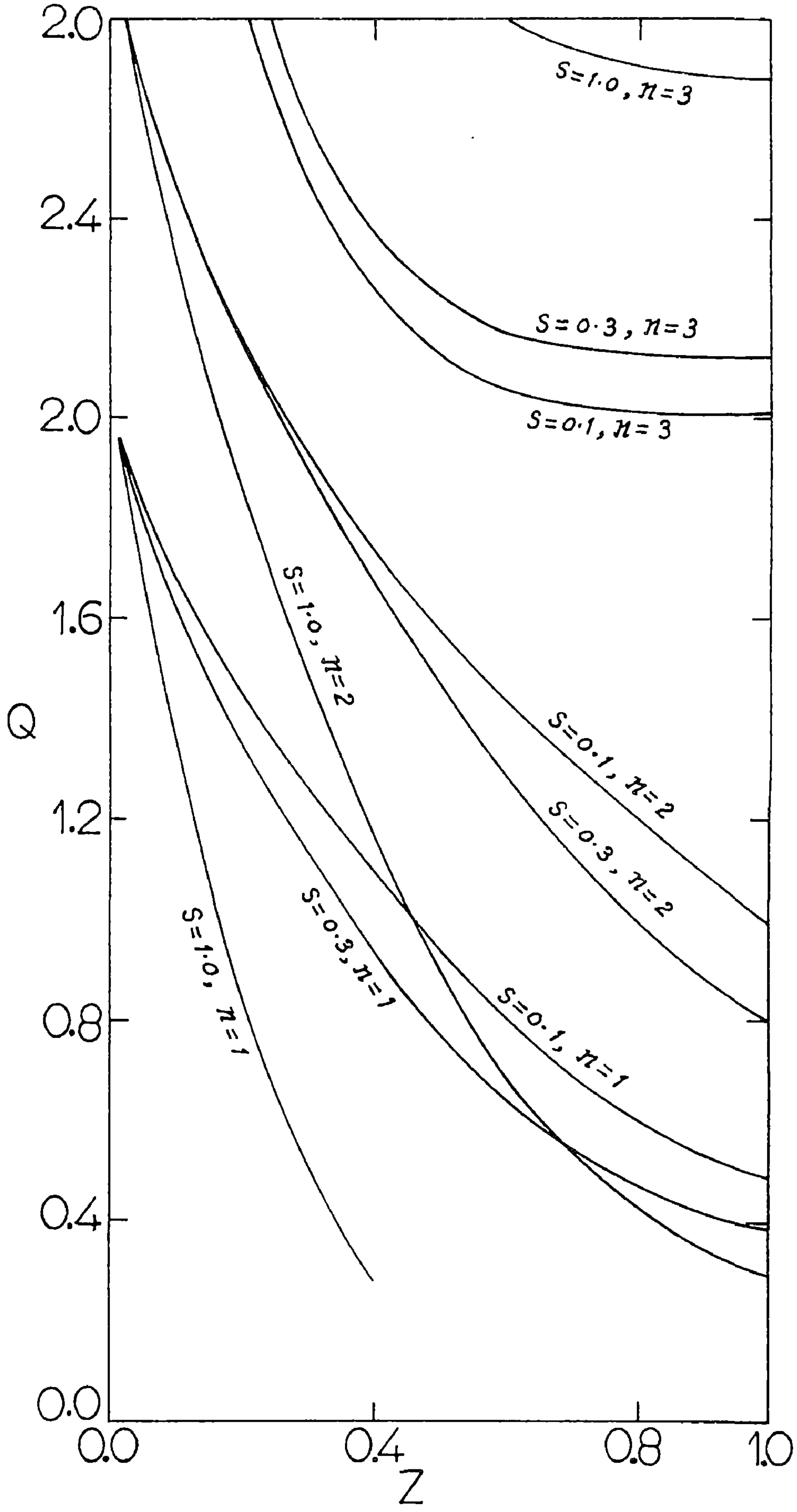

FIGURE 2.1 VARIATION OF FERMI LEVEL WITH Z IN THE HARTREE-FOCK APPROXIMATIONS FOR ZERO WIDTH OF d BAND AND SQUARE DENSITY OF STATES FOR s BAND. CURVES ARE PLOTTED FOR P=2.0.

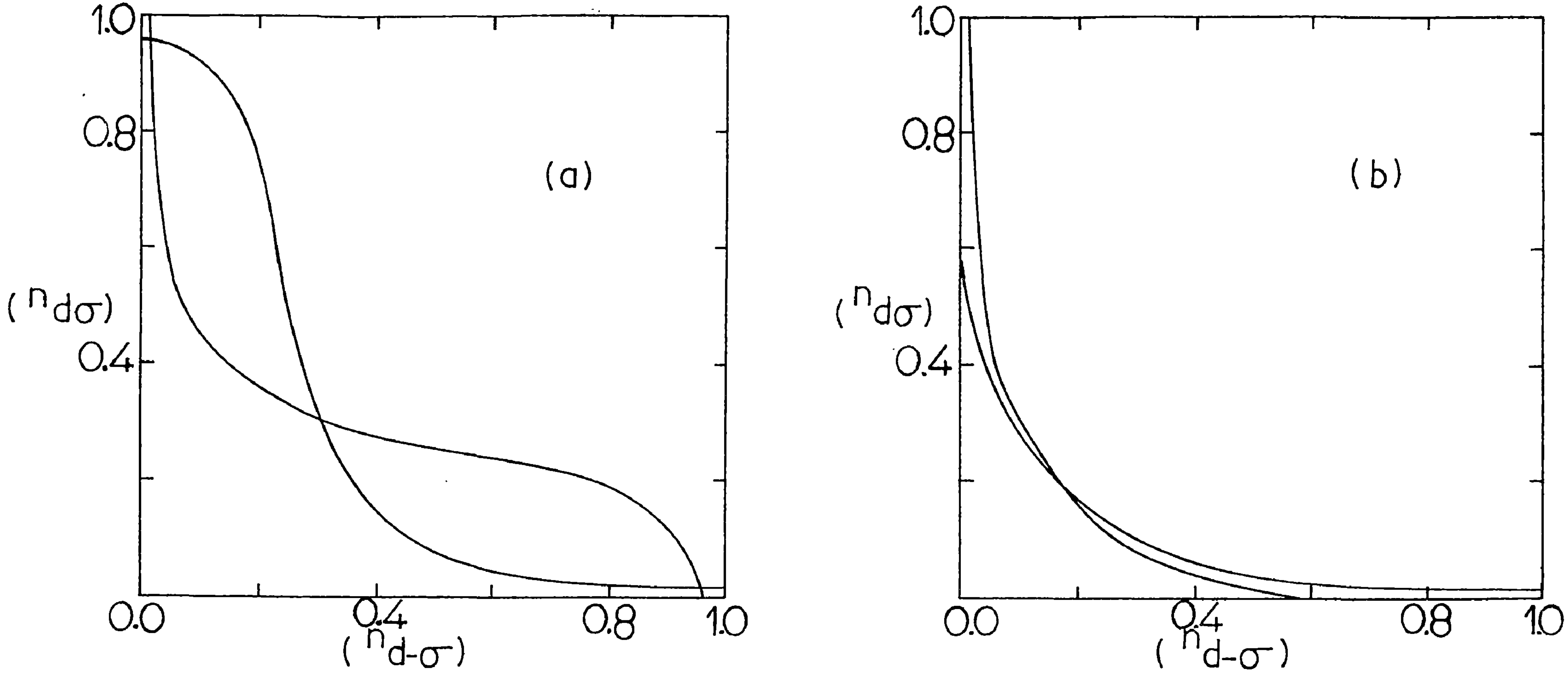

FIG. 2.2 SELF-CONSISTENT MAGNETIC SOLUTIONS IN THE HARTREE-FOCK APPROXIMATIONS FOR ZERO d-BAND WIDTH AND THE SQUARE DENSITY OF STATES FOR THE s BAND. THE PARAMETERS USED ARE (a) $P=2{\cdot}0$, $S=0{\cdot}3$, $n=2{\cdot}0$, $Z=0{\cdot}45$ AND $Q=1{\cdot}56$; (b) $P=2{\cdot}0$, $S=0{\cdot}3$, $n=2{\cdot}0$, $Z=0{\cdot}7$ AND $Q=1{\cdot}12$

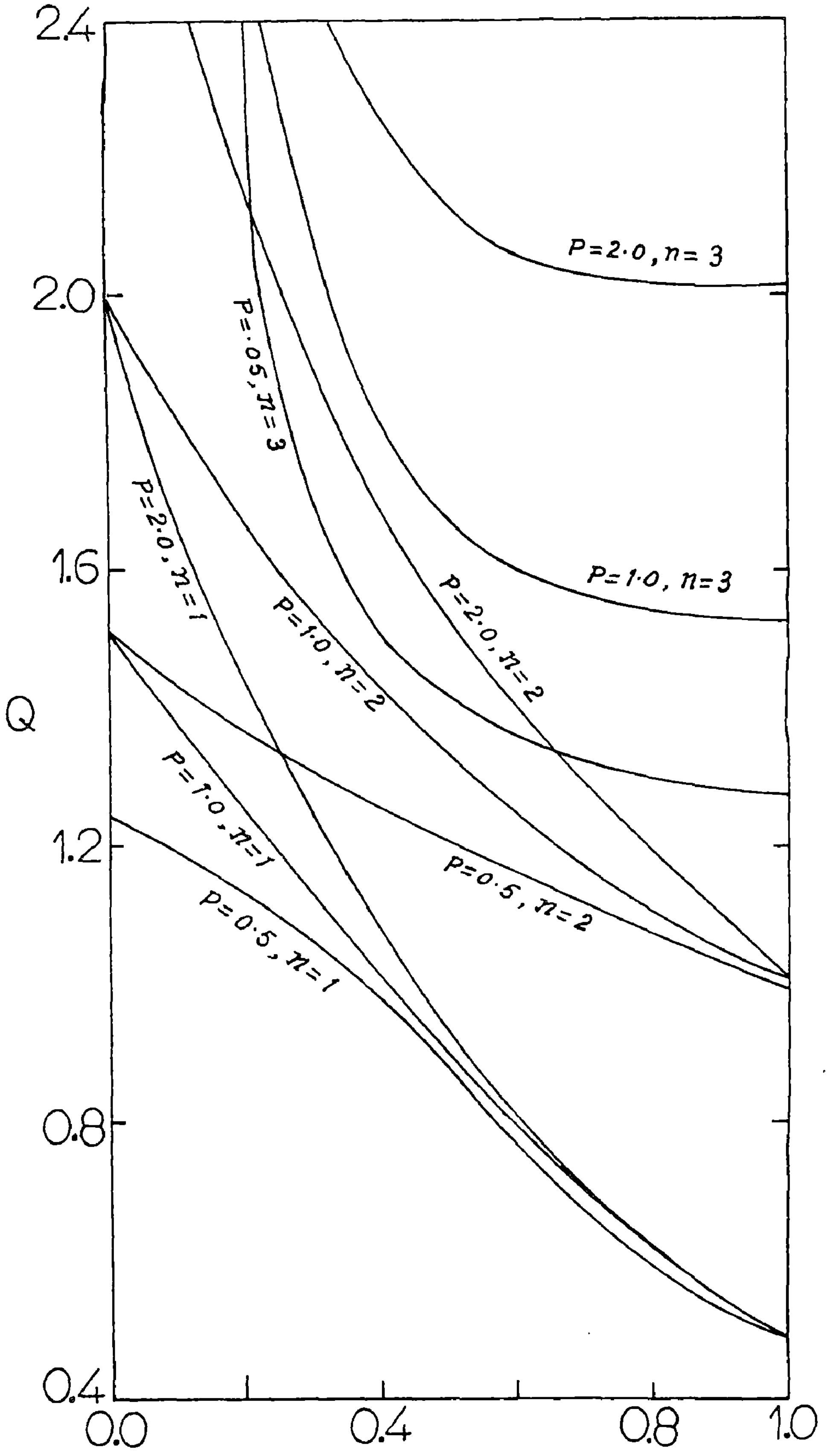

FIG. 2·3 VARIATION OF THE FERMI LEVEL WITH Z IN THE HARTREE-FOCK APPROXIMATION FOR A **ZERO** d-BAND WIDTH AND THE SQUARE DENSITY OF STATE FOR s BAND. CURVES ARE PLOTTED FOR S = 0·1.

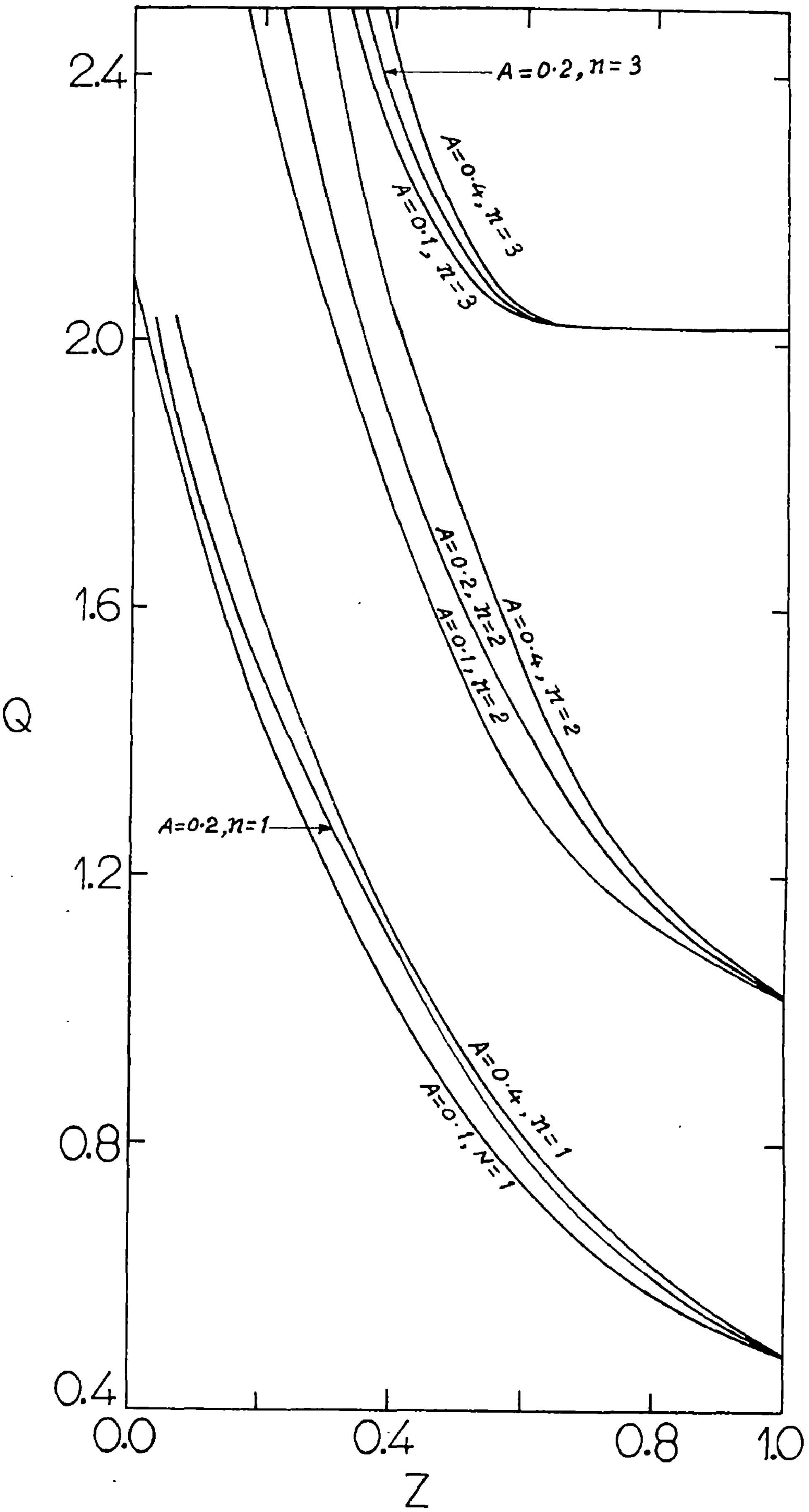

FIG. 2.4 VARIATION OF THE FERMI LEVEL WITH Z IN THE HARTREE-FOCK APPROXIMATION FOR A FINITE d-BAND WIDTH AND THE SQUARE DENSITY OF STATES FOR s BAND. CURVES ARE PLOTTED FOR P=2·0 AND S=0·1

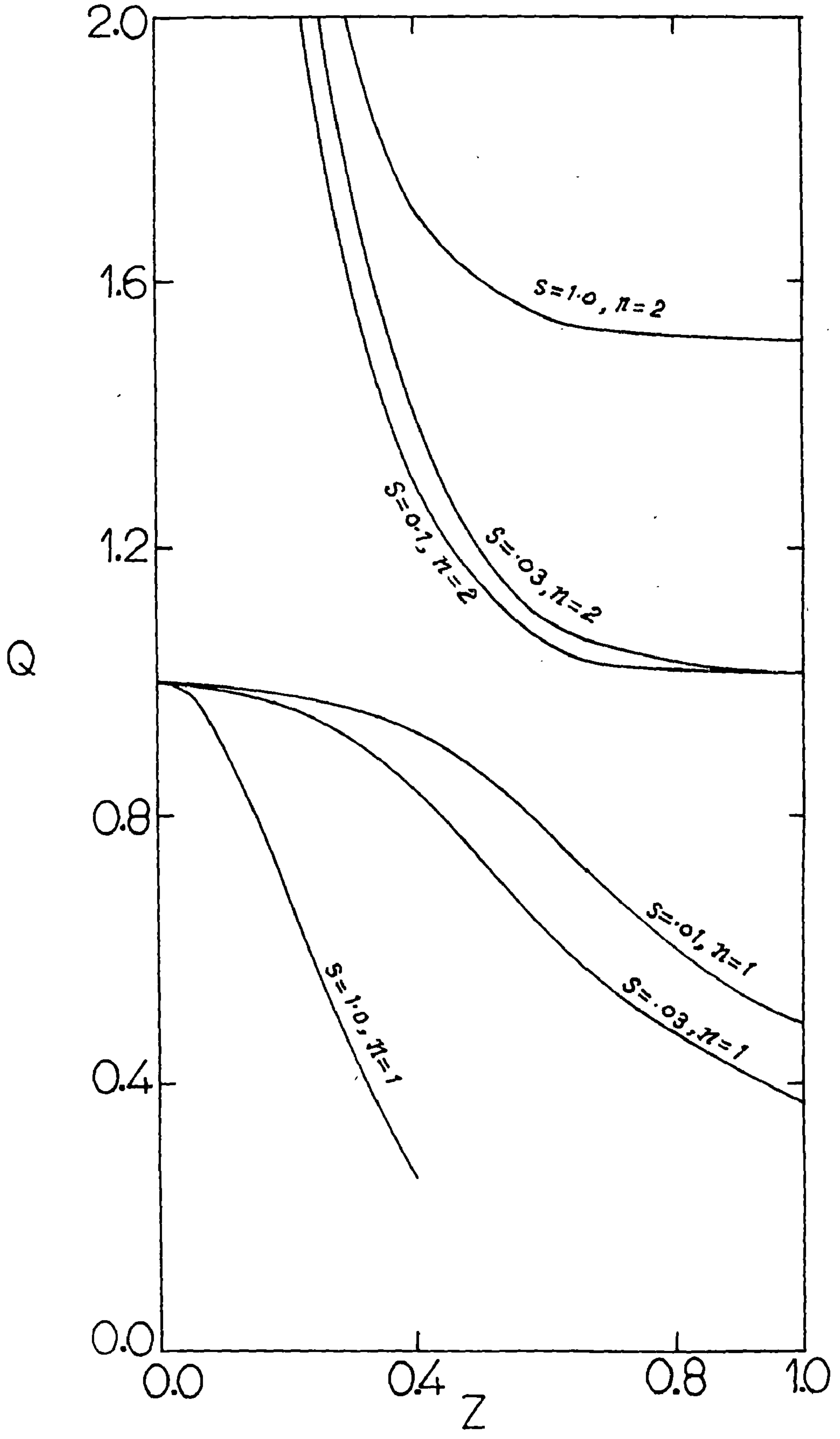

FIG. 2.5 VARIATION OF THE FERMI LEVEL WITH Z IN THE CORRELATION THEORY FOR THE ZERO d-BAND WIDTH AND THE SQUARE DENSITY OF STATES FOR THE s-BAND.

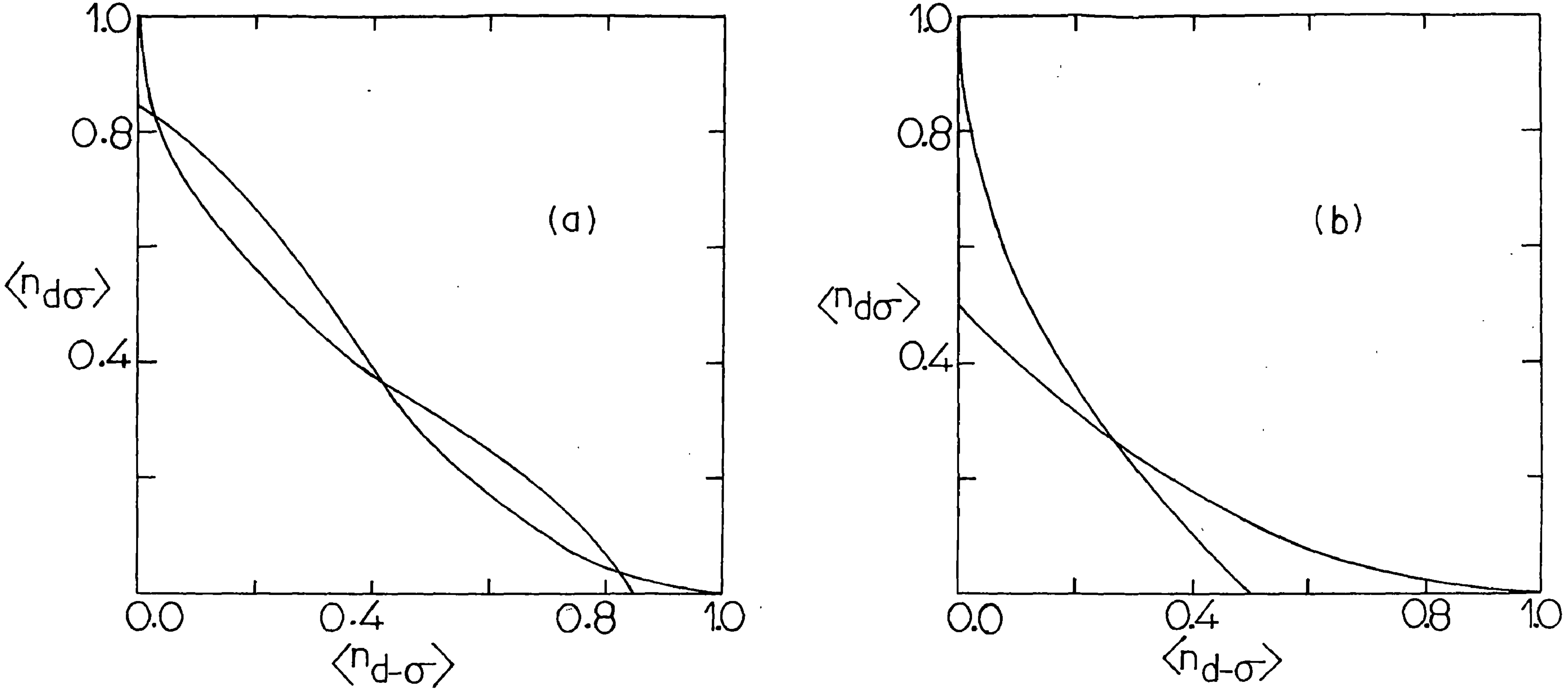

FIG-2·6 SELF-CONSISTENT MAGNETIC SOLUTIONS IN THE CORRELATION THEORY FOR ZERO d-BAND WIDTH AND THE SQUARE DENSITY OF STATES FOR THE s BAND. THE PARAMETERS USED ARE (a) $n=1, S=1{\cdot}0, Z=0{\cdot}1$ AND $Q=0{\cdot}91$; (b) $n=1, S=1{\cdot}0, Z=0{\cdot}2$ AND $Q=0{\cdot}68$.

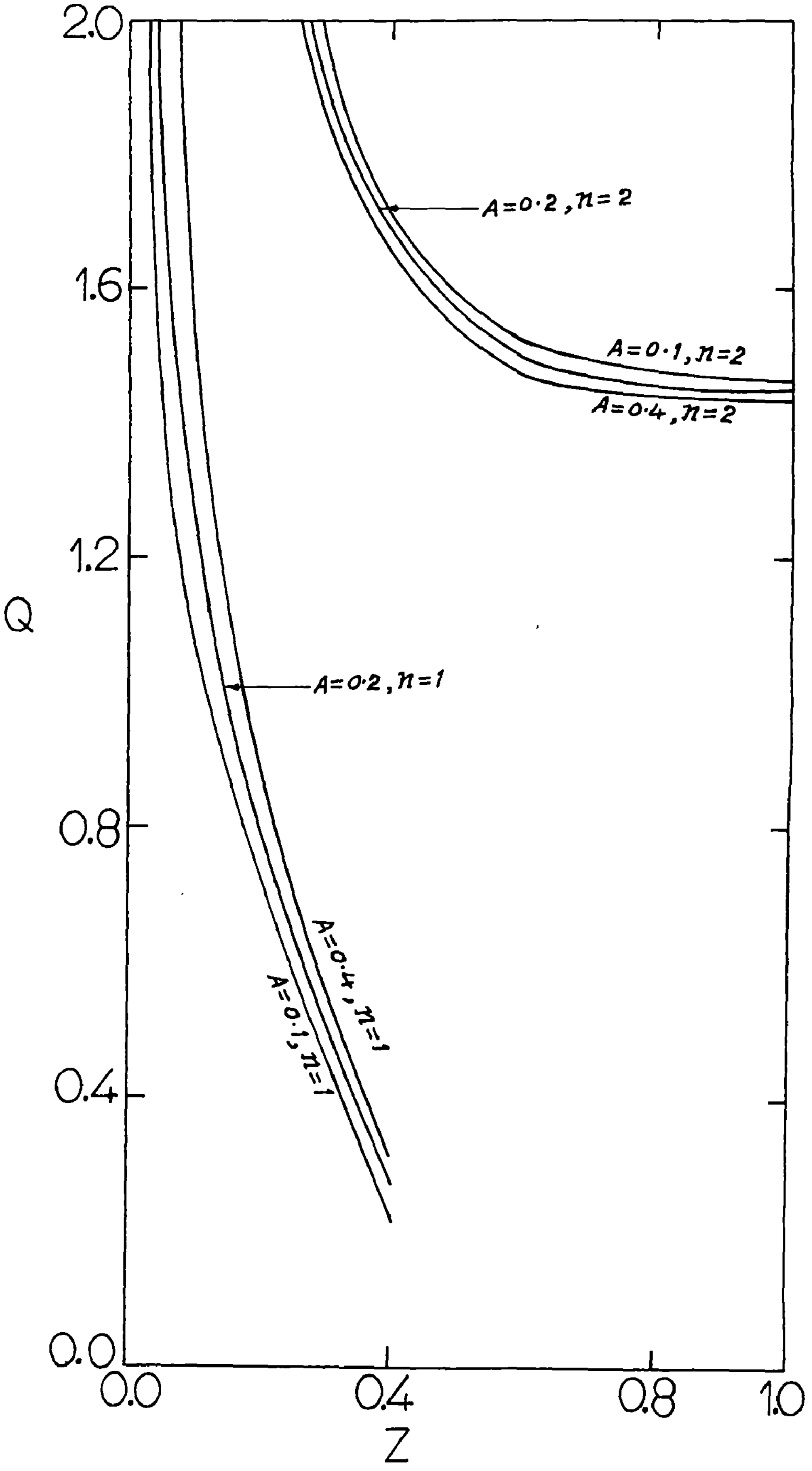

FIG. 2·7 VARIATION OF THE FERMI LEVEL WITH Z IN THE CORRELATION THEORY FOR A FINITE d-BAND WIDTH AND THE SQUARE DENSITY OF STATES FOR THE s BAND. CURVES ARE PLOTTED FOR S=1·0.

CHAPTER III

FERROMAGNETISM.II.INTERATOMIC COULOMB INTERACTION

I.INTRODUCTION

In this chapter we discuss the ferromagnetism in a single narrow energy band. The one band Hamiltonian (1.9) is extended by including a term corresponding to the interatomic Coulomb interaction. From Eq.(1.6), the general one band Hamiltonian in Wannier representation is given by

$$H = \sum_{ij\sigma} T_{ij}\, a^{\dagger}_{i\sigma} a_{j\sigma} + \frac{1}{2} \sum_{\substack{ijk\ell \\ \sigma\sigma'}} V_{ijk\ell}\, a^{\dagger}_{i\sigma} a^{\dagger}_{j\sigma'} a_{k\sigma'} a_{\ell\sigma} \qquad (3.1)$$

V_{ijkl} are in general four center integrals which are extremely difficult to compute. For Coulomb interaction, in narrow energy bands, three and four center integrals are very small in comparison to two and one center integrals. We therefore simplify (3.1) by retaining only one and two centre integrals. Of all the two center integrals we keep only one of them, namely, the interatomic Coulomb interaction V_{ijji} which is quite large in comparison to other two center integrals and for atomic wave functions its magnitude is about 30% to that of one center integral V_{iiii}.[34,53] Within this approximation Eq.(3.1) becomes

$$H = \sum_{ij\sigma} T_{ij}\, a_{i\sigma} a_{j\sigma} + \frac{I}{2} \sum_{i\sigma} n_{i\sigma} n_{i-\sigma} + \frac{1}{2} \sum_{\substack{ij \\ \sigma\sigma'}} K_{ij}\, n_{i\sigma} n_{j\sigma'} \qquad (3.2)$$

where $K_{ij} = V_{ijji}$ if $i \neq j$ and zero if $i = j$. We shall also assume that

$$K_{ij} = K \quad \text{if } i \text{ and } j \text{ are nearest neighbors}$$
$$= 0 \quad \text{Otherwise.}$$

In Section II, an approximate theory for correlation effects in electrons is developed. Here, we have evaluated one electron Green's function for the system described by the Hamiltonian (3.2). The higher order Green's functions appearing in the equations of motion of Green's function are decoupled within the Hartree-Fock approximation and within the approximations similar to that of Hubbard.[34] We also find the approximate solution of correlation problem in zero bandwidth limit. The same problem is then discussed for finite bandwidth case. In Sec. III, the occurrence of ferromagnetism for square density of states is discussed. Sec. IV summarizes our findings.

II. SOME APPROXIMATE SOLUTIONS

We consider the Green's function

$$G_{ik}^{\sigma}(\omega) = \langle\langle a_{i\sigma}, a_{k\sigma}^{\dagger} \rangle\rangle_{\omega} \quad (\eta = +1) \tag{3.3}$$

The knowledge of this Green's function enables one to evaluate the density of states per atom of spin σ, which is needed to study the condition for ferromagnetism. Substituting (3.3) into (1.14), putting $i = k$, $t - t' = 0$, and summing over i, one obtains for $\langle n_{\sigma} \rangle$, the mean number of the electrons per

$\langle\langle n_{i-\sigma} n_{j\sigma'}, a_{i\sigma} a^{\dagger}_{k\sigma} \rangle\rangle_{\omega}$ into $\langle\langle n_{i-\sigma} a_{i\sigma} , a_{k\sigma} \rangle\rangle_{\omega}$ according to the following approximation

$$\langle\langle n_{i-\sigma} n_{j\sigma'} a_{i\sigma} , a^{\dagger}_{k\sigma} \rangle\rangle_{\omega} \simeq \langle n_{\sigma} \rangle \langle\langle n_{i-\sigma} a_{i\sigma} , a^{\dagger}_{k\sigma} \rangle\rangle_{\omega} \quad , \tag{3.16}$$

Within this approximations, Eq.(3.14) reduces to

$$\langle\langle n_{i-\sigma} a_{i\sigma} , a^{\dagger}_{k\sigma} \rangle\rangle_{\omega} = \frac{\langle n_{-\sigma} \rangle}{\omega+\mu-T_0-I-Knz} \left[\frac{\delta_{ik}}{2\pi} + \sum_{j\neq i} T_{ij} G^{\sigma}_{jk}(\omega) \right] . \tag{3.17}$$

In a similar way, if we write the equation of motion for $\langle\langle n_{j\sigma'} a_{i\sigma} , a^{\dagger}_{k\sigma} \rangle\rangle_{\omega}$ and decouple the four-operator Green's functions according to the approximations used by Hubbard[34] and six operator Green's functions into $\langle\langle n_{j\sigma'} a_{i\sigma} , a^{\dagger}_{k\sigma} \rangle\rangle_{\omega}$ according to the approximation used in Eq.(3.16), we get

$$\langle\langle n_{j\sigma'} a_{i\sigma} , a^{\dagger}_{k\sigma} \rangle\rangle_{\omega} = \frac{\langle n_{\sigma} \rangle}{\omega+\mu-T_0-I\langle n_{-\sigma} \rangle-Knz} \left[\frac{\delta_{ik}}{2\pi} + \sum_{j} T_{ij} G^{\sigma}_{jk}(\omega) \right] , \tag{3.18}$$

Substituting the values of Green's functions $\langle\langle n_{i-\sigma} a_{i\sigma} , a^{\dagger}_{k\sigma} \rangle\rangle_{\omega}$ and $\langle\langle n_{j\sigma'} a_{i\sigma} , a^{\dagger}_{k\sigma} \rangle\rangle_{\omega}$ from Eqs. (3.17) and (3.18) in Eq.(3.8) we find

$$(\omega+\mu-T_0)\; G^{\sigma}_{ik}(\omega) = \left\{1+f(\omega+\mu,\langle n_{-\sigma}\rangle)\right\}\left\{\frac{\delta_{ik}}{2\pi} + \sum_{\substack{j\\ i\neq j}} T_{ij}G^{\sigma}_{jk}(\omega)\right\} , \tag{3.19}$$

where

$$f(\omega,\langle n_{-\sigma}\rangle) = \frac{I\langle n_{-\sigma}\rangle}{\omega - T_0 - I - Knz} + \frac{Knz}{\omega - T_0 - I\langle n_{-\sigma}\rangle - Knz} . \tag{3.20}$$

The Fourier transform of the Green's function defined by Eq.(3.11) is, therefore, given by

$$G^{\sigma}(\vec{k},\omega) = \frac{1}{2\pi} \; \frac{1+f(\omega+\mu,\langle n_{-\sigma}\rangle)}{(\omega\pm\mu-\epsilon_{\vec{k}}) - (\epsilon_{\vec{k}}-T_0)\, f(\omega+\mu,\langle n_{-\sigma}\rangle)} \tag{3.21}$$

We shall now consider the correlation effects in the theory of ferromagnetism on the basis of this Green's function .

A. Approximate Solution in Zero Bandwidth Limit

In the limit of zero bandwidth $\epsilon_{\vec{k}} = T_0$ for all $\vec{k}$, hence, it follows that $T_{ij} = T_0\delta_{ij}$. After replacing $\epsilon_{\vec{k}}$ by T_0 in Eq.(3.21) the Green's function in zero bandwidth case is

$$G^{\sigma}(\vec{k},\omega) = \frac{1}{2\pi} \; \frac{F(\omega+\mu)}{(\omega+\mu-T_0)(\omega+\mu-T_0-I-Knz)(\omega+\mu-T_0-I\langle n_{-\sigma}\rangle-Knz)} \tag{3.22}$$

atom of spin σ

$$\langle n_\sigma \rangle = \frac{1}{N} \sum_i \langle a^\dagger_{i\sigma} \, a_{i\sigma} \rangle$$

$$= \frac{i}{N} \lim_{\epsilon \to 0^+} \sum_i \int_{-\infty}^{\infty} \frac{G^\sigma_{ii}(\omega + i\epsilon) - G^\sigma_{ii}(\omega - i\epsilon)}{e^{\beta\omega} + 1}$$

(3.4

This shows that

$$\rho_\sigma(\omega) = \frac{i}{N} \lim_{\epsilon \to 0^+} \sum_i \left[G^\sigma_{ii}(\omega + i\epsilon) - G^\sigma_{ii}(\omega - i\epsilon) \right] , \qquad (3.5$$

gives the density of (pseudoparticle) states per atom of spin σ .

For the Hamiltonian (3.2), one finds

$$[a_{i\sigma} , H]_- = \sum_j T_{ij} \, a_{j\sigma} + I \, n_{i-\sigma} a_{i\sigma} + \sum_{j\sigma'} K_{ij} n_{j\sigma'} \, a_{i\sigma} \qquad (3.6$$

and

$$[n_{i\sigma} , H]_- = \sum_j T_{ij} \, (a^\dagger_{i\sigma} \, a_{j\sigma} - a^\dagger_{j\sigma} \, a_{i\sigma}). \qquad (3.7$$

Therefore, the Eq.(1.13) for $G^\sigma_{ij}(\omega)$ comes out to be

$$(\omega + \mu) G^\sigma_{ik}(\omega) = \frac{\delta_{ik}}{2\pi} + \sum_j T_{ij} \, G^\sigma_{jk}(\omega) + I \, \langle\langle n_{i-\sigma} a_{i\sigma} , a^\dagger_{k\sigma}$$

$$+ \sum_{j\sigma'} K_{ij} \langle\langle n_{j\sigma'} a_{i\sigma} , a^\dagger_{k\sigma} \rangle\rangle_\omega \qquad (3.8$$

Now we make the Hartree-Fock approximation in which the higher order Green's functions appearing in Eq.(3.8) are decoupled as

$$\begin{aligned} \langle\langle n_{i-\sigma} a_{i\sigma} , a^{\dagger}_{k\sigma} \rangle\rangle_{\omega} &\simeq \langle n_{i-\sigma} \rangle \; G^{\sigma}_{ik}(\omega) \\ \langle\langle n_{j\sigma} a_{i\sigma} , a^{\dagger}_{k\sigma} \rangle\rangle_{\omega} &\simeq \langle n_{j\sigma} \rangle \; G^{\sigma}_{ik}(\omega) \end{aligned} \qquad (3.9)$$

In this approximation, Eq.(3.8) turns out to be

$$(\omega+\mu-I\langle n_{-\sigma}\rangle - Knz)\, G^{\sigma}_{ik}(\omega) = \frac{\delta_{ik}}{2\pi} + \sum_{j} T_{ij}\, G^{\sigma}_{jk}(\omega) \qquad (3.10)$$

Here z is the number of nearest neighbors, and we have used the translational symmetry of the problem to write $\langle n_{i-\sigma}\rangle = \langle n_{-\sigma}\rangle$. We do not consider antiferromagnetic ordering. This equation may be solved by Fourier transformation. If we write

$$G^{\sigma}_{ij}(\omega) = \frac{1}{N} \sum_{\vec{k}} e^{i\vec{k}.(\vec{R}_i-\vec{R}_j)} G^{\sigma}(\vec{k},\omega) \qquad (3.11)$$

and

$$T_{ij} = \frac{1}{N} \sum_{\vec{k}} \epsilon_{\vec{k}}\, e^{i\vec{k}.(\vec{R}_i-\vec{R}_j)} \qquad (3.12)$$

we obtain from Eq.(3.10)

$$G^{\sigma}(\vec{k},\omega) = \frac{1/2\pi}{\omega+\mu-\epsilon_{\vec{k}} - I\langle n_{-\sigma}\rangle - Knz} \qquad (3.13)$$

The poles of one-particle Green's function give the energies of quasiparticles. Eq.(3.13), therefore, shows that the band

Here

$$F(\omega) = (\omega)^2 - (2T_0 + I + Knz)\,\omega$$

$$+ I^2 \langle n_{-\sigma}\rangle (1-\langle n_{-\sigma}\rangle) - T_0(I+T_0+Knz) , \qquad (3.23)$$

We substitute the value of $G^{\sigma}(\vec{k},\omega)$ from (3.22) in Eq.(3.5) to get the density of states per atom of spin σ

$$\rho_{\sigma}(\omega) = \frac{I^2\langle n_{-\sigma}\rangle(1-\langle n_{-\sigma}\rangle)}{(I+Knz)(I\langle n_{-\sigma}\rangle + Knz)}\,\delta(\omega - T_0 + \mu)$$

$$+ \frac{Knz}{I\langle n_{-\sigma}\rangle + Knz}\,\delta(\omega + \mu - T_0 - I\langle n_{-\sigma}\rangle - Knz)$$

$$+ \frac{I\langle n_{-\sigma}\rangle}{(I+Knz)}\,\delta(\omega + \mu - T_0 - I - Knz) . \qquad (3.24)$$

This expression shows that system behaves as though it has three energy levels at $T_0 - \mu$, $(T_0 + In_{-\sigma} + Knz - \mu)$ and $(T_0 + I + Knz - \mu)$containing

$$I^2 \langle n_{-\sigma}\rangle(1-\langle n_{-\sigma}\rangle)/(I+Knz)(I\langle n_{-\sigma}\rangle + Knz),$$

$Knz/(I\langle n_{-\sigma}\rangle + Knz)$, and $I\langle n_{-\sigma}\rangle/(I+Knz)$ states per atom for spin σ, respectively. This result differs strikingly from that of Hubbard. According to Hubbard, the system behaves as though it has two energy levels at T_0 and $T_0 + I$ containing $(1-\langle n_{-\sigma}\rangle)$ and $\langle n_{-\sigma}\rangle$ states respectively. It should be noted that because of interatomic interaction, the number of states in a particular energy level depends upon structure is modified, the energy of the $(\vec{k},\sigma)$ state now being $\epsilon_{\vec{k}}-\mu+I\langle n_{-\sigma}\rangle+Knz$, which reduces to Hubbard's expression in the limit $k\to 0$.

Now, we shall go beyond the Hartree-Fock approximation by writing down the equations of motion (Eq.(1.14)) for the higher order Green's functions $\langle\langle n_{i-\sigma}\, a_{i\sigma}\,,\, a^{\dagger}_{k\sigma}\rangle\rangle_{\omega}$ and $\langle\langle n_{j\sigma}\, a_{i\sigma}\,,\, a^{\dagger}_{k\sigma}\rangle\rangle_{\omega}$. The equation of motion for $\langle\langle n_{i-\sigma}\, a_{i\sigma}\,,\, a^{\dagger}_{k\sigma}\rangle\rangle_{\omega}$ is given by

$$(\omega+\mu-T_0-I)\langle\langle n_{i-\sigma}\, a_{i\sigma}\,,\, a^{\dagger}_{k\sigma}\rangle\rangle_{\omega}$$

$$=\langle n_{-\sigma}\rangle\frac{\delta_{ik}}{2\pi}+\sum_{\substack{j\\ i\neq j}}T_{ij}\langle\langle n_{i-\sigma}\, a_{j\sigma}\,,\, a^{\dagger}_{k\sigma}\rangle\rangle_{\omega}$$

$$+\sum_{\substack{j\\ i\neq j}}T_{ij}\Big\{\langle\langle a^{\dagger}_{i-\sigma}\, a_{j-\sigma}\, a_{i\sigma}\,,\, a^{\dagger}_{k\sigma}\rangle\rangle_{\omega}$$

$$-\langle\langle a^{\dagger}_{j-\sigma}\, a_{i-\sigma}\, a_{i\sigma}\,,\, a^{\dagger}_{k\sigma}\rangle\rangle_{\omega}\Big\}$$

$$+\sum_{j\sigma}K_{ij}\langle\langle n_{i-\sigma}\, n_{j\sigma}\, a_{i\sigma}\,,\, a^{\dagger}_{k\sigma}\rangle\rangle_{\omega}\qquad(3.14)$$

where

$$T_0=T_{ii}=\frac{1}{N}\sum_{\vec{k}}\epsilon_{\vec{k}}\qquad(3.15)$$

We decouple the four operator Green's functions $\langle\langle n_{i-\sigma}\, a_{j\sigma}\,,\, a^{\dagger}_{k\sigma}\rangle\rangle_{\omega}$, $\langle\langle a^{\dagger}_{i-\sigma}\, a_{j-\sigma}\overset{a_{i\sigma}}{_{\wedge}}\,,\, a^{\dagger}_{k\sigma}\rangle\rangle_{\omega}$ and $\langle\langle a^{\dagger}_{j-\sigma}\, a_{i-\sigma}\overset{a_{i\sigma}}{_{\wedge}}\,,\, a^{\dagger}_{k\sigma}\rangle\rangle_{\omega}$ according to the approximations used by Hubbard,[34] and six-operator Green's function the strength of interaction parameters I and K, while these are independent of the strength of interatomic interactions when interatomic interaction is neglected.

By finding out the density of states in each energy level, one can find out the number of electrons occupying a given energy level at absolute zero and, hence, the ground state energy of the system. Comparing the energies of paramagnetic and ferromagnetic states, one can find out their relative stability. In the Hubbard model, it can be shown that for n = 1, the energy of both paramagnetic and ferromagnetic states is the same and hence the probability of occurrence of both the states is equal. In the present case, we find that the energy of the ferromagnetic state is smaller than that of the paramagnetic state, and therefore the ferromagnetic state is more stable then the paramagnetic state. Here and in what follows, for the purpose of calculation, we take $T_o = 0$, i.e. we measure the band energy from the middle of the band, and consider a f.c.c lattice. The value of intraatomic interaction parameter I is taken to be 10 eV and to study the interatomic correlation effect the parameter K is varied from 0 to 3 eV.

B. Finite Bandwidth Case

The general nature of the solution given by Eq.(3.21) will now be investigated for the finite bandwidth case. The expression (3.21) for $G^{\sigma}(\vec{k},\omega)$ may be resolved into partial fractions:

$$G^{\sigma}(\vec{k},\omega) = \frac{1}{2\pi}\left[\frac{A_{\vec{k}\sigma}^{(1)}}{\omega-\omega_{\vec{k}\sigma}^{(1)}} + \frac{A_{\vec{k}\sigma}^{(2)}}{\omega-\omega_{\vec{k}\sigma}^{(2)}} + \frac{A_{\vec{k}\sigma}^{(3)}}{\omega-\omega_{\vec{k}\sigma}^{(3)}}\right] \tag{3.25}$$

Here $\omega_{\vec{k}\sigma}^{(1)} > \omega_{\vec{k}\sigma}^{(2)} > \omega_{\vec{k}\sigma}^{(3)}$ are the roots of the equation

$$\begin{aligned}&(\omega+\mu-\epsilon_{\vec{k}})(\omega+\mu-T_o-I-Knz)(\omega+\mu-T_o-I\langle n_{-\sigma}\rangle - Knz)\\ &\quad-(\epsilon_{\vec{k}}-T_o)\{I\langle n_{-\sigma}\rangle(\omega+\mu-T_o-I\langle n_{-\sigma}\rangle - Knz)\\ &\qquad+2Knz(\omega+\mu-T_o-I-Knz)\} = 0\end{aligned} \tag{3.26}$$

and

$$A_{\vec{k}\sigma}^{(1)} = \frac{F(\omega_{\vec{k}\sigma}^{(1)}+\mu)}{(\omega_{\vec{k}\sigma}^{(1)}-\omega_{k\sigma}^{(2)})(\omega_{\vec{k}\sigma}^{(1)}-\omega_{\vec{k}\sigma}^{(3)})} \tag{3.27}$$

$$A_{\vec{k}\sigma}^{(2)} = \frac{F(\omega_{\vec{k}\sigma}^{(2)}+\mu)}{(\omega_{\vec{k}\sigma}^{(2)}-\omega_{\vec{k}\sigma}^{(1)})(\omega_{\vec{k}\sigma}^{(2)}-\omega_{\vec{k}\sigma}^{(3)})} \tag{3.28}$$

$$A_{\vec{k}\sigma}^{(3)} = \frac{F(\omega_{\vec{k}\sigma}^{(3)}+\mu)}{(\omega_{\vec{k}\sigma}^{(3)}-\omega_{\vec{k}\sigma}^{(1)})(\omega_{\vec{k}\sigma}^{(3)}-\omega_{\vec{k}\sigma}^{(2)})} \tag{3.29}$$

From (3.25) and (3.5), the density of states per atom of spin σ is given by

$$\rho_{\sigma}(\omega) = \frac{1}{N} \sum_{\vec{k}} \Big\{ A_{\vec{k}\sigma}^{(1)}\, \delta(\omega-\omega_{k\sigma}^{(1)}) + A_{\vec{k}\sigma}^{(2)}\, \delta(\omega-\omega_{\vec{k}\sigma}^{(2)}) + A_{k\sigma}^{(3)}\, \delta(\omega-\omega_{k\sigma}^{(3)}) \Big\} \qquad (3.30)$$

The expression (3.30) for density of states per atom of spin σ shows that the system behaves as though it has three bands with dispersion laws. $\omega = \omega_{\vec{k}\sigma}^{(1)}$, $\omega = \omega_{\vec{k}\sigma}^{(2)}$, and $\omega = \omega_{\vec{k}\sigma}^{(3)}$. From Eqs. (3.27) - (3.29), it can be shown that $A_{\vec{k}\sigma}^{(1)} + A_{\vec{k}\sigma}^{(2)} + A_{\vec{k}\sigma}^{(3)} = 1$. This equality and Eqs. (3.27) - (3.29) show that the effect of $A_{\vec{k}\sigma}^{(n)}$ cannot be given any simplar interpretation beyond the statement that they regulate the density of states in each band in such a way that the total number of states in all three bands is just one. The general form of the bands $\omega_{\vec{k}\sigma}^{(1)}$, $\omega_{\vec{k}\sigma}^{(2)}$ and $\omega_{\vec{k}\sigma}^{(3)}$ is shown in Fig.3.1. The variation of bandwidth of different bands with K is shown in Table 3.1. We note that the bandwidth of lowest and highest bands increases as K decreases, while bandwidth of middle band diminishes as K decreases. This middle band disappears when K → 0.

Now, an expression more explicit than (3.30) will be given for the density of states. If $F(\omega_{\vec{k}\sigma}^{(1)}+\mu)$ and $F(\omega_{\vec{k}\sigma}^{(3)}+\mu)$ are positive and $F(\omega_{\vec{k}\sigma}^{(2)}+\mu)$ is negative*, then by applying the property of δ-function

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* We have seen that this condition is actually satisfied.

$$\delta\left\{g(x)\right\} = \sum_{n} \frac{\delta(x - a_n)}{|g'(a_n)|} \qquad (3.31)$$

where a_n are the roots of the equation $g(x) = 0$ and $|g'(a_n)|$ is the modulus of derivative of $g(x)$ with respect to x at a_n, the density of states can be written as

$$\rho_{\sigma}(\omega) = P\left\{g(\omega+\mu, \langle n_{-\sigma}\rangle)\right\} \qquad (3.32)$$

Here

$$g(\omega, \langle n_{-\sigma}\rangle) = \frac{\omega + T_0 + f(\omega, \langle n_{-\sigma}\rangle)}{1 + f(\omega, \langle n_{-\sigma}\rangle)} \qquad (3.33)$$

and

$$P(\omega) = \frac{1}{N} \sum_{\vec{k}} \delta(\omega - \epsilon_{\vec{k}}) \qquad (3.34)$$

is the density of states corresponding to the band structure $\epsilon_{\vec{k}}$.

Thus, $\rho_{\sigma}(\omega)$ can be obtained from $P(\omega)$ by the transformation given by Eqs.(3.32) and (3.33). This transformation is illustrated graphically in Fig.3.2 which shows a typical $g(\omega)$ curve and the projection of $P(\omega)$ into $\rho_{\sigma}(\omega-\mu)$. The curve $g(\omega, \langle n_{-\sigma}\rangle)$ splits into three parts. These parts are separated by infinities of $g(\omega, \langle n_{-\sigma}\rangle)$ at $\omega = \omega^+$ and $\omega = \omega^-$, ω^+ and ω^- ($\omega^+ > \omega^-$) are the roots of the equation

$$(\omega - T_0)(\omega - T_0 - I - Knz) + I^2 \langle n_{-\sigma}\rangle (1 - \langle n_{-\sigma}\rangle) = 0 \qquad (3.35)$$

The values of ω^{+} and ω^{-} are given in Table 3.2 for different values of K. This table illustrates that these infinities come closer as K decreases and the width of the middle band is reduced. In the limit K → 0, both infinities merge together and the second band disappears. It is quite clear that the appearance of middle band is due to the effect of interatomic interaction within the decoupling scheme used here.

In the paramagnetic states ($\langle n_{-\sigma} \rangle = \langle n_{\sigma} \rangle = n/2$) of the system, it is found by Hubbard that for square density of states, the first band is completely full for n = 1 and therefore, the system behaves as an insulator. We find that in the present case the system in the paramagnetic state behavess as an insulator only at some critical value $n = n_c$. The value of n_c depends on the value of K. Table 3.3 shows the variation of n_c with K. It is clear from the Table that n_c increases as K decreases and it becomes equal to 1 as K → 0

III. CONDITION FOR FERROMAGNETISM

In Sec.II, we have seen that in case of zero bandwidth, the ferromagnetic state is more stable than the paramagnetic state. In this section, we shall find out the possibility of the occurrence of ferromagnetism in the case of finite bandwidth. We use the general condition [34,53]

$$-\frac{1}{2} \geqslant \int_{-\infty}^{\mu} \frac{\partial}{\partial n} P\left\{ g(\omega, n/2)\right\} d\omega \qquad (3.36)$$

which must be satisfied for a system to exist in the ferromagnetic state. The chemical potential is determined by the condition

$$n = \langle n_{\sigma}\rangle + \langle n_{-\sigma}\rangle \tag{3.37}$$

and $\langle n_{\sigma}\rangle$ is given by

$$\langle n_{\sigma}\rangle = \int_{-\infty}^{\mu} P\{g(\omega, n-\langle n_{\sigma}\rangle)\}\, d\omega \tag{3.38}$$

It is difficult to manifest the condition (3.36) without reference to some specific density of states function $P(\omega)$. We examine the condition (3.36) for a square density of states defind by

$$P(\omega) = \frac{1}{\Delta} \quad \text{if } T_0 - \frac{1}{2}\Delta < \omega < T_0 + \frac{1}{2}\Delta \tag{3.39}$$

$$= 0 \text{ Otherwise}$$

For this case, density of state $\rho_{\sigma}(\omega)$ can be written as

$$\rho_{\sigma}(\omega) = \frac{1}{\Delta}\sum_{\alpha=1}^{6}(-1)^{\alpha+1}\,\theta\,(\omega+\mu-\omega_{\alpha}^{\sigma}) \tag{3.40}$$

where $\omega_1^{\sigma} < \omega_3^{\sigma} < \omega_5^{\sigma}$ and $\omega_2^{\sigma} < \omega_4^{\sigma} < \omega_6^{\sigma}$ are the roots of the cubic equations

$$g(\omega, \langle n_{-\sigma}\rangle) = T_0 - \Delta/2 \tag{3.41}$$

and

$$g(\omega, \langle n_{-\sigma}\rangle) = T_0 + \Delta/2 \tag{3.42}$$

respectively. The density of states given by Eq.(3.40) when used in Eq.(3.36), leads to the following condition for ferromagnetism.

$$-\frac{1}{2} > \frac{1}{\Delta} \int_{-\infty}^{\mu} \sum_{\alpha=1} (-1)^{\alpha} \frac{\partial \omega_{\alpha}^{\sigma}}{\partial n} \delta(\omega - \omega_{\alpha}^{\sigma}) \, d\omega \qquad (3.43)$$

It is not easy to evaluate the right hand side of inequality (3.43) analytically. We have evaluated it numerically.* It is found that when the Fermi level lies in the lowest band, ferromagnetism is not possible, but when it lies in the middle band, ferromagnetism is possible. This result is quite different from Hubbard's conclusion that for a square density of states ferromagnetism is not possible One may, therefore, infer that the interatomic interaction should play an important role in determining the behavior of ferromagnetic metals.

IV. CONCLUSIONS

In the preceding sections, we have investigated an approximate model for electron correlation in transition metals. It is found that one band splits up into three bands. The middle band occurs only because we consider the interatomic interactions. The system behaves as an insulator at certain critical value n_c of n. The value of n_c depends on K. Conditions for the ferromagnetism for the square density of

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*Calculations are performed for K = 0.1, 1 and 3eV, bandwidth = 4 eV and 2 eV, and $0<n<1$.

states are quite different from Hubbard's conclusion which is based on the assumption that interatomic interaction is negligible. We should mention here that Hubbard's decoupling approximation, which we have used, is not suitable for the Hamiltonian (3.2) which emphasizes intersite correlations. To have a better insight about the effect of interatomic coulomb interaction, one must use a decoupling scheme which takes into account the correlation between different lattice sites. However, our conclusions show that intersite correlations may be important to explain the magnetic properties of transition metals, and should not be neglected.

Table 3.1: Comparison of bandwidths of different bands for different values of K[a,b]

K (eV)	Δ_1 (eV)	Δ_2 (eV)	Δ_3 (eV)
0.0	2.0	0.0	2.0
0.1	1.79	0.76	1.45
0.3	1.49	1.64	0.87
0.5	1.28	2.14	0.58
0.7	1.13	2.46	0.41
0.9	1.01	2.68	0.31
1.0	0.96	2.77	0.27
2.0	0.64	3.26	0.10
3.0	0.50	3.45	0.05

[a] Δ_1, Δ_2 and Δ_3 are the bandwidths of the bands $\omega = \omega^{(1)}_{\vec{k}\sigma}$, $\omega = \omega^{(2)}_{\vec{k}\sigma}$, and $\omega = \omega^{(3)}_{\vec{k}\sigma}$ respectively.

[b] Calculations are performed for $T_o = 0$, $I = 10$ eV, $z = 12$, $\langle n_{-\sigma} \rangle = n/2 = 0.5$, and the bandwidth of the unperturbed band ($\omega = \epsilon_{\vec{k}}$) is taken equal to 4.0 eV.

Table 3.2: Positions of infinities of $g(\omega, \langle n_{-\sigma} \rangle)^a$

K (eV)	ω^+ (eV)	ω^- (eV)
0.0	5.0	5.0
0.1	8.12	3.08
0.5	14.24	1.76
1.0	20.80	1.20
2.0	33.25	0.75
3.0	45.45	0.55

[a] Calculations are performed for $T_0 = 0$, $I = 10$ eV, $\langle n_{-\sigma} \rangle = n/2 = 0.5$ and $z = 12$.

Table 3.3: Critical value n_c for different values of K[a]

n_c	K (eV)
1.0	0.0
0.84	0.1
0.58	0.5
0.35	1.0
0.21	2.0
0.16	3.0

[a] Calculations are performed for $T_0 = 0$, $I = 10$ eV, $\langle n_{-\sigma} \rangle = \langle n_{\sigma} \rangle = n/2$, $z = 12$, and the bandwidth of the unperturbed band equal to 4 eV.

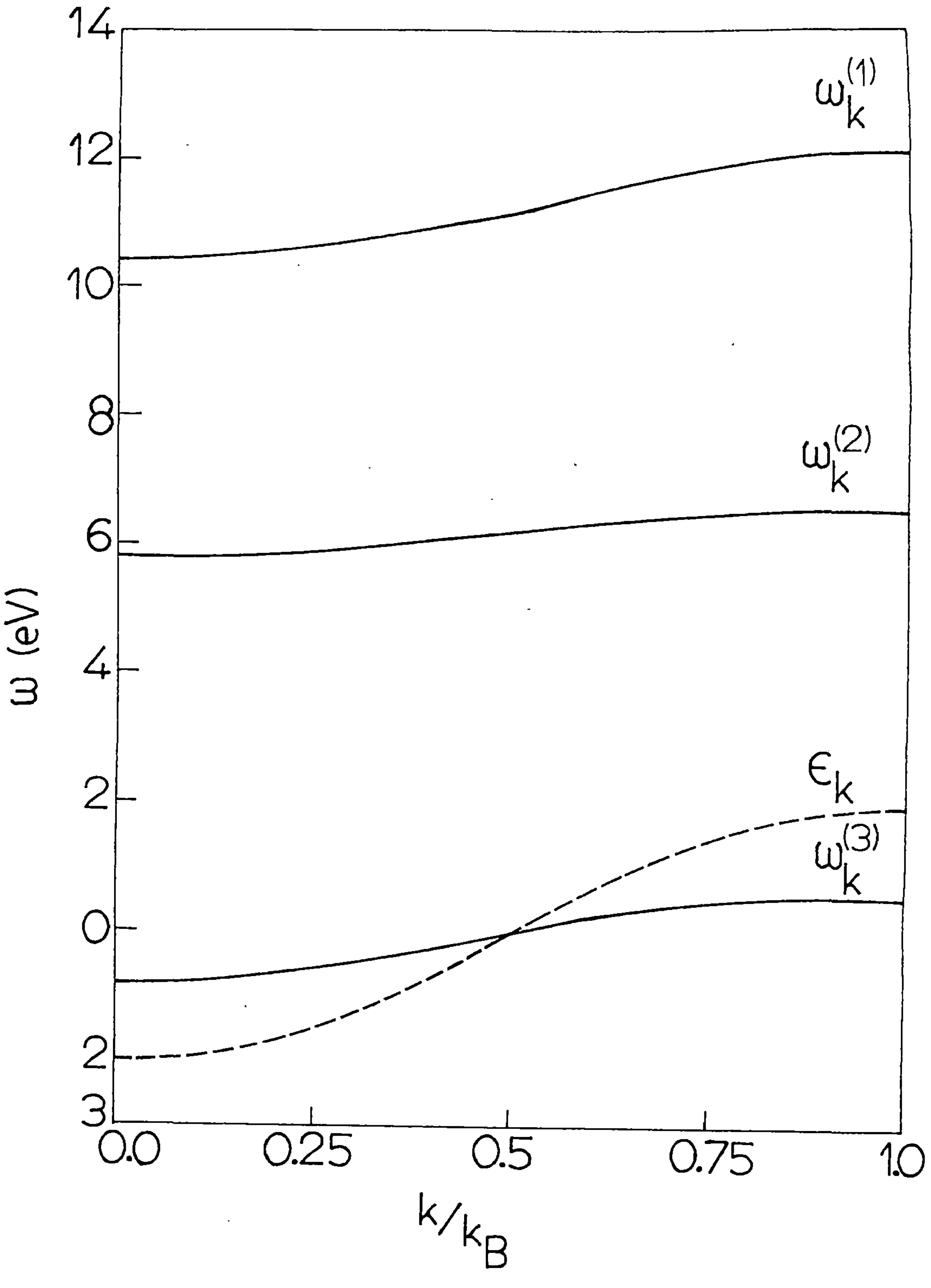

FIG. 3.1 TYPICAL PERTURBED BAND STRUCTURE IS SHOWN. $\omega = \omega_{k\sigma}^{(1)}$, $\omega_{k\sigma}^{(2)}$, AND $\omega = \omega_{k\sigma}^{(3)}$ ARE THREE PERTURBED ENERGY BANDS. DASHED CURVE REPRESENTS THE UNPERTURBED BAND. k_B IS THE WAVE VECTOR AT THE BOUNDARY OF THE BRILLOUIN ZONE. THE PARAMETERS CORRESPONDING TO THIS FIGURE ARE $I = 10eV$, $k = 0{\cdot}1eV$, $z = 12$, $\langle n_{-\sigma} \rangle = \frac{1}{2} n = 0{\cdot}5$.

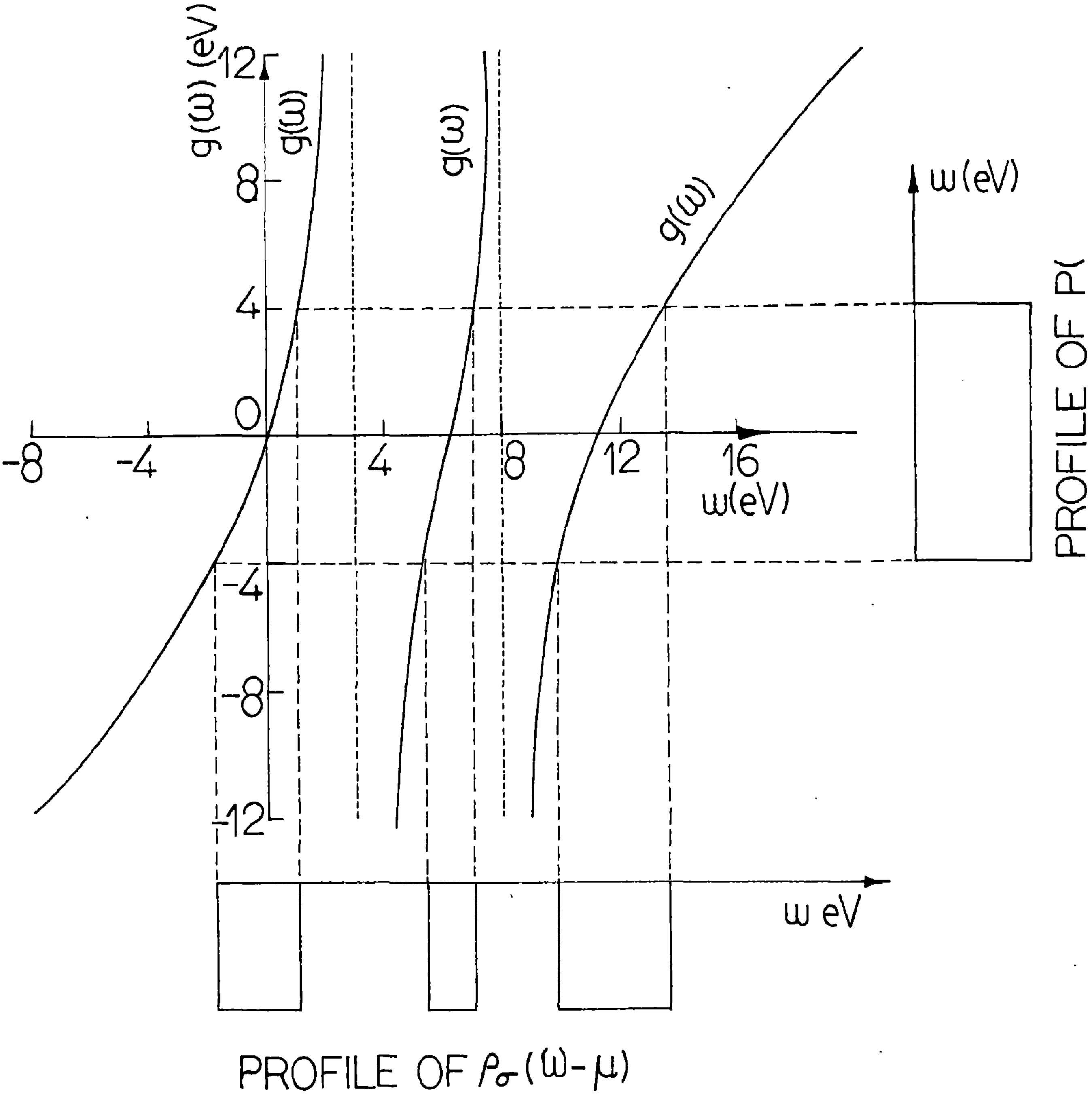

FIG. 3.2 TYPICAL $g(\omega,\langle n_{-\sigma}\rangle)$ CURVE IS SHOWN. THE PROJECTION OF THE UNPERTURBED DENSITY-OF-STATES FUNCTION $P(\omega)$ INTO THE PERTURBED DENSITY OF STATES $\rho_\sigma(\omega-\mu)$ IS INDICATED. THE PARAMETERS CORRESPONDING TO THIS FIGURE ARE THE SAME AS IN FIG. 3·1.

CHAPTER IV

THE DYNAMICAL SUSCEPTIBILITY IN NARROW ENERGY BANDS

I. INTRODUCTION

The dynamical susceptibility $\chi(\vec{q},\omega)$ of a metal is a quantity of considerable interest because it can be used to discuss a variety of problems:[6] it determines the cross section for inelastic scattering of neutrons, its poles give the frequencies of the spin waves and the condition $\chi^{-1}(\vec{q}, 0) = 0$ gives the criteria for the stability of magnetic phases. The properties of $\chi(\vec{q}, \omega)$ for the itinerant electron model based on the Hubbard Hamiltonian have been discussed within the random phase approximation by Izuyama et al.[61] and Doniach.[107] The validity of random phase approximation (RPA) is doubtful in the strongly correlated systems. Recently Sakurai,[39] and Hubbard and Jain[41] have gone beyond RPA to treat the strongly correlated systems.

The Hubbard Hamiltonian takes into account only the intraatomic interaction. The effect of inclusion of interatomic interactions on the Hubbard Hamiltonian has been discussed by several authors.[50-53] However there has been no systematic investigation on the dynamical susceptibility for a Hamiltonian which takes into account both intra as well as interatomic interactions.*

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* Englert and Antonoff (ref.62) have discussed the dynamical susceptibility within RPA by taking into account the interatom interactions.

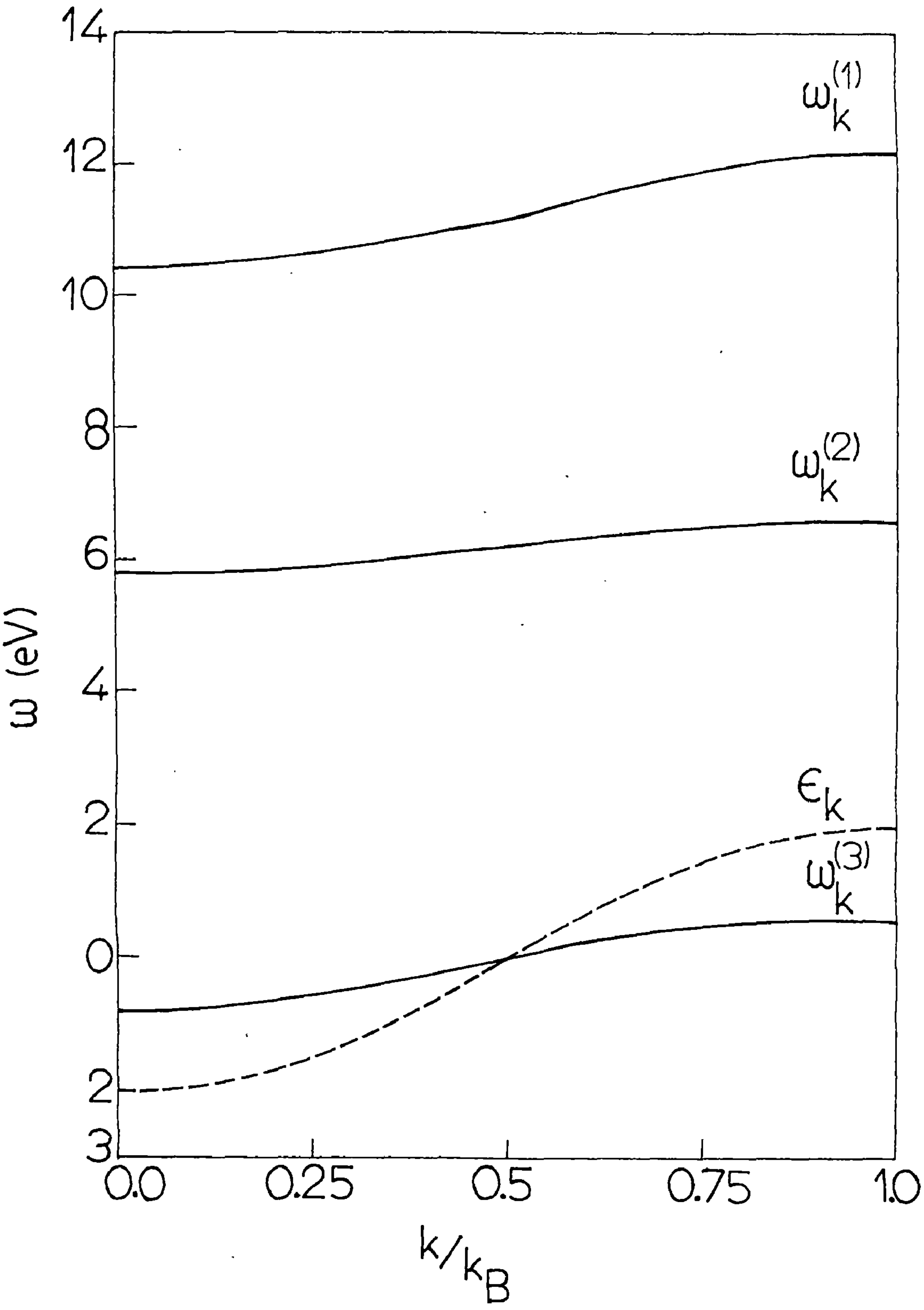

FIG. 3.1 TYPICAL PERTURBED BAND STRUCTURE IS SHOWN. $\omega=\omega_{k\sigma}^{(1)}$, $\omega_{k\sigma}^{(2)}$, AND $\omega=\omega_{k\sigma}^{(3)}$ ARE THREE PERTURBED ENERGY BANDS. DASHED CURVE REPRESENTS THE UNPERTURBED BAND. k_B IS THE WAVE VECTOR AT THE BOUNDARY OF THE BRILLOUIN ZONE. THE PARAMETERS CORRESPONDING TO THIS FIGURE ARE $I=10eV$, $k=0{\cdot}1eV$, $z=12$, $\langle n_{-\sigma}\rangle=\frac{1}{2}n=0{\cdot}5$.

assumption in narrow energy bands.

We concentrate our attention to the dynamical susceptibility $\chi_{-+}(\vec{q}, \omega)$ corresponding to a process with spin flip. It is given by [61]

$$\chi_{-+}(\vec{q}, \omega) = -2\pi (g\mu_B N)^2 \langle\langle n^{-}(\vec{q})^{+} , n^{+}(\vec{q})^{-} \rangle\rangle_{-\omega}(\eta = -1), \tag{4.2}$$

where g is the gyromagnetic ratio of an electron and μ_B is the Bohr magneton. The spin density operators $n^{\sigma}(\vec{q})^{\sigma'}$ are defined as

$$n^{\sigma}(\vec{q})^{\sigma'} = \frac{1}{N} \sum_{\vec{k}} n_{\vec{k}}^{\sigma\sigma'}(\vec{q}) \tag{4.3}$$

$$n_{\vec{k}}^{\sigma\sigma'}(\vec{q}) = a^{\dagger}_{\vec{k}+\vec{q}\sigma} \; a_{\vec{k}\sigma'} .$$

The Bloch operators $a_{\vec{k}\sigma}$ and $a^{\dagger}_{\vec{k}\sigma}$ are defined by

$$\begin{aligned} a_{\vec{k}\sigma} &= \frac{1}{\sqrt{N}} \sum_{i} e^{i\vec{k}.\vec{R}i} \, a_{i\sigma} , \\ a^{\dagger}_{\vec{k}\sigma} &= \frac{1}{\sqrt{N}} \sum_{i} e^{-i\vec{k}.\vec{R}i} \, a^{\dagger}_{i\sigma} . \end{aligned} \tag{4.4}$$

We shall restrict our analyses to cases where number of electrons per atom n<1 since the cases n>1 could equivalently be treated in terms of holes in the band.

In Sec.II we obtain the dynamical susceptibility using the random phase approximation. Instability of the paramagnetic state against the ferro and the antiferromagnetic states is discussed. In Sec. III we derive an expression for the dynamical susceptibility for strongly correlated systems and discuss the stability of magnetic states and spin wave dispersions. In Sec. IV we summarize our findings.

II. WEAK INTRAATOMIC INTERACTION THEORY

For the sake of comparison with the results of the strong intraatomic interaction theory developed in the next section it is desirable to investigate the results obtained by applying the RPA which is justified only when the intraatomic interaction I is small as compared to the band width α $(I \ll \alpha)^*$. To evaluate the dynamical susceptibility $\chi^{-+}(\vec{q}, \omega)$ we follow a procedure similar to that of Izuyama et al.[61] We first evaluate the retarded Green's function

$$\langle\langle n^{-+}(\vec{q}) \, , \, n^{+-}(-\vec{q}) \rangle\rangle_{\omega} = \frac{1}{N} \sum_{\vec{k}} \langle\langle n^{-+}_{\vec{k}}(\vec{q}) \, , \, n^{+-}(-\vec{q}) \rangle\rangle_{\omega} \qquad (4.5)$$

This retarded Green's function may be obtained by its equation of motion. For each term of the sum of the right hand side

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* In fact RPA is justified when all three interactions, intratomic interaction I, interatomic Coulomb interaction V_{ij} and the interatomic exchange interaction J_{ij} are small as compared to the bandwidth α. It can be shown (Ref.34) that $I > V_{ij} > J_{ij}$. Therefore $I \ll \alpha$ implies that $V_{ij}, J_{ij} \ll \alpha$.

of (4.5) we have

$$\omega \langle\langle \overset{-+}{n}_{\vec k}(\vec q)\ ,\ \overset{+-}{n}(-\vec q)\ \rangle\rangle_\omega = \frac{1}{2\pi}\langle[\overset{-+}{n}_{\vec k}(\vec q)\ ,\ \overset{+-}{n}(-\vec q)\,]_-\rangle$$

$$+\ \langle\langle[\overset{-+}{n}_{\vec k}(q)\ ,\ H'\,]_-,\ \overset{+-}{n}(-\vec q)\ \rangle\rangle_\omega\ .$$

(4.6)

For the Hamiltonian (4.1) the commutator $[\overset{-+}{n}_{\vec k}(q),\ H']_-$ consists of many terms and a rigorous treatment is prohibitively difficult. Accordingly we retain only those terms that can be transformed into a form like $a^{\dagger}_{\vec k\sigma}\ a_{\vec k\sigma}\ \ \overset{-+}{n}_{\vec k'}(\vec q)$ and ignore rest of them. Further the chain of successive Green's functions is cut off by the approximation.

$$\langle\langle a^{\dagger}_{\vec k\sigma}\ a_{\vec k\sigma}\ \overset{-+}{n}_{\vec k'}(\vec q)\ ,\ \overset{+-}{n}(-\vec q)\ \rangle\rangle_\omega \simeq \langle a^{\dagger}_{\vec k\sigma}\ a_{\vec k\sigma}\rangle\ \langle\langle \overset{-+}{n}_{\vec k'}(\vec q), \overset{+-}{n}(-\vec q)\rangle\rangle_\omega\ .$$

(4.7)

In this approximation, which is called RPA, the equation of motion (4.6) reduces to the form

$$\omega \langle\langle \overset{-+}{n}_{\vec k}(\vec q)\ ,\ \overset{+-}{n}(-\vec q)\ \rangle\rangle_\omega = \frac{1}{2\pi}\ \langle[\overset{-+}{n}_{\vec k}(\vec q),\ \overset{+-}{n}(-\vec q)\,]_-\ \rangle$$

$$+\Big[\epsilon_{\vec k} - \epsilon_{\vec k+\vec q} - (I+J_o)\ \sum_{\sigma}\sigma\,\langle\overset{\sigma\sigma}{n}(o)\rangle$$

$$+\ \frac{1}{N}\sum_{\vec k_1\sigma}(J_{\vec k_1-\vec k} - J_{\vec k_1-\vec k-\vec q})\langle a^{\dagger}_{\vec k_1\sigma}\ a_{\vec k_1\sigma}\ \rangle$$

$$-\ \frac{1}{N}\sum_{\vec k_1} K_{\vec k_1-\vec k-\vec q}\,\langle a^{\dagger}_{\vec k_1+}\ a_{\vec k_1+}\ \rangle$$

$$+ \frac{1}{N} \sum_{\vec{k}_1} K_{\vec{k}_1-\vec{k}} \langle a^{\dagger}_{\vec{k}_1-} \, a_{\vec{k}_1-} \rangle \Big] \langle\langle \overset{-+}{n}_{\vec{k}}(\vec{q}), \overset{+-}{n}(-\vec{q}) \rangle\rangle_{\omega}$$

$$+ \frac{1}{N} (I+J_q)(\langle a^{\dagger}_{\vec{k}+} \, a_{\vec{k}+} \rangle - \langle a^{\dagger}_{\vec{k}+\vec{q}-} \, a_{\vec{k}+\vec{q}-} \rangle)$$

$$\times \sum_{\vec{k}} \langle\langle \overset{-+}{n}_{\vec{k}}(\vec{q}) \, , \overset{+-}{n}(-\vec{q}) \rangle\rangle_{\omega}$$

$$+ \frac{1}{N} \sum_{\vec{k}_1} K_{\vec{k}_1-\vec{k}} (\langle a^{\dagger}_{\vec{k}_1+} \, a_{\vec{k}_1+} \rangle - \langle a^{\dagger}_{\vec{k}_1+\vec{q}-} a_{\vec{k}_1+\vec{q}-} \rangle)$$

$$\times \langle\langle \overset{-+}{n}_{\vec{k}_1}(\vec{q}) \, , \overset{+-}{n}(-\vec{q}) \rangle\rangle_{\omega} \quad , \qquad (4.8)$$

$K_{\vec{k}}$ and $J_{\vec{k}}$ are defined by

$$K_{ij} = \frac{1}{N} \sum_{\vec{k}} K_{\vec{k}} \, e^{i\vec{k}.(\vec{R}_i-\vec{R}_j)} \, , \qquad (4.9)$$

$$J_{ij} = \frac{1}{N} \sum_{\vec{k}} J_{\vec{k}} \, e^{i\vec{k}.(\vec{R}_i-\vec{R}_j)} \, . \qquad (4.10)$$

The quantities $V_{\vec{k}}$, $J_{\vec{k}}$ vary from $-V_o$,$-J_o$ to V_o,J_o inside a Brillouin zone. Hence one may expect the terms, which contain V's and J's under the summation sign, quite small in comparison to other terms. We neglect these terms and hope that such an approximation will not affect qualitatively the nature of the solutions because these solutions involve linear combination of the Green's functions $\langle\langle \overset{-+}{n}_{\vec{k}}(\vec{q}) , \overset{+-}{n}(-\vec{q}) \rangle\rangle_{\omega}$ for all $\vec{k}$.[62] By incorporating this approximation in Eq.(4.8) we get

$$\Big\{\omega - \epsilon_{\vec{k}} + \epsilon_{\vec{k}+\vec{q}} + (I + J_0) \sum_{\sigma} \sigma \langle \overset{\sigma\sigma}{n}(0) \rangle \Big\} \langle\langle \overset{-+}{n}_{\vec{k}}(\vec{q}) , \overset{+-}{n}(-\vec{q}) \rangle\rangle_{\omega}$$

$$= \frac{1}{2\pi} \langle [\overset{-+}{n}_{\vec{k}}(\vec{q}) , \overset{+-}{n}(-\vec{q})]_{-} \rangle$$

$$+ (I + J_{\vec{q}}) (\langle a^{\dagger}_{\vec{k}+} a_{\vec{k}+} \rangle - \langle a^{\dagger}_{\vec{k}+\vec{q}-} a_{\vec{k}+\vec{q}-} \rangle)$$

$$\times \langle\langle \overset{-+}{n}(\vec{q}), \overset{+-}{n}(-\vec{q}) \rangle\rangle_{\omega} .$$

Dividing both sides of this equation by $\Big\{\omega - \epsilon_{\vec{k}} + \epsilon_{\vec{k}+\vec{q}} + (I+J_0) \sum_{\sigma} \sigma \langle \overset{\sigma\sigma}{n}(0) \rangle \Big\}$ and summing up over all wave vector $\vec{k}$ we obtain the Green's function $\langle\langle \overset{-+}{n}(q), \overset{+-}{n}(-q) \rangle\rangle_{\omega}$ and hence the dynamical susceptibility

$$\chi_{-+}(\vec{q},\omega) = \frac{-g^2 \mu_B^2 \; \Gamma_{-+}(\vec{q},\omega)}{1 + \dfrac{I + J_{\vec{q}}}{N} \; \Gamma_{-+}(\vec{q},\omega)} , \qquad (4.12)$$

where $$\Gamma_{-+}(\vec{q},\omega) = \sum_{\vec{k}} \frac{\langle a^{\dagger}_{\vec{k}+\vec{q}-} a_{\vec{k}+\vec{q}-} \rangle - \langle a^{\dagger}_{\vec{k}+} a_{\vec{k}+} \rangle}{-\omega - \epsilon_{\vec{k}} + \epsilon_{\vec{k}+\vec{q}} + (I + J_0) \sum_{\sigma} \sigma \langle \overset{\sigma\sigma}{n}(0) \rangle} , \qquad (4.13)$$

An expression similar to (4.12) has also been obtained by Englert and Antonoff.[62] In absence of interatomic interactions it reduces to an expression obtained by Izuyama et al.[61] The averages $\langle a^{\dagger}_{\vec{k}\sigma} a_{\vec{k}\sigma}\rangle$ appearing in Eq.(4.13) can be obtained from the knowledge of one particle Green's function $\langle\langle a_{\vec{k}\sigma}, a^{\dagger}_{\vec{k}\sigma}\rangle\rangle_{\omega}$, $(\eta = +1)$. for the Hamiltonian (4.1), its equation of motion is given by

$$(\omega + \mu - \epsilon_{\vec{k}})\langle\langle a_{\vec{k}\sigma}, a^{\dagger}_{\vec{k}\sigma}\rangle\rangle_{\omega} = \frac{1}{2\pi} + \frac{I}{N}\sum_{\vec{k}_1\vec{k}_2} \langle\langle a^{\dagger}_{\vec{k}_1-\sigma} a_{\vec{k}+\vec{k}_1-\vec{k}_2-\sigma} a_{\vec{k}_2\sigma}, a^{\dagger}_{\vec{k}\sigma}\rangle\rangle_{\omega}$$

$$+ \frac{1}{N}\sum_{\substack{\vec{k}_1\vec{k}_2\\ \sigma_1}} K_{\vec{k}_1} \langle\langle a_{\vec{k}_2\sigma_1} a_{\vec{k}_1+\vec{k}_2\sigma_1} a_{\vec{k}-\vec{k}_1\sigma}, a^{\dagger}_{\vec{k}\sigma}\rangle\rangle_{\omega}$$

$$+ \frac{1}{N}\sum_{\substack{\vec{k}_1\vec{k}_2\\ \sigma_1}} J_{\vec{k}_1} \langle\langle a^{\dagger}_{\vec{k}_2\sigma_1} a_{\vec{k}-\vec{k}_1\sigma_1} a_{\vec{k}_1+\vec{k}_2\sigma}, a^{\dagger}_{\vec{k}\sigma}\rangle\rangle_{\omega} .$$

(4.14)

We decouple the higher order Green's functions according to the following scheme

$$\langle\langle a^{\dagger}_{\vec{k}_1\sigma_1} a_{\vec{k}_2\sigma_1} a_{\vec{k}_3\sigma}, a^{\dagger}_{\vec{k}\sigma}\rangle\rangle_{\omega}$$

$$\simeq \langle n_{\vec{k}_1\sigma_1}\rangle \Big[\delta_{\vec{k}_1\vec{k}_2} \langle\langle a_{\vec{k}_3\sigma}, a^{\dagger}_{\vec{k}\sigma}\rangle\rangle_{\omega}$$

$$- \delta_{\vec{k}_1\vec{k}_3}\,\delta_{\sigma_1\sigma} \langle\langle a_{\vec{k}_2\sigma}, a^{\dagger}_{\vec{k}\sigma}\rangle\rangle_{\omega}\Big] ,$$

(4.15)

When we incorporate this approximation, called the Hartree-Fock approximation, in Eq.(4.14), we obtain the Green's function $\langle\langle a_{\vec{k}\sigma}, a^{\dagger}_{\vec{k}\sigma}\rangle\rangle_{\omega}$ as

$$\langle\langle a_{\vec{k}\sigma}, a^{\dagger}_{\vec{k}\sigma}\rangle\rangle_{\omega} = \frac{1/2\pi}{\left\{\omega+\mu-\epsilon_{\vec{k}} - I\langle n^{-\sigma-\sigma}(o)\rangle - K_o n + J_o\langle n^{\sigma\sigma}(o)\rangle - \frac{1}{N}\sum\limits_{\vec{k}_1} K_{\vec{k}-\vec{k}_1}\langle a^{\dagger}_{\vec{k}_1-\sigma}\ a_{\vec{k}_1-\sigma}\rangle\right\}} \qquad (4.16)$$

where $n = \sum\limits_{\sigma}\langle n^{\sigma\sigma}(o)\rangle$. If we neglect the last term in the denominator as we have done earlier to obtain the dynamical susceptibility, we get

$$\langle\langle a_{\vec{k}\sigma}, a^{\dagger}_{\vec{k}\sigma}\rangle\rangle_{\omega} = \frac{1/2\pi}{\omega+\mu-\epsilon_{\vec{k}} - I\langle n^{-\sigma-\sigma}(o)\rangle - K_o n + J_o(n^{\sigma\sigma}(o)\rangle} . \qquad (4.17)$$

By substituting the value of $\langle a_{\vec{k}\sigma}, a^{\dagger}_{\vec{k}\sigma}\rangle\rangle_{\omega}$ in Eq. (1.14) we obtain

$$\langle a^{\dagger}_{\vec{k}\sigma}\ a_{\vec{k}\sigma}\rangle = f(\epsilon_{\vec{k}} + I\langle n^{-\sigma-\sigma}(o)\rangle + K_o n - J_o\langle n^{\sigma\sigma}(o)\rangle - \mu), \qquad (4.18)$$

where $f(\omega) = (e^{\beta\omega} + 1)^{-1}$.

The denominator of the susceptibility (4.12), gives the dispersion relations of spin waves and the conditions for the stability of magnetic phases. Spin wave excitations have been discussed by Englert and Antonoff[62] and Izuyama et al.[61] Recently Penn[77] has discussed the stability of magnetic phases for Hubbard model in the self consistent field approximation. Here we shall discuss the effect of interatomic interactions on the instability of the paramagnetic state against the ferro and the antiferromagnetic states. The instability of the paramagnetic state against a spin density of wave vector $\vec{q}$ occurs when the susceptibility $\chi(\vec{q},o) = \chi_{-+}(\vec{q},o)$ in the paramagnetic state diverges. From Eq.(4.12) the paramagnetic susceptibility $\chi(\vec{q},o)$ is given by

$$\chi(\vec{q},o) = \frac{-g^2\mu_B^2 \; \Gamma(\vec{q},o)}{1+ \dfrac{I + J_{\vec{q}}}{N} \; \Gamma(\vec{q},o)} \tag{4.19}$$

$$\text{where } \Gamma(\vec{q},o) = \sum_{\vec{k}} \frac{\langle a^{\dagger}_{\vec{k}+\vec{q}} \; a_{\vec{k}+\vec{q}} \rangle - \langle a^{\dagger}_{\vec{k}} \; a_{\vec{k}} \rangle}{\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}}} \tag{4.20}$$

$$\text{and } \langle a^{\dagger}_{\vec{k}} \, a_{\vec{k}} \rangle = f \left\{ \epsilon_{\vec{k}} + (I + 2K_o - J_o) \frac{n}{2} - \mu \right\} \tag{4.21}$$

Instability of the paramagnetic state against the spin density wave of wave vector $\vec{q}$ occurs when

$$1 + \frac{I + J_{\vec{q}}}{N} \sum_{\vec{k}} \frac{\langle a^{\dagger}_{\vec{k}+\vec{q}} \; a_{\vec{k}+\vec{q}} \rangle - \langle a^{\dagger}_{\vec{k}} \; a_{\vec{k}} \rangle}{\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}}} \leq 0$$

In the absence of interatomic interactions this result reduces to that obtained by Morris and Cornwell.[40] For a fixed value of n, the chemical potential μ is determined by

$$\frac{n}{2} = \frac{1}{N} \sum_{\vec{k}} f\left\{ \epsilon_{\vec{k}} + (I + 2K_o - J_o)\frac{n}{2} - \mu \right\} \tag{4.22}$$

A. Instability of the Paramagnetic State against the Ferromagnetic state

(i) Zero bandwidth case

The paramagnetic instability against the ferromagnetic state occurs when the static susceptibility $\chi(oo)$ in the paramagnetic state diverges. From Eqs.(4.19) - (4.21), $\chi(oo)$ is given by

$$\chi(oo) = \frac{-g^2 \mu_B^2 \, \Gamma(oo)}{1 + \frac{I + J_o}{N} \Gamma(oo)} \tag{4.23}$$

where
$$\Gamma(oo) = \sum_{\vec{k}} \frac{\partial \langle a^{\dagger}_{\vec{k}} a_{\vec{k}} \rangle}{\partial \epsilon_{\vec{k}}}$$

$$= \beta \sum_{\vec{k}} \frac{e^{\beta\left\{ \epsilon_{\vec{k}} + (I + 2K_o - J_o)\frac{n}{2} - \mu \right\}}}{\left[e^{\beta\left\{ \epsilon_{\vec{k}} + (I + 2K_o - J_o)\frac{n}{2} - \mu \right\}} + 1 \right]^2} \tag{4.24}$$

For zero bandwidth $\epsilon_{\vec{k}} = 0$ for all $\vec{k}$. From Eq.(4.22)

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$$\frac{n}{2} = \frac{1}{e^{\beta\{(I + 2K_o - J_o)\frac{n}{2} - \mu\}} + 1.}$$

Therefore from (4.24), we get

$$\Gamma(oo) = -\frac{\beta N(2-n)n}{4}$$

which on substituting in (4.23) gives

$$\chi(oo) = \frac{C}{T - T_c} \tag{4.25}$$

where $C = \dfrac{Ng^2\mu_B^2\ (2-n)\,n}{4k_B}$ and $T_c = \dfrac{(I + J_o)\ (2-n)\,n}{4k_B}$

are the Curie constant and the Curie temperature respectively. In the absence of intraatomic interaction I and for one electron per atom $(n = 1)$ the value of T_c is given by $J\beta_c = 4/z$ where J $(J = J_o/z)$ is the nearest neighbor exchange interaction and z is the number of nearest neighbors. For sc, bcc and fcc lattices the values of $J\beta_c$ are 0.66, 0.5 and 0.33 respectively. These values can be compared with values 0.5972, 0.3903 and 0.2492 obtained by high temperature series expansion of the susceptibility for the spin 1/2 Heisenberg model.[108] The values of $J\beta_c$ obtained here are just double of those obtained by the molecular field theory of the Heisenberg model.

(ii) Finite Bandwidth Case

(a) Zero Temperature theory

At absolute zero of temperature, the occupation number $\langle a^{\dagger}_{\vec{k}} a_{\vec{k}} \rangle$ can be written as

$$\langle a^{\dagger}_{\vec{k}} a_{\vec{k}} \rangle = \theta\{\mu - \epsilon_{\vec{k}} - (I + 2K_o - J_o)\, n/2\} \qquad (4.26)$$

Therefore from Eq.(4.23) and (4.24), the susceptibility (oo) is given by

$$\chi(oo) = \frac{N g^2 \mu_B^2\, \rho\{\mu - (I + 2K_o - J_o)\, n/2\}}{1 - (I + J_o)\, \rho\{\mu - (I + 2K_o - J_o)\, n/2\}} \qquad (4.27)$$

where $\rho(\omega) = \frac{1}{N} \sum_{\vec{k}} \delta(\omega - \epsilon_{\vec{k}})$ is the density of states for the band $\epsilon_{\vec{k}}$. The denominator of Eq.(4.27) gives the Stoner criterion for the instability of the paramagnetic state.

$$1 - (I + J_o)\rho\{\mu - (I + 2K_o - J_o)\, n/2\} \leqslant 0 \qquad (4.28)$$

(b) Finite temperature theory

At finite temperature we shall consider only the half filled band case (n = 1). In this case Eqs.(4.22) - (4.24) are considerably simplified . Indeed (4.22) is satisfied for $\mu = (I + 2K_o - J_o)\, n/2$ and Eq.(4.23) takes the form

$$\chi(oo) = \frac{g^2\mu_B^2\,\beta \sum\limits_{\vec{k}} \dfrac{e^{\beta\epsilon_{\vec{k}}}}{(e^{\beta\epsilon_{\vec{k}}}+1)^2}}{1 - \dfrac{\beta(I+J_o)}{N}\sum\limits_{\vec{k}} \dfrac{e^{\beta\epsilon_{\vec{k}}}}{(e^{\beta\epsilon_{\vec{k}}}+1)^2}} \qquad (4.29)$$

Instability of the paramagnetic state occurs at

$$1 - \frac{\beta(I+J_o)}{N}\sum_{\vec{k}} \frac{e^{\beta\epsilon_{\vec{k}}}}{(e^{\beta\epsilon_{\vec{k}}}+1)^2} = 0$$

For square density of states,

$$\begin{aligned}\rho(\omega) &= 1/\alpha \quad \text{if } -\alpha/2 < \omega < \alpha/2 \\ &= 0 \qquad \text{Otherwise},\end{aligned}$$

it gives the Curie temperature as

$$T_c = \frac{\alpha}{4k_B\tanh^{-1}\left\{\dfrac{\alpha}{(I+J_o)}\right\}} \qquad (4.30)$$

In Fig.4.1 we have shown the variation of $4k_BT_c/I$ as a function of α/I for various values of J_o/I. General features of the curves show that as the bandwidth increases the transition temperature decreases.

B. Instability of the Paramagnetic State against the Antiferromagnetic State

(i) Zero bandwidth case

Instability of the paramagnetic state against the antiferromagnetic state occurs when the denominator of the paramagnetic susceptibility $\chi(\vec{Q},o)$ becomes zero. Here $\vec{Q}$ is half the reciprocal lattice vector. From Eqs.(4.19) - (4.21) we have

$$\chi(\vec{Q},o) = \frac{g^2\mu_B^2 \sum_{\vec{k}\sigma} \sigma f\left\{-\sigma\epsilon_{\vec{k}} + (I + 2K_o - J_o)\, n/2\right\} / 2\epsilon_{\vec{k}}}{1 - \frac{I-J_o}{N} \sum_{\vec{k}\sigma} \sigma f\left\{-\sigma\epsilon_{\vec{k}} + (I+2K_o-J_o)n/2\right\} / 2\epsilon_{\vec{k}}} \tag{4.31}$$

Here we have made use of the fact that $\epsilon_{\vec{k}+\vec{Q}} = -\epsilon_{\vec{k}}$ and $J_{\vec{Q}} = -J_o$ when T_{ij} and J_{ij} are nonzero only when i and j are nearest neighbor lattice sites. For $\epsilon_{\vec{k}} = 0$, with the help of Eq.(4.22), the above expression reduces to the Curie Weiss law

$$\chi(\vec{Q},0) = \frac{C}{T - T_N} \tag{4.32}$$

where the Neel temperature $T_N = \dfrac{(I - J_o)\beta(2-n)n}{4k_B}$. If we compare the Neel temperature T_N with the Curie temperature T_c obtained in the section A, we see that for positive J_o, $T_c > T_N$ and for negative J_o, $T_c < T_N$. This result can only be obtained by the combined effect of intraatomic and interatomic exchange interactions. Either of these two interactions alone cannot give such type of behavior. This behavior of the model suggests that perhaps the combined effect of intra as well as interatomic interactions may be fruitful to explain the magnetic phase diagrams of the rare earth elements.[109]

(ii) Finite Bandwidth Case

(a) Zero temperature theory

From Eq.(4.31), at absolute zero the instability of the paramagnetic state is given by

$$1-\frac{I-J_0}{2}\int d\epsilon\,\frac{\rho(\epsilon)}{\epsilon}\sum_{\sigma}\sigma\quad\theta\{-\sigma\epsilon+-(I+2K_0-J_0)n/2\}<0 \tag{4.33}$$

For square density of states it reduces to

$$\frac{I}{\alpha}\geqslant\frac{J_0}{\alpha}+\frac{1}{\ln|(1-n)|} \tag{4.34}$$

The sign of equality in (4.34) gives the boundary line between the para and the antiferromagnetic states. In Fig.4.2 we have plotted I/α versus n for various values of J_0/α. In the region above the dashed curves antiferromagnetic states are more stable than the paramagnetic state while in the region below the dashed curves the paramagnetic states are more stable than the antiferromagnetic states. We have also shown by solid line the boundary between the para and the ferromagnetic states (from (4.28) for square density of states the boundary line between para and ferromagnetic state is given by $I/\alpha = 1 - J_0/\alpha$). The region above the solid lines corresponds to the stability of the ferromagnetic state against the paramagnetic state and in the region below the solid lines the reverse holds good. These curves show that positive values of J_0 are favorable to the ferromagnetism while antiferromagnetism is favored for negative values of J_0. For half filled band the paramagnetic state is always unstable against the ferro or antiferromagnetic states where $1 < J_0/\alpha < 0$, for $< J_0/\alpha < 1$ paramagnetic state is more stable than both ferro and antiferromagnetic states when $I/\alpha < 1 - J_0/\alpha$. Thus the prediction of Penn that for half filled band the paramagnetic state is not possible, no more holds good when we take interatomic interaction into account.

(b) Finite temperature theory

For half filled band, from Eq.(4.31) the instability of paramagnetic state against the antiferromagnetic state is given by

$$1 - \frac{I - J_0}{2N} \sum_{\vec{k}} \frac{\tanh \beta \, \epsilon_{\vec{k}}/2}{\epsilon_{\vec{k}}} \leq 0 \qquad (4.35)$$

In the absence of interatomic interactions, this inequality has recently been obtained by Langer et al.[93] For simple cubic lattice they have plotted the transition temperature as a function I. From ~~his~~ their curve it is clear that if we replace I by $(I - J_o)$, then for each value of I the transition temperature decreases for positive J_o and increases for negative J_o.

III. STRONG INTRAATOMIC INTERACTION THEORY

In this section we develop a theory for the systems where the intraatomic interaction I is very large in absolute magnitude as compared to the interatomic couplings T_{ij}, K_{ij} and J_{ij}. In Hamiltonian (4.1) I represants the energy required to bring two electrons into the same atomic state consequently for sufficiently large I ($\gg |T_{ij}|, |K_{ij}|, |J_{ij}|$ such doubly occupied atomic states cannot occur in the low lying states of the entire system. Because of the exclusion of doubly occupied states, the intraatomic interactions serve to reduce the phase space available to the electronic system. In order to formulate this effect we first represent the states that are available to the system as vectors in a Hilbert space S_o. Correspondingly, the observable are represented by a set of operators Q_o On S_o. We then take account of the fact that the intraatomic interaction exclude state vectors from a well defined set in S_o, which means that they confine the states to a subspace, S of S_o. Consequently the observables are now represented by operators Q on S. These are related to the corresponding primitive operators Q_o by the formula.

$$Q = PQ_oP \tag{4.36}$$

where P is the projection operator for S. The algebra of the set Q is quite different from that of Q_o. This difference represents the changes in the properties of the system due to correlations introduced by intraatomic interaction. In otherwords the effect of intraatomic interaction is built into our formalism through the new algebra of the operators on the reduced Hilbert space S.

Let $b_{\vec{k}\sigma}$, $b^{\dagger}_{\vec{k}\sigma}$ and $\overset{\sigma\sigma'}{\nu}(\vec{k})$ be the operators in the subspace S corresponding to the operators $a_{\vec{k}\sigma}$, $a^{\dagger}_{\vec{k}\sigma}$ and $\overset{\sigma\sigma'}{n}(\vec{k})$ in the space S_o. It can be shown that the operators $b_{\vec{k}\sigma}$, $b^{\dagger}_{\vec{k}\sigma}$ and $\overset{\sigma\sigma'}{\nu}(\vec{k})$ satisfy the algebraic relations[51]

$$[b_{\vec{k}\sigma}, b^{\dagger}_{\vec{k}'\sigma'}]_+ = (\delta_{\vec{k}\vec{k}'} - \overset{-\sigma-\sigma}{\nu}(\vec{k}'-\vec{k}))\delta_{\sigma\sigma'} + \delta_{\sigma-\sigma'}\overset{\sigma-\sigma}{\nu}(\vec{k}'-\vec{k}),$$

$$[b_{\vec{k}\sigma}, b_{\vec{k}'\sigma'}]_+ = [b^{\dagger}_{\vec{k}\sigma}, b^{\dagger}_{\vec{k}'\sigma'}]_+ = 0, \tag{4.37}$$

$$[b_{\vec{k}\sigma}, \overset{\sigma_1\sigma_2}{\nu}(\vec{k})]_- = \frac{1}{N} b_{\vec{k}-\vec{k}'\sigma_2}\delta_{\sigma\sigma_1}.$$

In terms of the operators in the subspace S the Hamiltonian (4.1) can be written as

$$H = \sum_{\vec{k}\sigma} \epsilon_{\vec{k}} b^{\dagger}_{\vec{k}\sigma} b_{\vec{k}\sigma} + N \sum_{\vec{k}} \tilde{K}_{\vec{k}} \nu_{\vec{k}} \nu_{-\vec{k}} + N \sum_{\vec{k}} \tilde{J}_{\vec{k}} \vec{S}_{\vec{k}} \cdot \vec{S}_{-\vec{k}}, \tag{4.38}$$

where
$$\tilde{K}_{\vec{k}} = \frac{2K_{\vec{k}} - J_{\vec{k}}}{4} \tag{4.39}$$

Here we discuss the dynamical susceptibility for a model Hamiltonian

$$H = \sum_{ij\sigma} T_{ij}\, a_{i\sigma}^{\dagger}\, a_{j\sigma} + \frac{I}{2} \sum_{i\sigma} n_{i\sigma}\, n_{i-\sigma}$$

$$+ \frac{1}{2} \sum_{\substack{ij \\ \sigma\sigma'}} K_{ij}\, n_{i\sigma} n_{j\sigma'} + \frac{1}{2} \sum_{\substack{ij \\ \sigma\sigma'}} J_{ij} a_{i\sigma}^{\dagger}\, a_{j\sigma'}\, a_{i\sigma'}\, a_{j\sigma} \qquad (4.1)$$

It is obtained from the one band Hamiltonian (3.1) by neglecting all V_{ijkl} corresponding to three and four center integrals. Of all the two center integrals we have retained only two of them, namely the interatomic Coulomb interaction $V_{ijji} = K_{ij}$ and the interatomic exchange interaction $V_{ijij} = J_{ij}$. This Hamiltonian differs from that of (3.2) by the inclusion of fourth term, corresponding to interatomic exchange interaction, on the right hand side of (4.1). The parameters I,K,J and T may be taken as phenomenological quantities. In relating their values to properties of real solids, one should realize that these parameters contain contributions due to indirect interactions involving other bands, for example, the interaction between magnetic electrons in a metal is screened by conduction electrons in a higher conduction band. Here we shall assume that I,K and T are positive and J is either positive or negative. We also assume that $T_{ii} = K_{ii} = J_{ii} = 0$. Throughout this treatment we shall assume that T_{ij}, K_{ij} and J_{ij} are nonzero only when i and j are nearest neighbors. It is a reasonable

$$\tilde{J}_{\vec{k}} = - J_{k/4} \tag{4.40}$$

$$\nu_{\vec{k}} = \sum_{\sigma} \overset{\sigma\sigma}{\nu}(\vec{k}), \tag{4.41}$$

and $$\vec{S}_{\vec{k}} = \sum_{\sigma} \left\{ \overset{\sigma-\sigma}{\nu}(\vec{k}), -i\sigma \overset{\sigma-\sigma}{\nu}(\vec{k}), \sigma \overset{\sigma\sigma}{\nu}(\vec{k}) \right\} . \tag{4.42}$$

The dynamical susceptibility $\chi_{-+}(\vec{q}, \omega)$ is given by

$$\chi_{-+}(\vec{q}, \omega) = - (g \mu_B N)^2 \langle\langle \overset{-+}{\nu}(\vec{q}), \overset{+-}{\nu}(-\vec{q}) \rangle\rangle_{-\omega} . \tag{4.43}$$

To evaluate $\chi_{-+}(q, \omega)$ we proceed in a manner similar to that adopted in Sec. II. We write down the equation of motion for the Green's function $\langle\langle \overset{-+}{\nu}_{\vec{k}}(\vec{q}), \overset{+-}{\nu}(-\vec{q}) \rangle\rangle_{\omega}$, $\left(\overset{\sigma\sigma'}{\nu}_{\vec{k}}(\vec{q}) = b^{\dagger}_{\vec{k}+\vec{q}\sigma} \; b_{\vec{k}\sigma'}\right)$,

$$\omega \langle\langle \overset{-+}{\nu}_{\vec{k}}(\vec{q}) , \overset{+-}{\nu}(-\vec{q}) \rangle\rangle_{\omega} = \frac{1}{2\pi} \langle \left[\overset{-+}{\nu}_{\vec{k}}(\vec{q}), \overset{+-}{\nu}(-\vec{q}) \right]_- \rangle + \langle\langle \left[\overset{-+}{\nu}_{\vec{k}}(\vec{q}), H \right]_- , \overset{+-}{\nu}(-\vec{q}) \rangle\rangle_{\omega} \tag{4.44}$$

For the Hamiltonian (4.38) we have

$$\left[\overset{-+}{\nu}_{\vec{k}}(\vec{q}), H \right]_- = - \sum_{\vec{k}_1} \epsilon_{\vec{k}_1} \left(\delta_{\vec{k}+\vec{q},\vec{k}_1} - \overset{-\sigma-\sigma}{\nu}(\vec{k}+\vec{q}-\vec{k}_1) \right) b^{\dagger}_{\vec{k}_1\sigma} \; b_{\vec{k}-\sigma}$$
$$- \sum_{\vec{k}_1} \epsilon_{\vec{k}_1} \overset{\sigma-\sigma}{\nu}(\vec{k}+\vec{q}-\vec{k}_1) \; b^{\dagger}_{\vec{k}_1-\sigma} \; b_{\vec{k}-\sigma}$$
$$- 2 \sum_{\vec{k}_1\sigma_1} \tilde{K}_{\vec{k}_1} \overset{\sigma_1\sigma_1}{\nu}(-\vec{k}_1) \; b^{\dagger}_{\vec{k}+\vec{q}+\vec{k}_1\sigma} \; b_{\vec{k}-\sigma}$$

$$- 4 \sum_{\vec{k}_1} \tilde{J}_{\vec{k}_1} \nu^{\sigma -\sigma}(-\vec{k}_1)\, b^{\dagger}_{\vec{k}+\vec{q}+\vec{k}_1 -\sigma}\, b_{\vec{k}-\sigma}$$

$$-4 \sum_{\vec{k}_1\sigma} \tilde{J}_{\vec{k}_1} \nu^{\sigma\sigma}(-\vec{k}_1)\, b^{\dagger}_{\vec{k}+\vec{q}+\vec{k}_1\sigma}\, b_{\vec{k}-\sigma}$$

$$+\epsilon_{\vec{k}}\, b^{\dagger}_{\vec{k}+\vec{q}\sigma}\, b_{\vec{k}-\sigma} - \sum_{\vec{k}_1} \epsilon_{\vec{k}_1}\, b^{\dagger}_{\vec{k}+\vec{q}\sigma}\, b_{\vec{k}_1-\sigma}\, \nu^{\sigma -\sigma}(\vec{k}_1-\vec{k})$$

$$+ \sum_{\vec{k}_1} \epsilon_{\vec{k}_1}\, b^{\dagger}_{\vec{k}+\vec{q}\sigma}\, b_{\vec{k}_1\sigma}\, \nu^{\sigma-\sigma}(\vec{k}_1-\vec{k})$$

$$+ 2\sum_{\vec{k}_1\sigma_1} \tilde{K}_{\vec{k}_1}\, b^{\dagger}_{\vec{k}+\vec{q}\sigma}\, b_{\vec{k}+\vec{k}_1-\sigma}\, \nu^{\sigma_1\sigma_1}(\vec{k}_1)$$

$$+ 4\sum_{\vec{k}_1} \tilde{J}_{\vec{k}_1}\, b^{\dagger}_{\vec{k}+\vec{q}\sigma}\, b_{\vec{k}+\vec{k}_1\sigma}\, \nu^{\sigma -\sigma}(\vec{k}_1)$$

$$- 2\sum_{\vec{k}_1\sigma} \tilde{J}_{\vec{k}_1}\, b^{\dagger}_{\vec{k}+\vec{q}\sigma}\, b_{\vec{k}+\vec{k}_1-\sigma}\, \nu^{\sigma\sigma}(\vec{k}_1) \quad .$$

The right hand side of the above equationcontains many terms so that a rigrous treatment is difficult. We retain only few terms by making on ansatz for the spin density operator

$$\nu^{\sigma\sigma'}(\vec{k}) = \nu^{\sigma\sigma'}(o)\, \delta_{\vec{k},o} + \nu^{\sigma\sigma'}(\vec{q})\, \delta_{\vec{k},\vec{q}} \qquad (4.45)$$

and replacing the operators $b^{\dagger}_{\vec{k}\sigma}\ b_{\vec{k}\sigma'}$, which are multiplied by $\nu^{\sigma-\sigma}(\vec{q})$ or $\nu^{\sigma-\sigma}_{\vec{k}}(\vec{q})$, by $\langle b^{\dagger}_{\vec{k}\sigma}\ b_{\vec{k}\sigma} \rangle \delta_{\vec{k}\vec{k}'}\delta_{\sigma\sigma'}$. In this approximation the equation of motion (4.44) becomes,

$$\omega \langle\langle \nu^{-+}_{\vec{k}}(\vec{q}), \nu^{+-}(-\vec{q})\rangle\rangle_{\omega} = \frac{1}{2\pi}\langle[\nu^{-+}_{\vec{k}}(\vec{q}) , \nu^{+-}(-\vec{q})]_{-}\rangle$$

$$+ A^{-+}_{\vec{k}\vec{q}}\langle\langle \nu^{-+}_{\vec{k}}(\vec{q}) , \nu^{+-}(-\vec{q}) \rangle\rangle_{\omega}$$

$$+ \frac{B^{-+}_{\vec{k}\vec{q}}}{N}\sum_{\vec{k}_1}\langle\langle \nu^{-+}_{\vec{k}_1}(\vec{q}) , \nu^{+-}(-\vec{q}) \rangle\rangle_{\omega} \quad (4.46)$$

$$A^{-+}_{\vec{k}\vec{q}} = \epsilon_{\vec{k}}(1-\langle \nu^{--}(o)\rangle) - \epsilon_{\vec{k}+\vec{q}}(1-\langle \nu^{++}(o)\rangle) + 4\,\tilde{J}_o \sum_{\sigma} \sigma \langle \nu^{\sigma\sigma}(o)\rangle$$

$$(4.47)$$

$$B^{-+}_{\vec{k}\vec{q}} = (\epsilon_{\vec{k}+\vec{q}} + 4\,\tilde{J}_{\vec{q}})\langle b^{\dagger}_{\vec{k}+\vec{q}-}\; b_{\vec{k}+\vec{q}-}\rangle$$

$$- (\epsilon_{\vec{k}} + 4\,\tilde{J}_{\vec{q}})\langle b^{\dagger}_{\vec{k}+}\; b_{\vec{k}+}\rangle \quad (4.48)$$

The first term on the right hand side of Eq.(4.46) is given by

$$\langle|\nu^{-+}_{\vec{k}}(\vec{q}) , \nu^{+-}(-\vec{q})|_{-}\rangle = \langle b^{\dagger}_{\vec{k}+\vec{q}-}\; b_{\vec{k}+\vec{q}-}\rangle - \langle b^{\dagger}_{\vec{k}+}\; b_{\vec{k}+}\rangle$$

$$- \sum_{\vec{k}}\Big\{\langle b^{\dagger}_{\vec{k}_1+}\; \nu^{++}(\vec{k}-\vec{k}_1)\; b_{\vec{k}+}\rangle$$

$$- \langle b^{\dagger}_{\vec{k}+\vec{q}-}\; \nu^{--}(\vec{k}_1-\vec{k})\; b_{\vec{k}_1+\vec{q}-}\rangle\Big\}$$

The correlation functions inside the curly brackets corresponds to creation of two electrons and two holes of the same spin simultaneously. We assume that there is a very small probability of occurrence of such processes and hence we neglect these terms. The equation of motion (4.46) takes the form

$$(\omega - A^{-+}_{\vec{k}\vec{q}})\,\langle\langle \nu^{-+}_{\vec{k}}(\vec{q})\,,\nu^{+-}(-\vec{q})\rangle\rangle_{\omega}$$

$$= (\langle b^{\dagger}_{\vec{k}+\vec{q}-}\;b_{\vec{k}+\vec{q}-}\rangle - \langle b^{\dagger}_{\vec{k}+}\;b_{\vec{k}+}\rangle)/2\pi$$

$$+\frac{B^{-+}_{\vec{k}\vec{q}}}{N}\sum_{\vec{k}}\langle\langle \nu^{-+}_{\vec{k}}(\vec{q})\,,\nu^{+-}(-\vec{q})\rangle\rangle_{\omega} \qquad (4.49)$$

when we devide both sides of the above equation by $(\omega - A^{-+}_{\vec{k}\vec{q}})$ and sum over $\vec{k}$, we get the Green's function $\langle\langle \nu^{-+}(\vec{q})\,,\nu^{+-}(-\vec{q})\rangle\rangle_{\omega}$ and hence the dynamical susceptibility

$$\chi_{-+}(q,\omega) = \frac{g^2\mu_B^2\sum_{k}\dfrac{\langle b^{\dagger}_{\vec{k}+\vec{q}-}\;b_{\vec{k}+\vec{q}-}\rangle - \langle b^{\dagger}_{\vec{k}+}\;b_{\vec{k}+}\rangle}{\omega + A^{-+}_{\vec{k}\vec{q}}}}{1+\dfrac{1}{N}\sum_{\vec{k}}\dfrac{B^{-+}_{\vec{k}\vec{q}}}{\omega + A^{-+}_{\vec{k}\vec{q}}}} \qquad (4.50)$$

The averages $\langle b^{\dagger}_{\vec{k}\sigma}\;b_{\vec{k}\sigma}\rangle$ can be obtained from the knowledge of one particle Green's function $\langle\langle b_{\vec{k}\sigma}\,,b^{\dagger}_{\vec{k}\sigma}\rangle\rangle_{\omega}(\eta = +1)$. It is given as[51]

$$\langle\langle b_{\vec{k}\sigma}\,,b^{\dagger}_{\vec{k}\sigma}\rangle\rangle_{\omega} = \frac{\frac{1}{2\pi}\,(1-\langle \nu^{-\sigma-\sigma}(0)\rangle)}{\omega + \mu - \epsilon_{\vec{k}}\,(1-\langle\nu^{-\sigma-\sigma}(0)\rangle) - 2\tilde{K}^{\nu}_{0} - 2\tilde{J}_{0}\sigma\sum_{\sigma}\sigma\langle\nu^{\sigma\sigma}(0)\rangle}$$

(4.51)

where $\nu = \sum_{\sigma} < \nu^{\sigma\sigma}(o) >$ is the number of electrons per atom. From the poles of the Green's function (4.51), the single particle energies are given by

$$\omega_{\vec{k}\sigma} = \epsilon_{\vec{k}} \;(1 - < \nu^{-\sigma-\sigma}(o) >) + 2\tilde{K}_o \nu + 2J_o \sigma \sum_{\sigma} \sigma \; < \nu^{\sigma\sigma}(o) > \tag{4.52}$$

In Eq.(4.52) the factor $(1 - < \nu^{-\sigma-\sigma}(o) >)$ represents a band narrowing due to restrictions imposed on the electronic motion by the exclusion of doubly occupied atomic states, while the terms $2\tilde{K}_o \nu$ and $2J_o \sigma \sum_{\sigma} \sigma < \nu^{\sigma\sigma}(o) >$ represent additional contributions to the energy of the electron due to interatomic Coulomb and exchange interactions. When we substitute the value of the Green's function in Eq.(1.14) we get the average $< b^{\dagger}_{\vec{k}\sigma} \; b_{\vec{k}\sigma} >$ as

$$< b^{\dagger}_{\vec{k}\sigma} \; b_{\vec{k}\sigma} > = (1 - < \nu^{-\sigma-\sigma}(o) >) \; f \left\{ \epsilon_{\vec{k}} \,(1 - < \nu^{-\sigma-\sigma}(o) >) + 2\tilde{K}_o \nu + 2J_o \sigma \sum_{\sigma} \sigma < \nu^{\sigma\sigma}(o) > - \mu \right\} \tag{4.53}$$

From Eq.(4.36) we have $<Q> = <Q_o>$, where on the left hand side the ensemble average is taken over the states in space S_o while on the right hand side average is over the states in subspace S. To compare the results of this section to the results of weak interaction theory, hereafter we shall replace the ensemble average of the operators in subspace S by the ensemble average of the operators in space S_o.

In the limit of zero bandwidth, the dynamical susceptibility (4.50) reduces to

$$\chi(\vec{q},\omega) = \frac{g^2\mu_B^2 \sum_\sigma \sigma \langle n^{\sigma\sigma}(o)\rangle}{(J_o - J_{\vec{q}}) \sum_\sigma \sigma \langle n^{\sigma\sigma}(o)\rangle - \omega} \qquad (4.54)$$

This is an expression which one obtains for Heisenberg model under the random phase approximation.[62] It should be noted that the dynamical susceptibility obtained in the weak interaction theory also reduces to the same form in the limit of zero bandwidth.

For a system with small number of electrons (n<<1) and $J_{\vec{q}} >> \alpha/2$, Eq.(4.50) takes the form

$$\chi_{-+}(q,\omega) = \frac{-g^2\mu_B^2 \sum_{\vec{k}} \dfrac{\langle a^{\dagger}_{\vec{k}+\vec{q}-} a_{\vec{k}+\vec{q}-}\rangle - \langle a^{\dagger}_{\vec{k}+} a_{\vec{k}+}\rangle}{-\omega - \epsilon_{\vec{k}} + \epsilon_{\vec{k}+\vec{q}} + J_o \sum_\sigma \langle n^{\sigma\sigma}(o)\rangle}}{1 + \dfrac{J_q}{N} \sum_{\vec{k}} \dfrac{\langle a^{\dagger}_{\vec{k}+\vec{q}-} a_{\vec{k}+\vec{q}-}\rangle - \langle a^{\dagger}_{\vec{k}+} a_{\vec{k}+}\rangle}{-\omega - \epsilon_{\vec{k}} + \epsilon_{\vec{k}+\vec{q}} + J_o \sum_\sigma \sigma \langle n^{\sigma\sigma}(o)\rangle}} \qquad (4.55)$$

and (4.53) becomes

$$\langle a^{\dagger}_{k\sigma} a_{k\sigma}\rangle = f\{\epsilon_k + K_o n - J_o\langle n(o)\rangle - \mu\} \qquad (4.56)$$

Eqs.(4.55) and (4.56) are the same as Eqs.(4.12) and (4.18) provided I = 0. This similarity between strong and weak intraatomic interaction theories is very similar to that pointed out by Kanamori.[33] He has shown that for a system of electrons interacting by strong intraatomic interaction, the random phase approximation is good provided the density of electrons is small and the bare intraatomic interaction is replaced by some effective intraatomic interaction.

The static paramagnetic susceptibility $\chi(\vec{q},o)$ which is needed to discuss the instability of paramagnetic state against the spin density wave of wave vector $\vec{q}$ is given by (from Eq.(4.50))

$$\chi(\vec{q},o) = \chi_{-+}(\vec{q},o) = \frac{g^2\mu_B^2 \sum_{\vec{k}} \left(\langle a^{\dagger}_{\vec{k}+\vec{q}}\, a_{\vec{k}+\vec{q}} \rangle - \langle a^{\dagger}_{\vec{k}}\, a_{\vec{k}} \rangle\right) / A_{\vec{k}\vec{q}}}{1 + \frac{1}{N} \sum_{\vec{k}} \frac{B_{\vec{k}\vec{q}}}{A_{\vec{k}\vec{q}}}} \qquad (4.57)$$

where

$$A_{\vec{k}\vec{q}} = (\epsilon_{\vec{k}} - \epsilon_{\vec{k}+q})\,(1 - n/2) \qquad (4.58)$$

$$B_{\vec{k}\vec{q}} = (\epsilon_{\vec{k}+\vec{q}} + 4J_{\vec{q}})\,\langle a^{\dagger}_{\vec{k}+\vec{q}}\, a_{\vec{k}+\vec{q}} \rangle - (\epsilon_{\vec{k}} + 4J_{\vec{q}})\langle a^{\dagger}_{\vec{k}}\, a_{\vec{k}} \rangle \qquad (4.59)$$

and $\langle a^{\dagger}_{\vec{k}}\, a_{\vec{k}} \rangle = (1-n/2)\, f\left\{ \epsilon_{\vec{k}}\,(1-n/2) + 2K_o n - \mu \right\}$ (4.60)

The chemical potential μ is determined by

$$n/2\,/(1-n/2) = \frac{1}{N}\sum_{\vec{k}} f\left\{\epsilon_{\vec{k}}(1-n/2) + 2K_o n - \mu\right\} \qquad (4.61)$$

A. Instability of the Paramagnetic State against the Ferromagnetic State

(i) Zero bandwidth Case

From Eqs. (4.57) to (4.60) the static paramagnetic susceptibility $\chi(oo)$ is given by

$$\chi(oo) = \frac{g^2\mu_B^2\,\beta\,(1-n/2)^2 \sum_{\vec{k}} \dfrac{e^{\beta\left\{\epsilon_{\vec{k}}(1-n/2) + 2\tilde{K}_o n - \mu\right\}}}{\left[1 + e^{\beta\left\{\epsilon_{\vec{k}}(1-n/2) + 2K_o n - \mu\right\}}\right]^2}}{1 - n + \dfrac{\beta(1-n/2)^2}{N}\sum_{\vec{k}} \dfrac{(\epsilon_{\vec{k}} + 4J_o)\, e^{\beta\left\{\epsilon_{\vec{k}}(1-n/2) + 2K_o n - \mu\right\}}}{\left[1 + e^{\beta\left\{\epsilon_{\vec{k}}(1-n/2) + 2K_o n - \mu\right\}}\right]^2}}$$

(4.62)

For $\epsilon_{\vec{k}} = 0$ with the help of Eq.(4.69) the above equation gives the Curie Weiss law given by Eq.(4.25) with $C = Ng^2\mu_B^2\, n/2k$ and $T_c = J_o n/2k_B$. When we compare the values of C and T_c with the values obtained in the weak intraatomic interaction theory $I = 0$, we see that both the Curie constant C and the Curie temperature T_c are enhanced in the strong intraatomic interaction theory. Recently in the absence of interatomic interaction (Hubbard model) Mattuck[110] has also reached to the conclusion that correlation effects enhances the critical temperature.

(ii) Finite bandwidth Case

(a) Zero temperature theory

At absolute zero of temperature the expression (4.62) reduces to

$$\chi(oo) = \frac{g^2\mu_B^2 N\,(1-n/2)\,\rho\left(\dfrac{\mu - 2\tilde{K}_0 n}{1-n/2}\right)}{1-n + (\mu - 2\tilde{K}_0 n + 4J_0(1-n/2))\,\rho\left(\dfrac{\mu - 2\tilde{K}_0 n}{1-n/2}\right)} \qquad (4.63)$$

Instability of the paramagnetic state is given by

$$1-n + \{\mu - 2K_0 n + 4J_0(1-n/2)\}\,\rho\left(\frac{\mu - 2K_0 n}{1-n/2}\right) \leq 0 \qquad (4.64)$$

In the absence of interatomic interaction the inequality (4.64) reduces to that obtained by Sakurai[39] and Hubbard and Jain[41] in the limit of strong intraatomic interaction. Sakurai has analysed the inequality and reached to the following conclusions.

(i) The paramagnetic state is unstable for a system with a small number of electrons if the density of states at the bottom of the band is large enough (For a nearly filled band the high density of states at the top of the band is required for the instability).

(ii) When the narrowed band is more than half filled, the paramagnetic state is always more stable than the ferromagnetic state.

In the presence of interatomic interactions both the conclusions of Sakurai are modified.

(i) When the number of electrons per atom is small ($n \ll 1$) the inequality (4.64) reduces to

$$1 + (\mu - 2\tilde{K}_o n + 4\tilde{J}_o)\rho(\mu - 2\tilde{K}_o n) < 0 \qquad (4.65)$$

For small number of electrons per atom the Fermi level lies below the middle of the narrowed band (i.e. $\mu < 2K_o n$), therefore the inequality (4.65) can be satisfied for the high density of states at the bottom of the band if $J_o > \mu - 2K_o n$, on the other hand if $J_o < \mu - 2K_o n$, the inequality is never satisfied whatever may be the value of the density of states.

(ii) For $n = 2/3$ the band is half filled because in that case Eq.(4.61) is satisfied for $\mu = 2K_o n$. For more than half filled band (i.e. $n > 2/3$ or $\mu > 2K_o n$) the paramagnetic state is stable if $\mu - 2K_o n > J_o(1 - n/2)$, but if $\mu - 2K_o n < J_o(1 - n/2)$ paramagnetic state may become unstable for large value of the density of states.

To be more specific, we shall discuss the inequality (4.64) for square density of states. In this case Eq.(4.61) gives the chemical potential

$$\mu = 2K_o\, n + \frac{\alpha}{2}\,(3/2n - 1), \qquad (4.66)$$

hence the inequality (4.64) becomes

$$J_o/\alpha > 0.5 \qquad (4.67)$$

(b) Finite temperature theory

We restrict our analysis to half filled narrowed band. As shown in subsection a for this case equation (4.61) is satisfied for $n_o = 2/3$. From (4.62) the condition for the paramagnetic instability is given by

$$1 + \frac{4\beta}{3N} \sum_{\vec{k}} \frac{(\epsilon_{\vec{k}} + 4\tilde{J}_o)\; e^{\beta\, \epsilon_{\vec{k}}/3}}{(e^{\beta\, \epsilon_{\vec{k}}/3} + 1)^2} \leqslant 0 \qquad (4.68)$$

For square density of states it gives the transition temperature

$$T_c = \frac{2\alpha/3}{4k_B \tanh^{-1}\left(\dfrac{2\alpha/3}{4/3J_o} \right)} \qquad (4.69)$$

This result is exactly similar to the result (4.30) obtained in the weak interaction theory if one replaces α by $2\alpha/3$ and $(I+J_o)$ by $4/3J_o$ in Eq.(4.30).

B. Instability of the Paramagnetic State against the Antiferromagnetic State

(i) Zero bandwidth case

The static paramagnetic susceptibility $\chi(\vec{Q},o)$, which is needed to discuss the instability of the paramagnetic state against the antiferromagnetic state can be obtained from Eq.(4.57). From Eqs.(4.57) - (4.60) we get

$$\chi(\vec{Q},o) = \frac{\frac{2-n}{4} \sum\limits_{\vec{k}\sigma} \sigma \, f\left\{ -\sigma \, \epsilon_{\vec{k}} (1-n/2) + 2K_o n \right\} / \epsilon_{\vec{k}}}{1-n + \frac{(2-n)\, J_o}{4N} \sum\limits_{\vec{k}\sigma} \sigma \, f\left\{ -\sigma \, \epsilon_{\vec{k}} (1-n/2) + 2K_o n \right\} / \epsilon_{\vec{k}}} \tag{4.70}$$

For zero bandwidth it gives the Curie Weiss law given by Eq.(4.32) with $C = g^2 \mu_B^2 N \, n/2k_B$ and $T_N = - \frac{J_o n}{2k_B}$.

When we compare this value of T_N with the value obtained in weak interaction theory for $I = 0$, we see that like Curie temperature, the Neel temperature is also enhanced due to strong correlations.

(ii) Finite bandwidth case

(a) Zero temperature theory

From (4.70) at absolute zero the instability of paramagnetic state occurs when

$$1 - n + \frac{(2-n)J_o}{4} \sum_{\sigma} \sigma \int d\epsilon \, \frac{\rho(\epsilon)}{\epsilon} \, \theta\left\{ \mu - 2K_o n + \sigma \, \epsilon (1-n/2) \right\} \leq 0 \, . \tag{4.71}$$

For square density of states it gives

$$\frac{J_0}{\alpha} \leq \frac{n - 1}{(1-n/2)\ \ln \left| \frac{2-n}{3n-2} \right|} \qquad (4.72)$$

The boundary line, given by the equality sign in (4.72) between the para and the antiferromagnetic state is shown in Fig.4.3. We have also shown the line $J_0/\alpha = 0.5$ given by (4.67) which gives the boundary line between para and ferromagnetic states. For $0 < J_0/\alpha < 0.5$ paramagnetic state is stable for all values of n. This can be compared with the result of the weak interaction theory (for $I = 0$) where paramagnetic state is stable for $0 < J_0/\alpha < 1.0$.

b. Finite temperature theory

For half filled band ($n = 2/3$, $= 2K_0\ n$) the paramagnetic instability occurs when

$$1 - \frac{4J_0}{3N} \sum_{\vec{k}} \tanh \frac{\beta E_{\vec{k}}/2}{E_{\vec{k}}} < 0 \qquad (4.73)$$

where $E_{\vec{k}} = 2/3\ \epsilon_{\vec{k}}$. The inequality (4.73) reduces to (4.35) if we replace $4J_0/3$ by $(I - J_0)$ and $E_{\vec{k}}$ by $\epsilon_{\vec{k}}$ in this inequality. Thus we see that the behavior of the system for half filled band is of the same type in both weak interaction ($n = 1$) and strong interaction ($n = 2/3$) theories.

C Spin-flip Excitations

The excitations of the system with spin flips are expressed as the poles of the dynamical susceptibility (4.50). In our case they contain Stoner like individual excitations and collective excitations called spin waves. Stoner excitations are given by

$$\omega_s + A^{-+}_{\vec{k}\vec{q}} = 0 \tag{4.74}$$

By substituting the value of $A^{-+}_{\vec{k}\vec{q}}$ from Eq.(4.47) we get

$$\omega_s = (\epsilon_{\vec{k}+\vec{q}} - \epsilon_{\vec{k}})\,(1-n/2) + \Big(J_o - \frac{\epsilon_{\vec{k}} + \epsilon_{\vec{k}+\vec{q}}}{2}\Big)\sum_{\sigma} \sigma \langle n^{\sigma\sigma}(o)\rangle \tag{4.75}$$

For $\vec{q} = 0$ it gives

$$\omega_s = (J_o - \epsilon_{\vec{k}})\sum_{\sigma} \sigma \,\langle n^{\sigma\sigma}(o)\rangle \tag{4.76}$$

It shows that if $J_o < \alpha/2$, there is no gap in the spectrum of Stoner excitations and therefore the spin waves given by

$$1 - \frac{1}{N}\sum_{\vec{k}} \frac{B^{-+}_{\vec{k}\vec{q}}}{\omega + A^{-+}_{\vec{k}\vec{q}}} = 0 \tag{4.77}$$

have finite life time in this region. For $J_o > \alpha/2$, a gap in the spectrum of Stoner excitations occurs at $\vec{q} = 0$ and hence for small values of $\vec{q}$ we get spin waves with infinite life time. Under the assumptions $J_o >> \alpha/2$, ω satisfying the condition

$$J_o \sum_{\sigma} \sigma \langle n^{\sigma\sigma}(o)\rangle >> |(\epsilon_{\vec{k}} - \epsilon_{\vec{k}+\vec{q}})(1-n/2)|,\ \omega,$$

and for small $\vec{q}$, we get from (4.77) the spin wave dispersion relations as

$$\omega_{\text{spin}} = (J_o - J_{\vec{q}})\langle S_o^z \rangle + \frac{1-n/2}{2N\langle S_o^z \rangle} \sum_{\vec{k}\sigma} \langle a^{\dagger}_{\vec{k}\sigma} a_{\vec{k}\sigma} \rangle (\vec{q}\cdot\vec{\nabla}_{\vec{k}})^2 \, \epsilon_{\vec{k}}$$

$$- \frac{(1-n/2)^2}{2NJ_o\langle S_o^z \rangle^2} \sum_{\vec{k}} (\langle a^{\dagger}_{\vec{k}+} a_{\vec{k}+} \rangle - \langle a^{\dagger}_{\vec{k}+\vec{q}-} a_{\vec{k}+\vec{q}-} \rangle)(\vec{q}\cdot\vec{\nabla}_{\vec{k}}\epsilon_{\vec{k}})^2$$

$$+ \; 0\,(q^4) + \ldots\ldots \qquad (4.78)$$

where $\langle S_o^z \rangle = \sum_{\sigma} \sigma \; \langle \overset{\sigma\,\sigma}{n(o)} \rangle$. Here we have assumed that $\epsilon_{\vec{k}} = \epsilon_{-\vec{k}}$. For small number of electrons per atom ($n \ll 1$) it reduces to an expression obtained within the random phase approximation[62] if one replaces J_o by $(I + J_o)$ in the third term on its right hand side.

IV. CONCLUSIONS

We have discussed the dynamical susceptibility for a model Hamiltonian which takes into account the interatomic Coulomb and exchange interaction over the Hubbard Hamiltonian. For weak intraatomic interaction we have obtained an expression for the dynamical susceptibility which is very similar to that of Englert and Antonoff.[62] It is found that in the presence of interatomic interactions the results of the Hubbard model are considerably modified. For example for the square density of states at absolute zero of temperature according to Hubbard model in half filled band ($n = 1$) the paramagnetic state is always unstable against the ferro and the antiferromagnetic states. In the presence of the interatomic interactions we find that it is possible to have a paramagnetic ground state for $J_0/\alpha>0$. At finite temperature for the zero bandwidth the C Curie-Weiss law is obtained. It is found that for positive J_0 the Curie temperature obtained from the Hubbard model increases while Neel temperature decreases. For negative J_0 these conclusions are reversed.

In the strong intraatomic interaction theory we have obtained an expression for the dynamical susceptibility which reduces to an expression obtained in the weak intraatomic interaction theory for $I = 0$, when the density of electrons is small ($n \ll 1$) and $J_q \gg \alpha/2$. Here also the results of the Hubbard model are modified. For example at absolute zero the Hubbard model predicts that for the square density of states the paramagnetic state is always more stable than the ferro and the antiferromagnetic states. Here we find that for $J_0/\alpha>0.5$ ferromagnetic state is stable for all values of n, for $0<J_0/\alpha<0.5$ the paramagnetic is stable for all values of n and for $J_0/\alpha<0$ both para and antiferromagnetic states are stable in regions shown in Fig.4.3. Whatever may be the density of states Hubbard model predicts that for $n>2/3$ paramagnetic state is more stable than the ferromagnetic state. Here we find that the paramagnetic state is unstable against the ferromagnetic states for higher density of states if $-2K_0n<J_0(1-n/$ For small number of electrons Hubbard model predicts that paramagnetic states is unstable against ferromagnetic state

if density of states at the bottom of the band is large. In presence of interatomic interactions if $J_o<(\quad -2K_o n)$, the paramagnetic state is always stable whatever may be the value of the density of states. Finite temperature theory shows that for zero bandwidth case Curie and Neel temperatures have higher values compared to the week intraatomic interaction theory for $I = 0$. For square density of states and for half filled narrowed band ($n = 2/3$) the expressions for Curie and Neel temperatures come out to be very similar to that obtained in weak interaction theory for $n = 1$. For $J_o/\alpha>0.5$ spin wave dispersions are found to be very similar to that obtained in weak intraatomic interaction theory.

Thus we see that interatomic interaction play an important role in the magnetic properties of the system. Our treatment is approximate and qualitative but if gives some insight into the effect of interatomic interactions and reveals that in any complete theory of magnetism interatomic interactions should not be neglected.

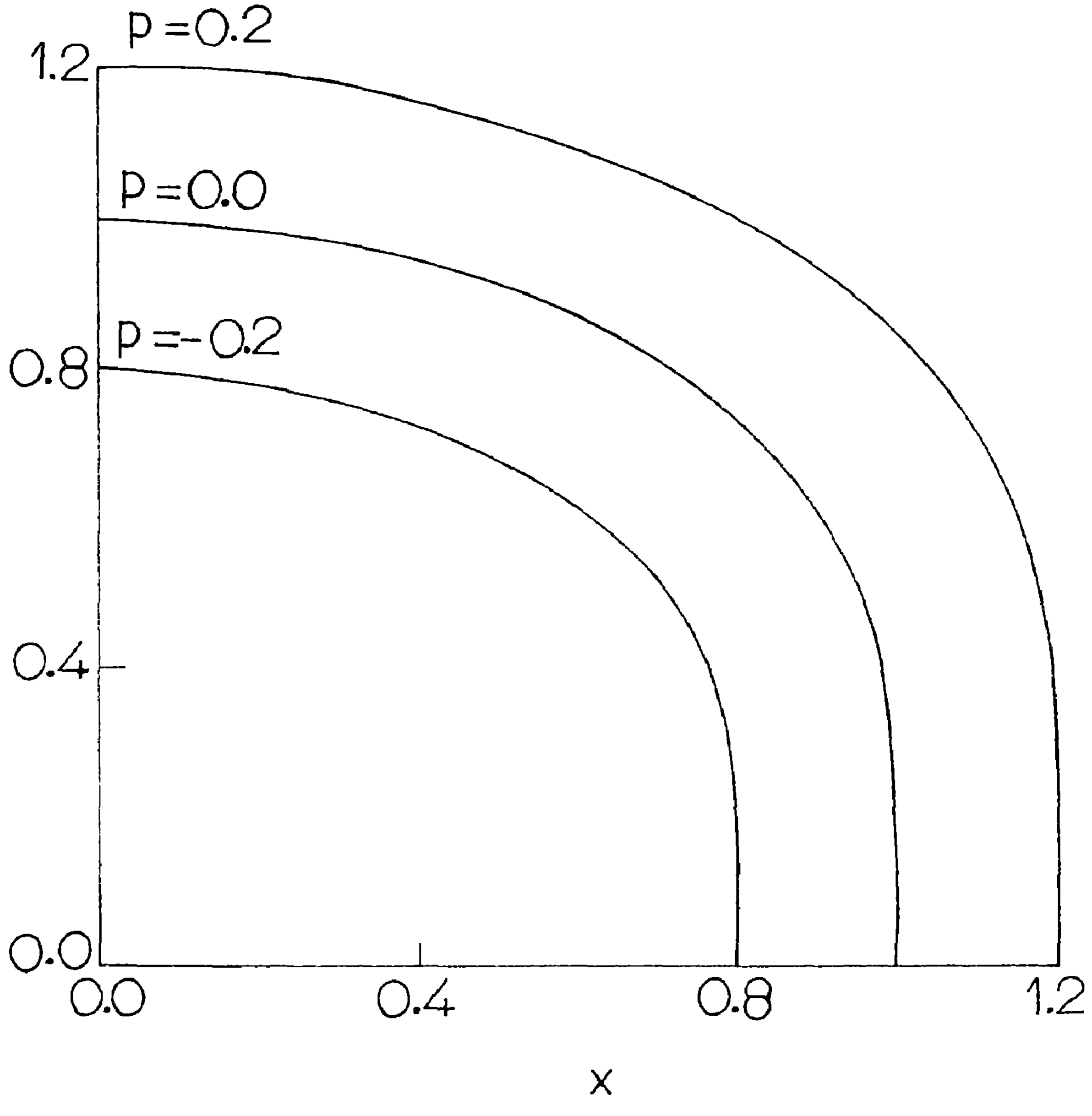

FIG. 4.1. A PLOT OF CRITICAL TEMPERATURE $(y = 4k_B T_c / I)$ AS A FUNCTION OF BAND WIDTH $(x = \alpha / I)$ FOR VARIOUS RATIO $p = J_0 / I$

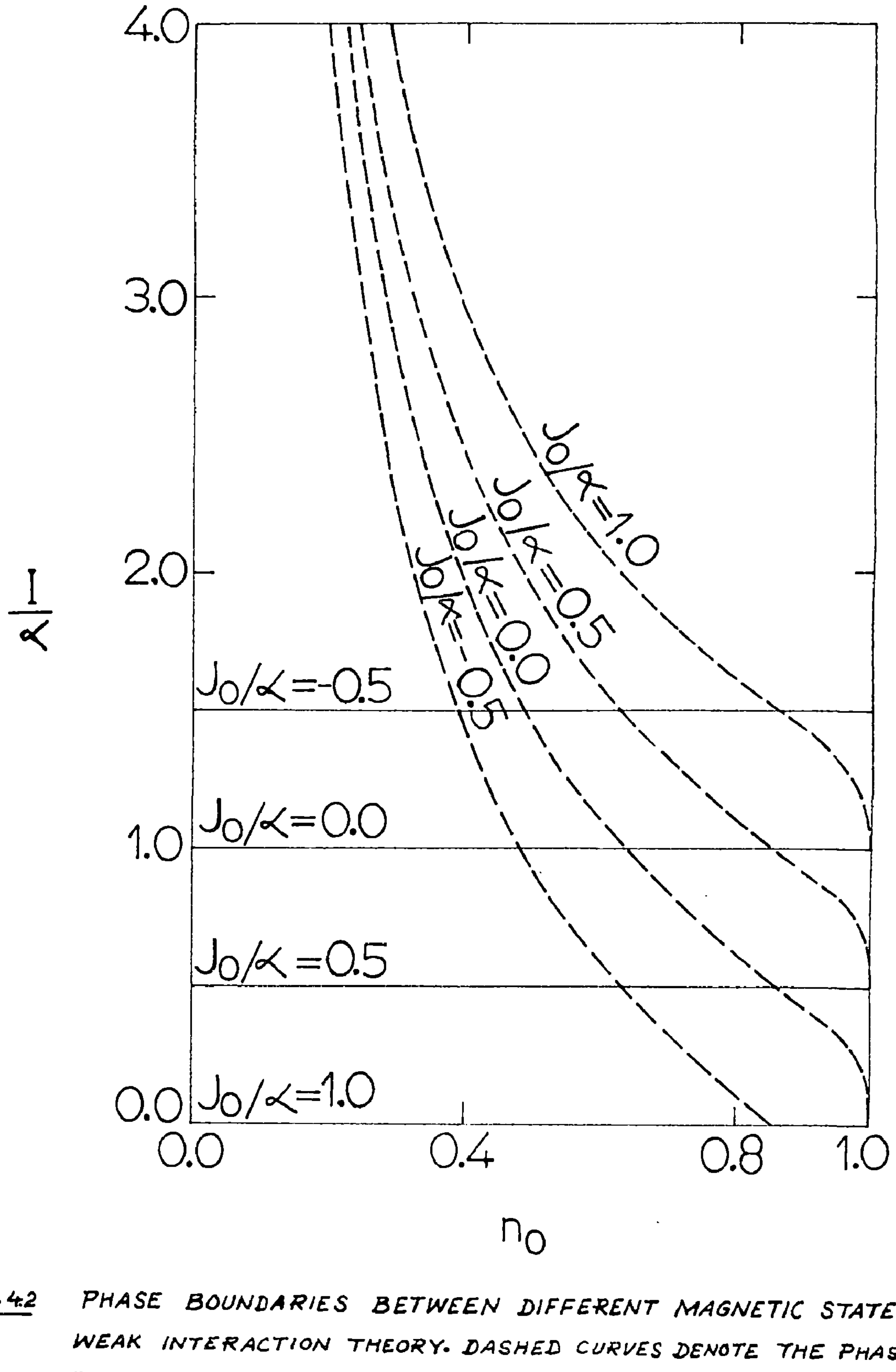

FIG. 4.2 PHASE BOUNDARIES BETWEEN DIFFERENT MAGNETIC STATES IN THE WEAK INTERACTION THEORY. DASHED CURVES DENOTE THE PHASE BOUNDARIES BETWEEN PARA AND THE ANTIFERROMAGNETIC STATES. SOLID LINES REPRESENT THE BOUNDARY BETWEEN THE PARA AND THE FERROMAGNETIC STATES.

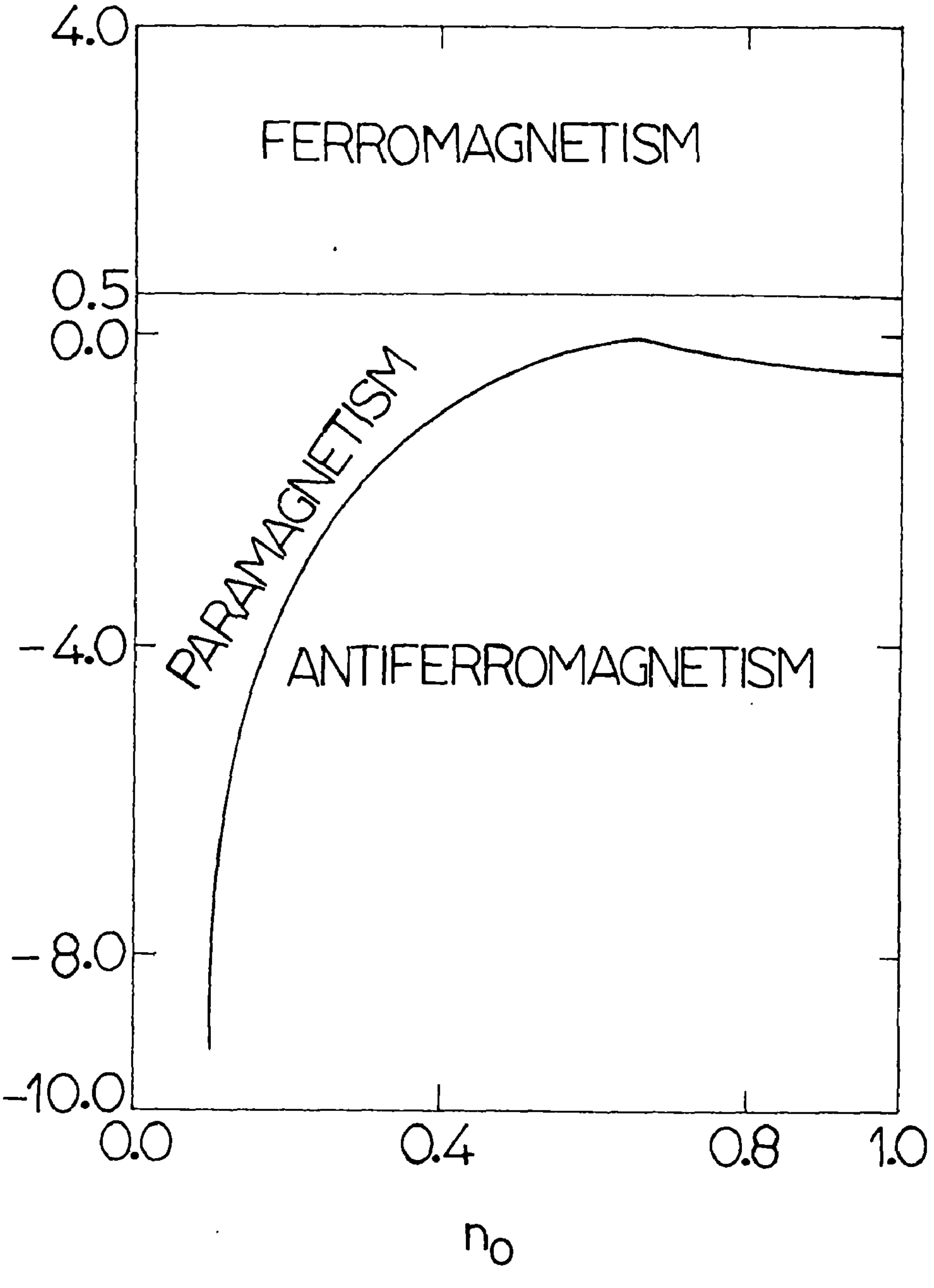

FIG.4.3 PHASE BOUNDARIES BETWEEN DIFFERENT MAGNETIC STATES IN STRONG INTERACTION THEORY.

CHAPTER V

METAL-NONMETAL TRANSITIONS

A. METAL-NONMETAL TRANSITIONS IN NARROW ENERGY BANDS

I. INTRODUCTION

In the preceding chapter we have discussed the dynamical susceptibility for a model Hamiltonian (4.1) which includes the interatomic Coulomb and exchange interactions in addition to the Hubbard Hamiltonian. Here we use this Hamiltonian to investigate the phenomenon of metal-nonmetal transitions. In Sec. II we examine this model with the help of one particle Green's function approach. The higher order Green's functions are decoupled in such a way that it is possible to take into account the correlation between an electron and a hole of opposite spin. In Sec. III we examine our solutions for ferromagnetic system having one electron per atom. We find two phase transitions at two different critical temperatures: T_M at which a ferromagnetic nonmetal changes into a ferromagnetic metal, and T_c at which the system becomes a paramagnetic metal. T_c is always higher than T_M. In Sec. IV we consider the antiferromagnetic system and find that, like ferromagnetic systems, two phase transitions do not occur. In Sec. V we summarise our conclusions.

II. GENERAL FORMULATION

We consider the one particle Green's function

$$G_{ij}^{\sigma\sigma'}(\omega) = \langle\langle a_{i\sigma} , a_{j\sigma'}^{\dagger} \rangle\rangle_{\omega} . \qquad (5.1)$$

The equation of motion (1.13) for this Green's function, for a system described by the Hamiltonian (4.1), is given by

$$(\omega+\mu)\, G_{ij}^{\sigma\sigma'}(\omega) = \frac{\delta_{ij}\delta_{\sigma\sigma'}}{2\pi} + \sum_{\ell} T_{i\ell}\, G_{\ell j}^{\sigma\sigma'}(\omega) + I\langle\langle n_{i-\sigma} a_{i\sigma} , a_{j\sigma'}^{\dagger} \rangle\rangle_{\omega}$$

$$+ \sum_{\ell\sigma_1} K_{i\ell} \langle\langle n_{\ell\sigma_1} a_{i\sigma} , a_{j\sigma'}^{\dagger} \rangle\rangle_{\omega}$$

$$+ \sum_{\ell\sigma_1} J_{i\ell} \langle\langle a_{\ell\sigma_1}^{\dagger} a_{i\sigma_1} a_{\ell\sigma} , a_{j\sigma'}^{\dagger} \rangle\rangle_{\omega} . \qquad (5.2)$$

The above equation contains the higher order Green's function of the form $\langle\langle a_{\ell\sigma_1}^{\dagger} a_{\ell\sigma_2} a_{i\sigma_3} , a_{j\sigma'}^{\dagger} \rangle\rangle_{\omega}$. These Green's functions are decoupled as follows

$$\langle\langle a_{\ell\sigma_1}^{\dagger} a_{\sigma_2} a_{i\sigma_3} , a_{j\sigma'}^{\dagger} \rangle\rangle_{\omega}$$

$$\langle a_{\ell\sigma_1}^{\dagger} a_{\ell\sigma_2} \rangle G_{ij}^{\sigma_3\sigma'}(\omega) - \langle a_{\ell\sigma_1}^{\dagger} a_{i\sigma_3} \rangle G_{j}^{\sigma_2\sigma'}(\omega) . \qquad (5.3)$$

The equation (5.3) includes the term like $\langle a_{\ell\sigma}^{\dagger} a_{i-\sigma} \rangle$ which takes into account the correlation between an electron and a hole of opposite spin. The importance of such anomalous correlation functions in the theory of magnetic systems has recently been stressed by Mattuck and Johanson, and Klein.[111] Under the approximation (5.3) the equation of motion (5.2) of $G_{ij}^{\sigma\sigma'}(\omega)$ becomes

$$
\begin{aligned}
(\omega+\mu)\, G_{ij}^{\sigma\sigma'}(\omega) = {} & \frac{\delta_{ij}\,\delta_{\sigma\sigma'}}{2\pi} + \sum_{\ell} T_{i\ell}\, G_{\ell j}^{\sigma\sigma'}(\omega) + I \langle n_{i-\sigma} \rangle G_{ij}^{\sigma\sigma'}(\omega) \\
& - I \langle a_{i-\sigma}^{\dagger}\, a_{i\sigma} \rangle\, G_{ij}^{-\sigma\sigma'}(\omega) + \sum_{\ell\sigma_1} K_{i\ell} \langle n_{\ell\sigma_1} \rangle\, G_{ij}^{\sigma\sigma'}(\omega) \\
& - \sum_{\ell\sigma_1} K_{i\ell} \langle a_{\ell\sigma_1}^{\dagger}\, a_{i\sigma} \rangle\, G_{ij}^{\sigma_1\sigma'}(\omega) \\
& + \sum_{\ell\sigma_1} J_{i\ell} \langle a_{\ell\sigma_1}^{\dagger}\, a_{i\sigma_1} \rangle\, G_{\ell j}^{\sigma\sigma'}(\omega) \\
& - \sum_{\ell\sigma_1} J_{i\ell} \langle a_{\ell\sigma_1}^{\dagger}\, a_{\ell\sigma} \rangle\, G_{ij}^{\sigma_1\sigma'}(\omega) \,. \qquad (5.4)
\end{aligned}
$$

We define the Fourier transform of the Green's function $G_{ij}^{\sigma\sigma'}(\omega)$ as

$$
G_{ij}^{\sigma\sigma'}(\omega) = \frac{1}{N} \sum_{\vec{k}_1\vec{k}_2} G_{\vec{k}_1\vec{k}_2}^{\sigma\sigma'}(\omega)\; e^{i\vec{k}_1\cdot\vec{R}_i - i\vec{k}_2\cdot\vec{R}_j} \,. \qquad (5.5)
$$

In terms of Fourier transform $G_{\vec{k}_1\vec{k}_2}^{\sigma\sigma'}$, the equation of motion (5.4) takes the form

$$
\begin{aligned}
(\omega+\mu-\epsilon_{\vec{k}})\, G_{\vec{k}\vec{k}'}^{\sigma\sigma'}(\omega) = {} & \frac{\delta_{\sigma\sigma'}\,\delta_{\vec{k}\vec{k}'}}{2\pi} - \frac{I}{N} \sum_{\vec{k}_1\vec{k}_2} \Big\{ \langle a_{\vec{k}_1-\sigma}^{\dagger}\, a_{\vec{k}_2\sigma} \rangle\, G_{\vec{k}+\vec{k}_1-\vec{k}_2,\,\vec{k}'}^{-\sigma\sigma'}(\omega) \\
& - \sum_{\vec{k}_1\vec{k}_2} \langle a_{\vec{k}_1-\sigma}^{\dagger}\, a_{\vec{k}+\vec{k}_1-\vec{k}_2-\sigma} \rangle\, G_{\vec{k}_2\vec{k}'}^{\sigma\sigma'}(\omega) \Big\}
\end{aligned}
$$

$$-\frac{1}{N}\sum_{\substack{\vec{k}_1\vec{k}_2\\ \sigma_1}} K_{\vec{k}_1}\Big\{\langle a^{\dagger}_{\vec{k}_2\sigma_1}\; a_{\vec{k}-\vec{k}_1\sigma}\rangle\, G^{\sigma_1\sigma'}_{\vec{k}_1+\vec{k}_2,\vec{k}'}(\omega)$$

$$-\langle a^{\dagger}_{\vec{k}_2\sigma_1}\; a_{\vec{k}_1+\vec{k}_2\sigma_1}\rangle\, G^{\vec{\sigma}\sigma'}_{\vec{k}-\vec{k}_1,\vec{k}'}(\omega)\Big\}$$

$$+\frac{1}{N}\sum_{\substack{\vec{k}_1\vec{k}_2\\ \sigma_1}} J_{\vec{k}_1}\Big\{\langle a^{\dagger}_{\vec{k}_2\sigma_1}\; a_{\vec{k}-\vec{k}_1\sigma_1}\rangle\, G^{\sigma\sigma'}_{\vec{k}_1+\vec{k}_2,\vec{k}'}(\omega)$$

$$-\langle a^{\dagger}_{\vec{k}_2\sigma_1}\; a_{\vec{k}_1+\vec{k}_2\sigma}\rangle\, G^{\sigma_1\sigma'}_{\vec{k}-\vec{k}_1,\vec{k}'}(\omega)\Big\}, \tag{5.6}$$

where, the Bloch operators $a_{\vec{k}\sigma}$ and $a^{\dagger}_{\vec{k}\sigma}$ are defined by (4.4), $\epsilon_{\vec{k}}$ is defined by (3.12), and $K_{\vec{k}}$ and $J_{\vec{k}}$ are defined by (4.10). For the correlation function $\langle a^{\dagger}_{\vec{k}\sigma}\; a_{\vec{k}'\sigma}\rangle$ we make an ansatz

$$\langle a^{\dagger}_{\vec{k}\sigma} a_{\vec{k}'\sigma}\rangle \simeq \langle a^{\dagger}_{\vec{k}\sigma}\; a_{\vec{k}\sigma}\rangle\, \delta_{\vec{k}\vec{k}'} + \langle a^{\dagger}_{\vec{k}\sigma} a_{\vec{k}+\vec{Q}\sigma}\rangle\, \delta_{\vec{k}',\vec{k}+\vec{Q}}\ , \tag{5.7}$$

where $\vec{Q}$ is half the smallest reciprocal lattice vector. This approximation corresponds to considering the spin density waves of wave vector $\vec{q} = 0$ or $\vec{q} = \vec{Q}$. Within the approximation (5.7), Eq.(5.6) becomes

$$(\omega+\mu-\epsilon_{\vec{k}}-A^{\sigma}_{\vec{k},0})\, G^{\sigma\sigma'}_{\vec{k}\vec{k}'}(\omega) + B^{\sigma}_{\vec{k},0}\, G^{-\sigma\sigma'}_{\vec{k}\vec{k}'}(\omega)$$

$$-A^{\sigma}_{\vec{k},\vec{Q}}\; G^{\sigma\sigma'}_{\vec{k}+\vec{Q},\vec{k}'}(\omega) + B^{\sigma}_{\vec{k},\vec{Q}}\; G^{-\sigma\sigma'}_{\vec{k}+\vec{Q},\vec{k}'}(\omega) = \frac{\delta_{\vec{k}\vec{k}'}\delta_{\sigma\sigma'}}{2\pi}, \tag{5.8}$$

where

$$A^{\sigma}_{\vec k\vec q} = I\, n_{\vec q}(-\sigma-\sigma) + K_{\vec q}\, n_{\vec q} - J_{\vec q}\, n_{\vec q}(\sigma,\sigma) - \frac{1}{N}\sum_{\vec k'} K_{\vec k-\vec k'} N^{\sigma\sigma}_{\vec k'+\vec q,\vec k'} + \frac{1}{N}\sum_{\vec k'} J_{\vec k-\vec k'} N^{-\sigma-\sigma}_{\vec k'+\vec q,\vec k'}\,, \tag{5.9}$$

$$B^{\sigma}_{\vec k\vec q} = (I+J_{\vec q})\, n_{\vec q}(-\sigma,\sigma) + \frac{1}{N}\sum_{\vec k'} K_{\vec k-\vec k'} N^{-\sigma\sigma}_{\vec k'+\vec q,\vec k'}\,, \tag{5.10}$$

$$n_{\vec q}(\sigma\sigma') = \frac{1}{N}\sum_{\vec k} N^{\sigma\sigma'}_{\vec k+\vec q,\vec k} \tag{5.11}$$

$$N^{\sigma\sigma'}_{\vec k,\vec k'} = \langle a^{\dagger}_{\vec k\sigma}\, a_{\vec k'\sigma'}\rangle\,, \tag{5.12}$$

$$n_{\vec q} = \sum_{\sigma} n_{\vec q}(\sigma\sigma) \tag{5.13}$$

We restrict our study to a system with nearest neighbor coupling. In this case the terms under the summation sign in Eqs.(5.9) and (5.10) are quite small in comparison to other terms. Further we assume that the system is magnetized in the x direction instead of conventional z axis. Such a system has also been considered by Morris and Cornwell.[40] For this system the average values of y and z components of the spin on each lattice site are zero. Since the components S^x_i, S^y_i, S^z_i of the spin operator $\vec S_i$ for an electron on the lattice site i are given by

$$\begin{aligned} S^x_i &= \frac{1}{2}\sum_{\sigma} a^{\dagger}_{i\sigma}\, a_{i-\sigma} \\ S^y_i &= -\frac{i}{2}\sum_{\sigma} \sigma\, a^{\dagger}_{i\sigma}\, a_{i-\sigma} \\ S^z_i &= \frac{1}{2}\sum_{\sigma} \sigma\, a^{\dagger}_{i\sigma}\, a_{i\sigma} \end{aligned} \tag{5.14}$$

we have $\langle a^{\dagger}_{i\sigma}\ a_{i-\sigma}\rangle = \langle a^{\dagger}_{i-\sigma}\ a_{i\sigma}\rangle$ and $\langle a^{\dagger}_{i\sigma}\ a_{i\sigma}\rangle = \langle a^{\dagger}_{i-\sigma} a_{i-\sigma}$

$$(5.15)$$

From Eqs. (4.4), (5.11) and (5.12) we have

$$n_{\vec{q}}(\sigma\,\sigma') = \frac{1}{N}\sum_{i}\langle a^{\dagger}_{i\sigma}\ a_{i\sigma'}\rangle\, e^{i\vec{q}\cdot\vec{R}_i}\ , \qquad (5.16)$$

and therefore from (5.15) we get

$$n_{\vec{q}}(\sigma\,,\,-\,\sigma) = n_{\vec{q}}(-\sigma\,,\,\sigma)\,;\ n_{\vec{q}}(\sigma\,,\,\sigma) = n_{\vec{q}}(-\,\sigma\,,\,-\,\sigma)\ . \qquad (5.17)$$

When we use (5.17) and drop the terms inside the summation sign in Eqs. (5.9) and (5.10), the equation (5.8) becomes

$$(\omega+\mu-\epsilon_{\vec{k}}-A_0)\,G^{\sigma\sigma}_{\vec{k}\vec{k}'}(\omega) + B_0\,G^{-\sigma\,\sigma}_{\vec{k}\vec{k}'}(\omega)$$

$$-\,A_{\vec{Q}}\ G^{\sigma\,\sigma}_{\vec{k}+\vec{Q},\vec{k}'} + B_{\vec{Q}}\ G^{-\,\sigma\,\sigma}_{\vec{k}+\vec{Q},\vec{k}'}\,(\omega) = \frac{\delta_{\vec{k}\vec{k}'}\,\delta_{\sigma\,\sigma'}}{2\pi}\ , \qquad (5.18)$$

where

$$A_{\vec{q}} = (I + 2V_{\vec{q}} - J_{\vec{q}})\, n_{\vec{q}}/2\ ,$$

$$B_{\vec{q}} = (I + J_{\vec{q}})\ \Delta_{\vec{q}}\ , \qquad (5.19)$$

and $\Delta_{\vec{q}} = n_{\vec{q}}(-\,\sigma\,,\,\sigma) = n_{\vec{q}}(\sigma\,,\,-\sigma)$.

III. FERROMAGNETIC SYSTEMS

In a ferromagnetic system the magnetude and the direction of magnetization are independent of the lattice site, therefore Eq.(5.16) gives $n_{\vec q}(\sigma, \sigma') = n_0(\sigma, \sigma')\, \delta_{\vec q,0}$. And Eq.(5.18) takes the form

$$(\omega+\mu-\epsilon_k-A_0)\, G^{\sigma\sigma'}_{\vec k\vec k'}(\omega) + B_0\, G^{-\sigma\sigma'}_{\vec k\vec k'}(\omega) = \frac{\delta_{\vec k\vec k'}\delta_{\sigma\sigma'}}{2\pi} \, . \qquad (5.20)$$

We solve this equation for $G^{\sigma\sigma'}_{\vec k\vec k'}(\omega)$ and get

$$G^{\sigma\sigma'}_{\vec k\vec k'}(\omega) = \frac{(\omega+\mu-\epsilon_{\vec k}-A_0)\delta_{\sigma\sigma'} - B_0\delta_{-\sigma\sigma'}}{(\omega+\mu-\epsilon_{\vec k}-A_0)^2 - B_0^2} \; \frac{\delta_{\vec k\vec k'}}{2\pi} \, . \qquad (5.21)$$

Poles of the Green's function $G^{\sigma\sigma'}_{\vec k\vec k'}(\omega)$ give two quasi-particle bands

$$\omega^{\pm}_{\vec k} = -\mu + \epsilon_{\vec k} + A_0 \pm B_0 \, . \qquad (5.22)$$

The bands $\omega^{+}_{\vec k}$ and $\omega^{-}_{\vec k}$ are separated by an energy gap

$$G = 2B_0 - \alpha \, , \qquad (5.23)$$

where α is the width of the band $\epsilon_{\vec k}$. When the lower band $\omega_{\vec k}$ is completely filled, the upper band $\omega_{\vec k}$ is completely empty, and the two bands are separated by a positive energy gap, the system behaves as a nonmetal otherwise it behaves as a metal. Hence to know whether a system with a given number of electrons per atom is a metal or nonmetal we must know the density of states in the bands. The density of states per atom for the energy ω and spin σ is given by (See Eqs(2.15) and (2.16))

$$\rho^{\sigma}(\omega) = \frac{1}{N} \lim_{\epsilon \to 0^{+}} \sum_{\vec{k}} \left[G^{\sigma\sigma}_{\vec{k}\vec{k}}(\omega + i\epsilon) - G^{\sigma\sigma}_{\vec{k}\vec{k}}(\omega - i\epsilon) \right] . \qquad (5.24)$$

By substituting the value of the Green's function $G^{\sigma\sigma}_{\vec{k}\vec{k}}(\omega)$ from Eq. (5.21) in Eq.(5.24) we get

$$\rho^{\sigma}(\omega) = \frac{1}{2} \sum_{\vec{k}} \left[\delta(\omega - \omega^{-}_{\vec{k}}) + \delta(\omega - \omega^{+}_{\vec{k}}) \right] . \qquad (5.25)$$

The above equation shows that number of states per atom in each band is equal to 1. ~~in each band~~. Therefore a system having one electron per atom behaves as a nonmetal if the two bands are separated by a positive gap and it makes transition from a nonmetal to metal when the gap goes to zero.

To evaluate the number of electrons per atom n_0 and the average x component of the spin per atom Δ_0 we require the knowledge of $\langle a^{\dagger}_{\vec{k}\sigma'}\, a_{\vec{k}\sigma} \rangle$. By substituting the value of the Green's function $G^{\sigma\sigma'}_{\vec{k}\vec{k}}(\omega)$ from Eq.(5.21) in Eq.(1.14) we obtain th correlation function as

$$\langle a^{\dagger}_{\vec{k}'\sigma'} \, a_{\vec{k}\sigma} \rangle = \int_{-\infty}^{\infty} f(\omega) \, \frac{\delta_{\vec{k}\vec{k}'}}{2} \Big[\{ \delta(\omega - \overset{-}{\omega}_{\vec{k}}) + \delta(\omega - \overset{+}{\omega}_{\vec{k}}) \} \, \delta_{\sigma\sigma'}$$

$$- \{ \delta(\omega - \overset{-}{\omega}_{\vec{k}}) - \delta(\omega - \overset{+}{\omega}_{\vec{k}}) \} \, \delta_{-\sigma\sigma'} \Big] \, d\omega \, . \tag{5.26}$$

With the help of Eq.(5.11), for one electron per atom, the above equation gives two self consistency conditions

$$1 = \frac{1}{N} \sum_{\vec{k}} \left[f(\epsilon_{\vec{k}} - \mu + A_o - B_o) + f(\epsilon_{\vec{k}} - \mu + A_o + B_o) \right] , \tag{5.27}$$

$$B_o = \frac{I + J_Q}{2N} \sum_{\vec{k}} \left[f(\epsilon_{\vec{k}} - \mu + A_o - B_o) - f(\epsilon_{\vec{k}} - \mu + A_o + B_o) \right] , \tag{5.28}$$

If T_{ij} is nonzero only when i and j are nearest neighbors, $\epsilon_{\vec{k}+\vec{Q}} = -\epsilon_{\vec{k}}$ and therefore

$$\sum_{\vec{k}} f(\epsilon_{\vec{k}}) = \sum_{\vec{k}} f(-\epsilon_{\vec{k}}) \, . \tag{5.29}$$

With the help of this relation Eq.(5.27) and (5.28) yield

$$\mu = A_o \, ,$$

and

$$B_o = \frac{I + J_Q}{2N} \sum_{\vec{k}} \tanh \left\{ \frac{\beta}{2} (\epsilon_{\vec{k}} + B_o) \right\}$$

$$= \frac{I + J_Q}{2} \int \eta(\epsilon) \tanh \{ \beta(\epsilon + B_o)/2 \} \, d\epsilon \, , \tag{5.30}$$

where $\eta(\epsilon) = \frac{1}{N} \sum_{\vec{k}} \delta(\omega - \epsilon_{\vec{k}})$ is the density of states per atom for the band $\epsilon_{\vec{k}}$. To discuss the solution of Eq.(5.30) one has to choose a particular form of the density of states. For convenience we choose a square density of states defined by $\eta(\epsilon) = 1/\alpha$ if $-\alpha/2 < \epsilon < \alpha/2$ and zero otherwise. For this type of density of states Eq.(5.30) takes the form

$$\Delta_0 = \frac{1}{\beta\alpha} \Big[\ln \cosh \frac{\beta}{2} \{ \alpha/2 + (I+J_0) \} - \ln \cosh \frac{\beta}{2} \{ -\alpha/2 + (I+J_0) \} \Big] . \tag{5.31}$$

We first examine the solution of Eq.(5.31) at absolute zero, For $\alpha/(I+J_0) < 1.0$, it has two solutions $\Delta_0 = 1/2$ and $\Delta_0 = 0$. In section V we shall show that energy of the system corresponding to the solution $\Delta_0 = 1/2$ is lower than that corresponding to $\Delta_0 = 0$. And therefore the solution $\Delta_0 = 1/2$ is a stable solution. Eq.(5.23) shows that for this solution band gap is greater than zero and so the system behaves as a ferromagnetic nonmetal. For zero bandwidth ($\epsilon_{\vec{k}} = 0$, for all $\vec{k}$) and in the absence of interatomic interaction Eq.(5.22) gives two states at $-\mu$ and $-\mu + I$. This result is in perfect agreement with the exact zero bandwidth result obtained by Hubbard.[34] For $\alpha/(I+J_0) > 1.0$ Eq.(5.31) has only one solution $\Delta_0 = 0$. This shows that for ferromagnetic system a first order phase transition occurs at $\alpha/(I+J_o) = 1.0$ where the long range order parameter changes discontinuously from a finite value 1/2 to zero.

To discuss the phenomena of metal-non-metal transition at finite temperatures we have shown that the finite temperature solution of Eq. (5.31) in Figs. 5.1 - 5.3. In Fig.5.1 we have plotted Δ_0 against $2k_BT/(I+J_o)$ for various values of $\alpha/(I+J_o)$. At zero temperature there is always a nonzero average magnetic moment ($\Delta_0 = 1/2$) and as the temperature increases the average magnetic moment gradually decreases and it disappears at a critical temperature T_c where a phase transition from a ferromagnetic state to a paramagnetic state occurs. In Fig.5.2 we show the plot of $\bar{G} = \frac{G}{I+J_o}$ versus $2K_BT/(I+J_o)$ for various values of $\alpha/(I+J_o)$. At zero temperature there is always a nonzero band gap (different for different $\alpha/(I+J_o)$) and as the temperature is raised the gap gradually disappears and the system undergoes a nonmetal-metal transition at a temperature T_M. The solutions of Eq.(5.31) for $\Delta_0 = 0$ and $\Delta_0 = \alpha/2(I+J_o)$ give the transition temperatures T_c and T_M as

$$T_c = \alpha/\{4k_B \tanh^{-1}(\alpha/2(I+J_o))\} , \qquad (5.32)$$

$$\frac{\alpha}{2k_BT_M} = \frac{I+J_o}{\alpha} \ln \cosh \left(\frac{\alpha}{2k_BT_M} \right) , \qquad (5.33)$$

The variations of $2k_BT_c/(I+J_o)$ and $2k_BT_M/(I+J_o)$ as a functions of $\alpha/(I+J_o)$ are shown in Fig.5.3. For finite bandwidth T_M is always less than T_c. It shows that a ferromagnetic nonmetal first changes into a ferromagnetic metal at T_M and then finally into a paramagnetic metal at $T = T_c$. All these curves are plotted for $\alpha/(I+J_o) < 1.0$. For $\alpha/(I+J_o) > 1.0$ only solution for Δ_0 is $\Delta_0 = 0$, and hence in this region the system behaves as a paramagnetic metal.

The expression (5.32) for the transition temperature T_c is the same as that obtained in the preceding chapter (Eq.(4.30)). It should be noted that interatomic exchange interaction alone can predict the existence of two phase transitions because everywhere I and J_o appear together in the form $(I+J_o)$. It will be shown in section V that, however, Hubbard model ($J_o = 0$) does not predict the two phase transitions because in this model for a system having one electron per atom, the ferromagnetic state is never the ground state.

IV. ANTIFERROMAGNETIC SYSTEMS

In antiferromagnetic systems, the spins in the neighboring lattice sites are aligned opposite to each other so that the average magnetization is zero. Therefore Eq.(5.16) gives

$$n_{\vec{q}}(\sigma, \sigma) = n_o(\sigma, \sigma)\, \delta_{\vec{q},o}$$

$$n_{\vec{q}}(\sigma, \sigma') = n_{\vec{Q}}(\sigma, \sigma')\, \delta_{\vec{q},\vec{Q}} \qquad \text{for } \sigma \neq \sigma'$$

and Eq.(5.18) takes the form

$$(\omega+\mu-\epsilon_{\vec{k}}-A_0)\,G^{\sigma\sigma'}_{\vec{k}\vec{k}'}(\omega) + B_Q\,G^{-\sigma\sigma'}_{\vec{k}+Q,\vec{k}'}(\omega) = \frac{\delta_{\vec{k}\vec{k}'}\delta_{\sigma\sigma'}}{2\pi} \tag{5.34}$$

In the reduced zone scheme we have

$$G^{\sigma\sigma'}_{\vec{k}+2\vec{Q},\vec{k}'}(\omega) = G^{\sigma\sigma'}_{\vec{k}\vec{k}'}(\omega) \tag{5.35}$$

By solving Eq.(5.34) for $G^{\sigma\sigma'}_{\vec{k}\vec{k}'}(\omega)$ and using the relation $\epsilon_{\vec{k}+\vec{Q}} = -\epsilon_{\vec{k}}$ we get

$$G^{\sigma\sigma'}_{\vec{k}\vec{k}'}(\omega) = \frac{(\omega+\mu+\epsilon_{\vec{k}}-A_0)\delta_{\vec{k}\vec{k}'}\delta_{\sigma\sigma'} - B_{\vec{Q}}\,\delta_{\vec{k}+\vec{Q},\vec{k}'}\delta_{-\sigma\sigma'}}{2\pi\left[(\omega+\mu-\epsilon_{\vec{k}}-A_0)(\omega+\mu+\epsilon_{\vec{k}}-A_0) - B^2_{\vec{Q}}\right]} \tag{5.36}$$

Poles of the Green's function $G^{\sigma\sigma'}_{\vec{k}\vec{k}'}(\omega)$ give the quasi-particle bands

$$\omega^{\pm}_{\vec{k}} = -\mu + A_0 \pm \sqrt{(\epsilon^2_{\vec{k}} + B^2_{\vec{Q}})} \tag{5.37}$$

The bands $\omega^{+}_{\vec{k}}$ and ω^{-}_{k} are separated by an energy gap

$$G = 2(I-J_0)\,\Delta_{\vec{Q}} \tag{5.38}$$

When we substitute the value of $G^{\sigma\sigma}_{\vec{k}\vec{k}}(\omega)$ from Eq.(5.36) in Eq.(5.24) we get the density of states per atom in each band equal to 1. Therefore for one electron per atom the system behaves as a nonmetal for positive band gap. Like the ferromagnetic system in this case the system cannot show two phase transitions because the band gap goes to zero only when the long range order parameter $\Delta_{\vec{Q}}$ goes to zero. The self-consistency conditions are given by

$$1 = \frac{1}{2N} \sum_{\vec{k}} \left[f\left(-\mu + A_0 - \sqrt{(\epsilon^2_{\vec{k}} + B^2_{\vec{Q}})}\right) + f\left(-\mu + A_0 + \sqrt{(\epsilon^2_{\vec{k}} + B^2_{\vec{Q}})}\right)\right], \quad (5.39)$$

$$\Delta_{\vec{Q}} = \frac{B_{\vec{Q}}}{2N} \sum_{\vec{k}} \frac{f\left(-\mu + A_0 - \sqrt{(\epsilon^2_{\vec{k}} + B^2_{\vec{Q}})}\right) - f\left(-\mu + A_0 + \sqrt{(\epsilon^2_{\vec{k}} + B^2_{\vec{Q}})}\right)}{\sqrt{(\epsilon^2_{\vec{k}} + B^2_{\vec{Q}})}} . \quad (5.40)$$

Equation (5.39) is satisfied for $\mu = A_0$ and therefore Eq.(5.40) becomes

$$1 = \frac{I-J_0}{2N} \sum_{\vec{k}} \frac{\tanh \frac{\beta}{2} \sqrt{(\epsilon^2_{\vec{k}} + (I-J_0)^2 \Delta^2_{\vec{Q}})}}{\sqrt{(\epsilon^2_{\vec{k}} + (I-J_0)^2 \Delta^2_{\vec{Q}})}} . \quad (5.41)$$

Recently this equation has been obtained by Langer et al.[93] in the absence of interatomic interactions, ($J_0 = 0$). They have plotted the order parameter $\Delta_{\vec{Q}}$ as a function of α/I at various temperatures. At absolute zero it is found that $\Delta_{\vec{Q}}$ changes from 1/2 → 0 as α/I changes from $0 \to \infty$. Thus we see that at absolute zero in antiferromagnetic system nonmetal-metal transition is not possible. At finite temperatures $\Delta_{\vec{Q}}$ goes to zero at some value of α/I and shows the nonmetal-metal transition.

V. STABILITY OF THE MAGNETIC PHASES

In the previous sections we have discussed the metal-nonmetal transition by assuming that the ground state is either ferromagnetic or antiferromagnetic. Here we find out the conditions under which a given ground state is ferromagnetic or antiferromagnetic. To determine the stability of the ground state we evaluate the ground state energy of different magnetic phases.

The ground state energy of the system described by the Hamiltonian (4.1) can be expressed in terms of the one particle Green's function. The equation of motion of the operator $a_{i\sigma}(t)$ for the Hamiltonian (4.1) is

$$\begin{aligned} i \frac{d}{dt} a_{i\sigma}(t) &= [a_{i\sigma}(t), H]_- \\ &= \sum_j (T_{ij} - \mu\delta_{ij}) a_{i\sigma}(t) + I\, n_{i-\sigma}(t)\, a_{i\sigma}(t) \\ &+ \sum_{j\sigma'} K_{ij}\, a_{i\sigma}(t) n_{j\sigma'}(t) + \sum_{j\sigma'} J_{ij}\, a^{\dagger}_{j\sigma'}(t) a_{i\sigma'}(t) a_{j\sigma}(t) . \end{aligned} \tag{5.42}$$

When we multiply the above equation by $a^{\dagger}_{i\sigma}$ from the left and sum over the lattice site i and spin σ we get

$$\begin{aligned} i \frac{d}{dt} \sum_{i\sigma} a^{\dagger}_{i\sigma} a_{i\sigma}(t) &= \sum_{ij\sigma} (T_{ij} - \mu\delta_{ij})\, a^{\dagger}_{i\sigma} a_{j\sigma}(t) \\ &+ I \sum_{i\sigma} a^{\dagger}_{i\sigma}\, a_{i\sigma}(t)\, n_{i-\sigma}(t) \end{aligned}$$

$$+ \sum_{i\,j\sigma\,\sigma'} K_{ij}\, a^{\dagger}_{i\sigma}\, a_{i\sigma}(t)\, n_{j\sigma'}(t)$$

$$+ \sum_{i\,j\sigma\,\sigma'} J_{ij}\, a^{\dagger}_{i\sigma}\, a^{\dagger}_{j\sigma'}(t)\, a_{i\sigma'}(t)\, a_{j\sigma}(t)\ . \qquad (5.42)$$

By taking the ensemble average of both the sides using Eq.(1.14), and taking the limit $t \to 0$ we get

$$\lim_{\epsilon\to 0^+} i \sum_{i\sigma} \int_{-\infty}^{\infty} \omega \frac{G^{\sigma\sigma}_{ii}(\omega+i\epsilon) - G^{\sigma\sigma}_{ii}(\omega-i\epsilon)}{e^{\beta\omega}+1}\, d\omega$$

$$= 2\langle H\rangle - i\sum_{i\,j\sigma} (T_{ij}+\mu\,\delta_{ij}) \lim_{\epsilon\to 0^+} \int_{-\infty}^{\infty} \frac{G^{\sigma\sigma}_{ji}(\omega+i\epsilon) - G^{\sigma\sigma}_{ji}(\omega-i\epsilon)}{e^{\beta\omega}+1}\, d\omega\ ,$$

Using the relations (3.12) and (5.5) we get the energy of the system per atom as

$$E = \frac{\langle H\rangle}{N} = \frac{i}{2N} \lim_{\epsilon\to 0^+} \sum_{\vec{k}\sigma} \int_{-\infty}^{\infty} \frac{(\omega+\mu+\epsilon_{\vec{k}})\,[G^{\sigma\sigma}_{\vec{k}\vec{k}}(\omega+i\epsilon) - G^{\sigma\sigma}_{\vec{k}\vec{k}}(\omega-i\epsilon)]}{e^{\beta\omega}+1}\, d\omega\ ,$$

$$(5.43)$$

It gives the ground state energy per atom as

$$E = \frac{i}{2N} \lim_{\epsilon\to 0^+} \sum_{\vec{k}\sigma} \int_{-\infty}^{0} (\omega+\mu+\epsilon_{\vec{k}})\,[G^{\sigma\sigma}_{\vec{k}\vec{k}}(\omega+i\epsilon) - G^{\sigma\sigma}_{\vec{k}\vec{k}}(\omega-i\epsilon)]\, d\omega\ .$$

$$(5.44)$$

Now we evaluate the expression (5.44) for para, ferro and antiferromagnetic states using square density of states.

From Eq.(5.18) the Green's function $G^{\sigma\sigma}_{\vec{k}\vec{k}}(\omega)$ for the paramagnetic state is given by

$$G^{\sigma\sigma}_{\vec{k}\vec{k}}(\omega) = \frac{1/2\pi}{\omega+\mu-\epsilon_{\vec{k}}-A_o} . \tag{5.45}$$

Using this Green's function in Eq.(5.44) we get the ground state energy of the paramagnetic state as

$$E_P = \frac{A_o}{2} . \tag{5.46}$$

Here we have used the relation $T_{ii} = \frac{1}{N} \sum_{\vec{k}} \epsilon_{\vec{k}} = 0.$

For ferromagnetic system the Green's function $G^{\sigma\sigma}_{\vec{k}\vec{k}}(\omega)$ is given by Eq.(5.21). By substituting this in Eq.(5.44) we get

$$E_F = \frac{1}{2N} \sum_{\vec{k}} \int_{-\infty}^{\infty} (\omega+\mu+\epsilon_{\vec{k}}) \{\delta(\omega+\mu-\epsilon_{\vec{k}}-A_o-B_o) + \delta(\omega+\mu-\epsilon_{\vec{k}}-A_o+B_o)\} d\omega . \tag{5.47}$$

For one electron per atom it has been shown in sec. III that $\mu = A_o$ and

$$\begin{aligned} \Delta_0 &= \frac{1}{2} \quad \text{for} \quad \frac{\alpha}{I+J_o} < 1.0 \\ &= 0 \quad \text{otherwise} . \end{aligned}$$

Hence Eq.(5.47) gives

$$E_F = \frac{A_o}{2} - \frac{I+J_o}{4} \qquad \text{for} \quad \frac{\alpha}{I+J_o} < 1.0$$

$$= E_P = \frac{A_o}{2} \qquad \text{otherwise .} \tag{5.48}$$

In an antiferromagnetic system, by substituting the value of the Green's function $G^{\sigma}_{\vec{K}\vec{K}}(\omega)$ from Eq.(5.36) in Eq.(5.44) we get

$$E_{AF} = \frac{1}{2N} \sum_{\vec{k}} \int_{-\infty}^{0} \frac{(\omega+\mu+\epsilon_{\vec{k}})}{\sqrt{(\epsilon_{\vec{k}}^2 + B_{\vec{Q}}^2)}} \Big[(\epsilon_{\vec{k}} + \sqrt{(\epsilon_{\vec{k}}^2 + B_{\vec{Q}}^2)})\delta \; \omega+\mu - \epsilon_{\vec{k}} - A_o - \sqrt{(\epsilon_{\vec{k}}^2 + B_{\vec{Q}}^2)} \}$$

$$+ (\sqrt{(\epsilon_{\vec{k}}^2 + B_{\vec{Q}}^2)} - \epsilon_{\vec{k}})\delta \{ \omega+\mu-\epsilon_{\vec{k}} - A_o + \sqrt{(\epsilon_{\vec{k}}^2 + B_{\vec{Q}}^2)} \} \Big] d\omega$$

$$\tag{5.49}$$

Using the relation $\mu = A_o$ for one electron per atom in Eq.(5.41) we get at absolute zero of temperature

$$1 = \frac{2(I - J_o)}{2\alpha} \int_0^{\alpha/2} \frac{d\epsilon}{\sqrt{(\epsilon^2 + B_{\vec{Q}}^2)}} . \tag{5.50}$$

When the relations (5.50) and $\mu = A_o$ are used in Eq.(5.49) it takes the form

$$E_{AF} = \frac{A_o}{2} - (I-J_o)\,\tilde{\Delta}_{\vec{Q}} - \frac{2}{\alpha} \int_0^{\alpha/2} \frac{\epsilon^2 d\epsilon}{\sqrt{(\epsilon^2 + B_{\vec{Q}}^2)}} . \tag{5.51}$$

Integrals in Eqs.(5.50) and (5.51) are easy to evaluate. After integration Eq.(5.50) gives

$$B_{\vec{Q}} = \frac{\alpha/2}{\operatorname{Sinh}\,(\alpha/(I-J_o))} . \qquad (5.52)$$

Using this relation in Eq.(5.51) and performing the integration we get

$$E_{AF} = \frac{A_o}{2} - \frac{\alpha}{4} \operatorname{Coth}\left(\frac{\alpha}{I-J_o}\right) . \qquad (5.53)$$

The energies of the para, ferro and antiferromagnetic states are evaluated from Eqs. (5.46), (5.48) and (5.53). The regions of stability of these magnetic phases are shown as a α/I vs J_o/I diagram in Fig.5.4. This figure clearly shows that for Hubbard model ($J_o/I = o$) the ground state is antiferromagnetic and hence in this model the question of two phase transitions in ferromagnetic system does not arise.

VI. CONCLUSIONS

In the preceding sections we have discussed the phenomena of metal-nonmetal transitions in ferromagnetic as well as in antiferromagnetic systems having one electron per atom. We found that in ferromagnetic system, for $\alpha/(I+J_o)<1.0$ two phase transitions occur at two different critical temperatures

T_c and T_M ($T_M < T_c$), for $\alpha/(I+J_0) > 1.0$ no phase transition is possible. Two phase transitions are possible only when the interatomic interaction is finite because in the absence of interatomic interaction (i.e. for Hubbard model) ground state is never the ferromagnetic state. At absolute zero of temperature a first order phase transition occurs at $\alpha/(I+J_0) = 1.0$ where the long range order parameter Δ_0 changes from 1/2 to zero and the system changes from a ferromagnetic nonmetal to paramagnetic metal.

In antiferromagnetic system, at absolute zero, phase transitions do not occur. The system remains antiferromagnetic nonmetal for all values of interaction parameters. At finite temperatures the antiferromagnetic nonmetal changes into a paramagnetic metal at some critical temperature. Like the ferromagnetic system, in this case two phase transitions do not occur because the band gap goes to zero only when the long range order parameter $\Delta_{\vec{Q}}$ goes to zero.

B. METAL-NONMETAL TRANSITIONS IN HYBRIDIZED s AND d BANDS

Mott[88] proposed a theory for metal-nonmetal transitions and predicted the existence of a nonmetal-metal transition under pressure when the lattice parameter passes through a critical value. Such a transition has not yet been observed.[94] Here we discuss qualitatively how the s-d hybridization stiffens the conditions for the pressure induced nonmetal-metal transition.

We consider a system described by the Hamiltonian (2.1). First we restrict our study to the case $I = 0$ i.e. we drop out the third term in (2.1). This term represents the Coulomb interaction between d electrons of opposite spin at the same lattice site. In this case equations of motion (2.8) - (2.11) for the s and d electron Green's functions are exactly soluble. s and d electron Green's functions are given by

$$G^{\sigma}_{\vec{k}\vec{k}}(\omega) = \frac{(\omega - E_{d\vec{k}})/2\pi}{(\omega-E_{\vec{k}})(\omega-E_{d\vec{k}}) - N|V_{\vec{k}d}|^2} , \qquad (5.54)$$

$$G^{\sigma}_{d\vec{k}}(\omega) = \frac{(\omega-E_{\vec{k}})/2\pi}{(\omega-E_{\vec{k}})(\omega-E_{d\vec{k}}) - N|V_{\vec{k}d}|^2} . \qquad (5.55)$$

These Green's functions are independent of the spin index σ and hence the system behaves as a paramagnet. The poles of the

A at which the transition from the nonmetallic to metallic state occurs. When we apply pressure on a nonmetallic substance, the lattice parameter decreases, consequently A increases, therefore a transition from nonmetallic to metallic state should occur at a critical pressure when A crosses the critical value determined by the choice of S and B. But it should be remembered that S increases as we increase the pressure, because the overlapping of s and d wavefunctions increases due to compression of the lattice. Fig. 5.6 clearly shows that this increase in S does not favor the nonmetal-metal transition. Thus the s-d interaction opposes the pressure induced nonmetal transition. This behavior of s-d hybridization may help in understanding the difficulty of observing the pressure induced nonmetal-metal transitions.

Now we extend our study to the Hamiltonian (2.2) with the intraatomic interaction $I \neq 0$. In chapter II we have investigated this Hamiltonian within the Hartree-Fock approximation. It is found that in this approximation, due to s-d hybridization, s and d bands give rise to two hybridized bands given by Eq.(2.24). Number of states per atom for each spin is found to be 1 in each hybridized band. Therefore, as we have seen earlier, a system having two electrons per atom in the s and d bands together, will show nonmetal-metal transition when the band gap between the lower and upper hybridized bands goes to zero. Here we shall consider only the paramagnetic case. Under the assumptions (2.33) and (2.41) the condition for zero band gap is given by

$$(A+1)^2 S^2 - A\left[\frac{A}{4}(A+2)B^2 + B\left(1+P\frac{\langle n_d\rangle}{2}\right) - \left(1+P\frac{\langle n_d\rangle}{2}\right)^2\right] = 0 \qquad (5.58)$$

where $P = \frac{I}{T_o}$ and $\frac{\langle n_d\rangle}{2} = \langle n_{d\sigma}\rangle = \langle n_{d-\sigma}\rangle$. The value of $\langle n_d\rangle$ must be evaluated self-consistently from Eqs. (2.50) and (2.51) in a way such that the total number of electrons $n = \langle n_d\rangle + \langle n_s\rangle = 2$. To do this we take   as a variable parameter and evaluate $\langle n_d\rangle$ self-consistently from Eq.(2.50). This value of $\langle n_d\rangle$ is substituted in Eq.(2.51) to get $\langle n_s\rangle$ and consequently n. The process is continued till we get n = 2. To obtain the transition curve this value of $\langle n_d\rangle$ corresponding to n = 2 is substituted in Eq.(5.58). For B = 2.0 we have plotted the transition curves between S and A for various values of P in Fig.5.8. The regions above and below a transition curve correspond to nonmetallic and metallic behaviors respectively. These curves show that as we increase the intraatomic interaction, the nonmetallic region increases, ~~and~~ thus tendency of a system towards nonmetallic behavior increases. This result one might have guessed in the very begining from the fact that the intraatomic interaction tries to keep apart the two electrons of opposite spins at the same lattice site and thus lowers the tendency of metallic behavior.

When the intraatomic interaction I is very large, the validity of the Hartree-Fock approximation is dubious. In this case one must take into account the effect of correlation between d electrons. We have already developed a correlation theory in chapter II. By proceding in a manner similar to the Hartree-Fock approximation, we have investigated the phenomenon of metal-nonmetal transition for $I \rightarrow \infty$ with the help of Eqs. (2.61)- (2.65). We find that nonmetal-metal transition occurs when the number of electrons in both s and d bands together is equal to 1.67. The transition curve coincides with the curve $P = 0$ in Fig.5.8.

In the absence of s-d hybridization it is easy to show from Eqs.(2.22), (2.23), (2.61) and (2.62) that in the Hartree-Fock theory, d and s bands are half filled when $\langle n_d \rangle = \langle n_s \rangle = 1.0$ and in the correlation theory they are half filled when $\langle n_d \rangle = 0.67$ and $\langle n_s \rangle = 1.0$ respectively. This shows that nonmetal-metal transition occurs in the presence of s-d hybridization only when the d and s bands are half filled.

above Green's functions give the hybridized bands

$$\omega^{\pm}_{\vec{k}} = \frac{1}{2} \left[\epsilon_{\vec{k}} + \epsilon_{d\vec{k}} \pm \sqrt{\left\{(\epsilon_{d\vec{k}} - \epsilon_{\vec{k}})^2 + 4N|V_{\vec{k}d}|^2\right\}}\right] - \mu . \quad (5.56)$$

The Green's functions (5.54) and (5.55), when substituted in the equations (2.15) and (2.16) give the number of states per atom for s and d electrons together in each hybridized band equal to unity for each spin. Thus if we choose a system with two electrons per atom in s and d bands together, the system will behave as a non-metal if there is a gap between the lower and upper hybrid bands, otherwise it will behave as a metal. A nonmetal-metal transition occurs when the band gap becomes zero. Under the assumptions (2.33) for $V_{\vec{k}d}$ and (2.41) for $\epsilon_{d\vec{k}}$, we obtain from (5.56) the following condition for zero band gap.

$$(A+1)^2 S^2 - A\left\{\frac{A}{4}(A+2)B^2 + B - 1\right\} = 0 \qquad (5.57)$$

Where $B = \alpha/T_0$ and $S = |v|/T_0$. Eq.(5.57) contains three parameters. By fixing a particular parameter, one can plot a transition curve for the remaining two parameters. In Figs.(5.5) to (5.7) we have plotted S - B, S - A and B - A curves for differen values of A, B and S respectively. In Figs. 5.5 and 5.6 the regions above and below a transition curve correspond to nonmetallic and metallic behaviors respectively while in Fig.5.7 situation is just the reverse. These curves show that for a particular choice of values of S and B we get a critical value of

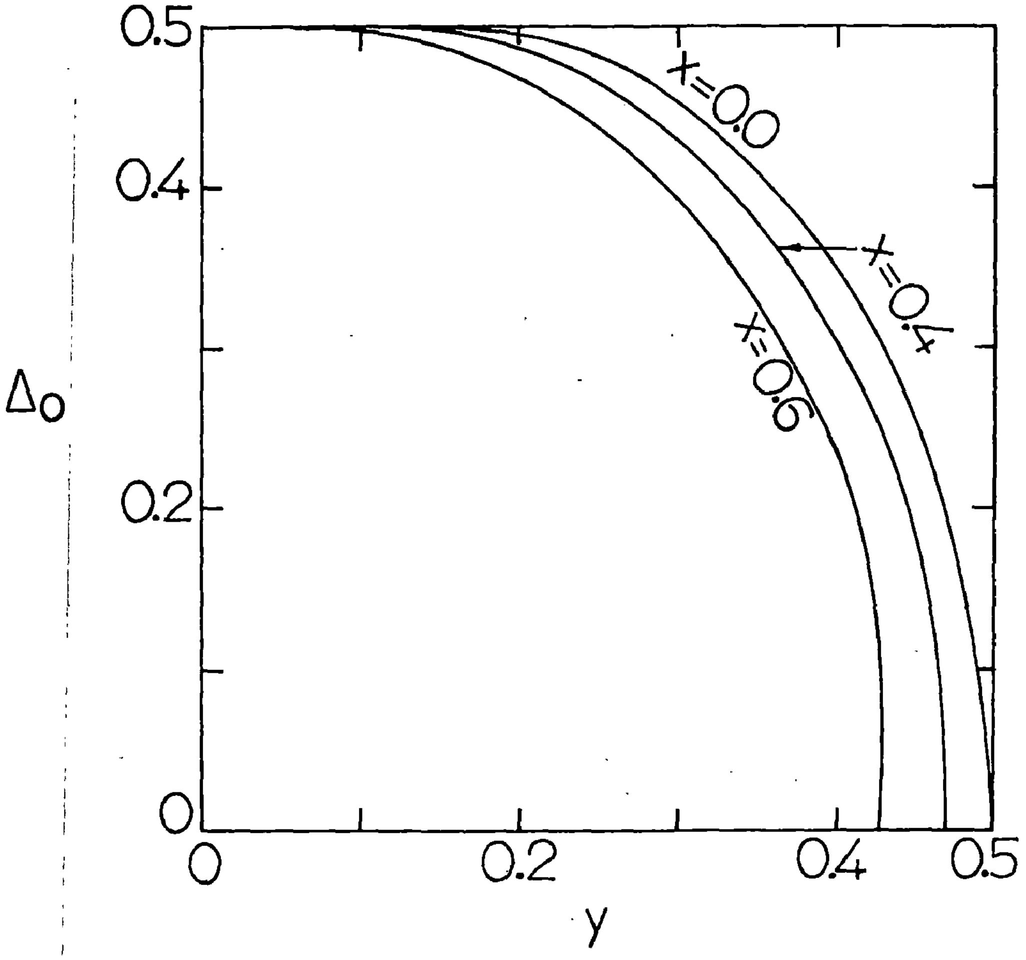

FIG. 5.1 A PLOT OF Δ_0 VERSUS $Y = 2k_B T/(I+J_0)$ FOR VARIOUS VALUES OF $x = K/(I+J_0)$.

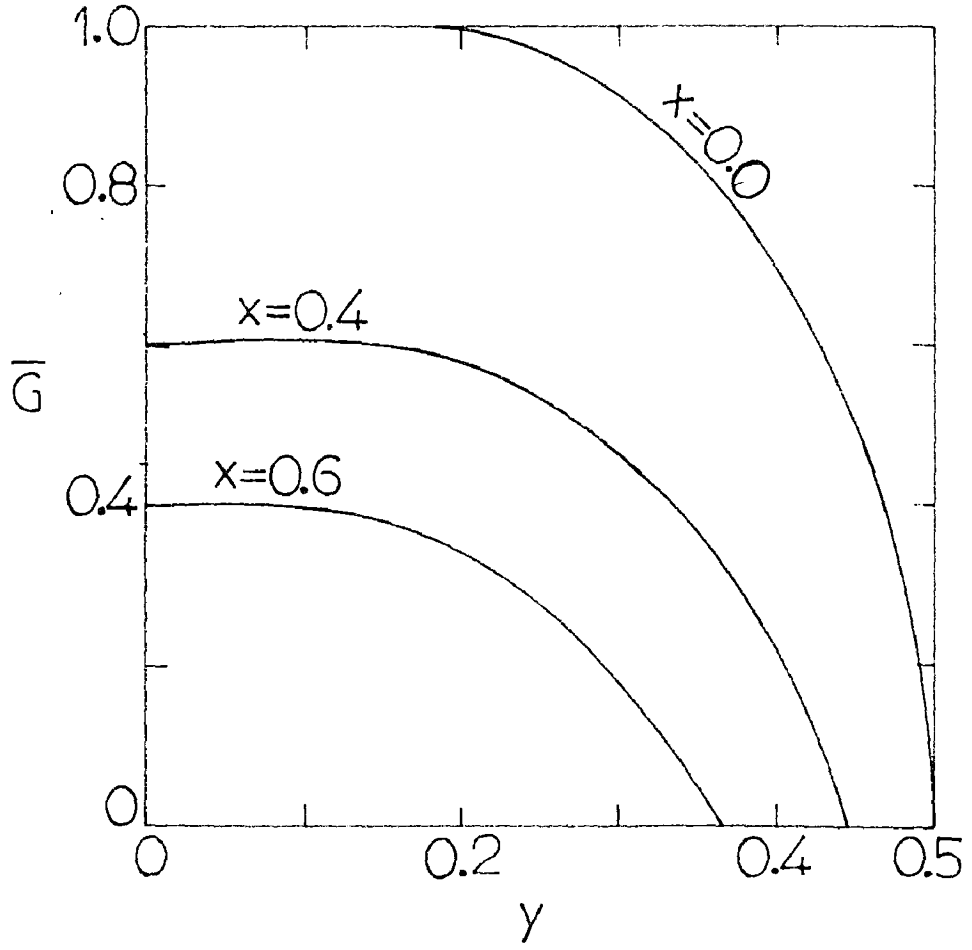

FIG. 5.2 A PLOT OF $\overline{G} = G/(1+J_0)$ VERSUS $y = 2k_B T/(1+J_0)$ FOR VARIOUS VALUES OF $x = \alpha/(1+J_0)$.

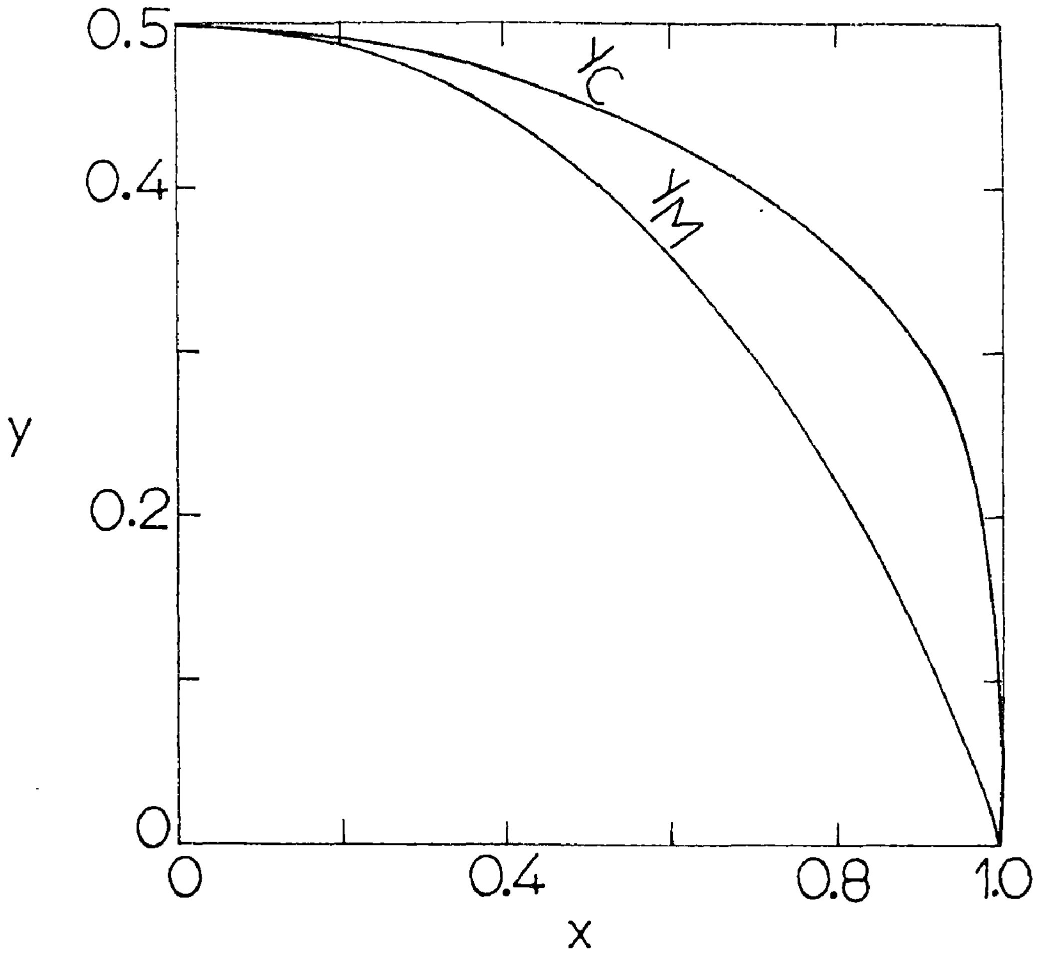

FIG. 5.3 VARIATION OF $Y_C = 2k_B T_C/(1+J_0)$ AND $Y_M = 2k_B T_M/(1+J_0)$ AS A FUNCTION OF $x = \alpha/(1+J_0)$

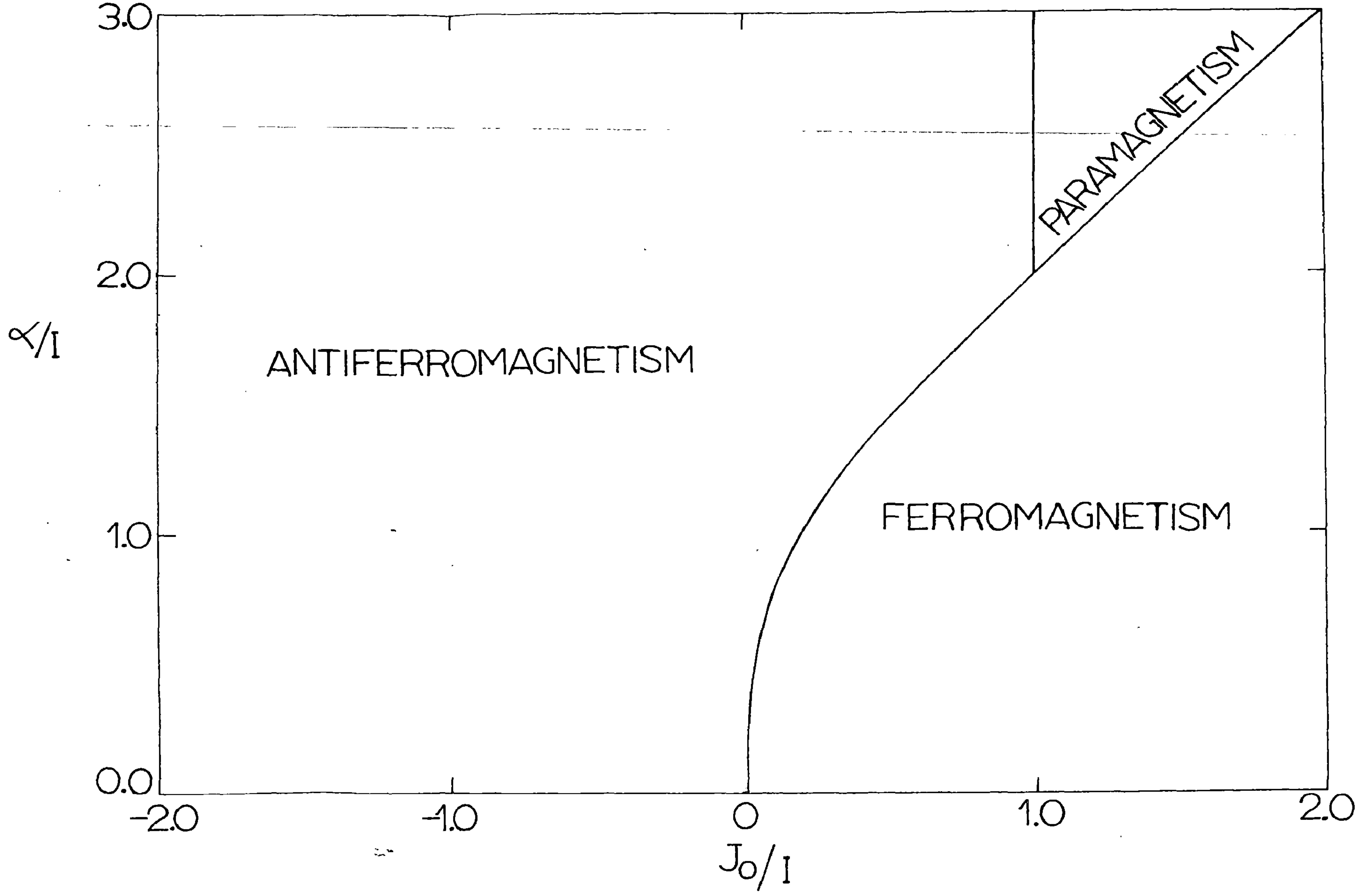

FIG. 5.4 PHASE BOUNDARIES BETWEEN PARA, FERRO AND ANTIFERRMAGNETIC STATES.

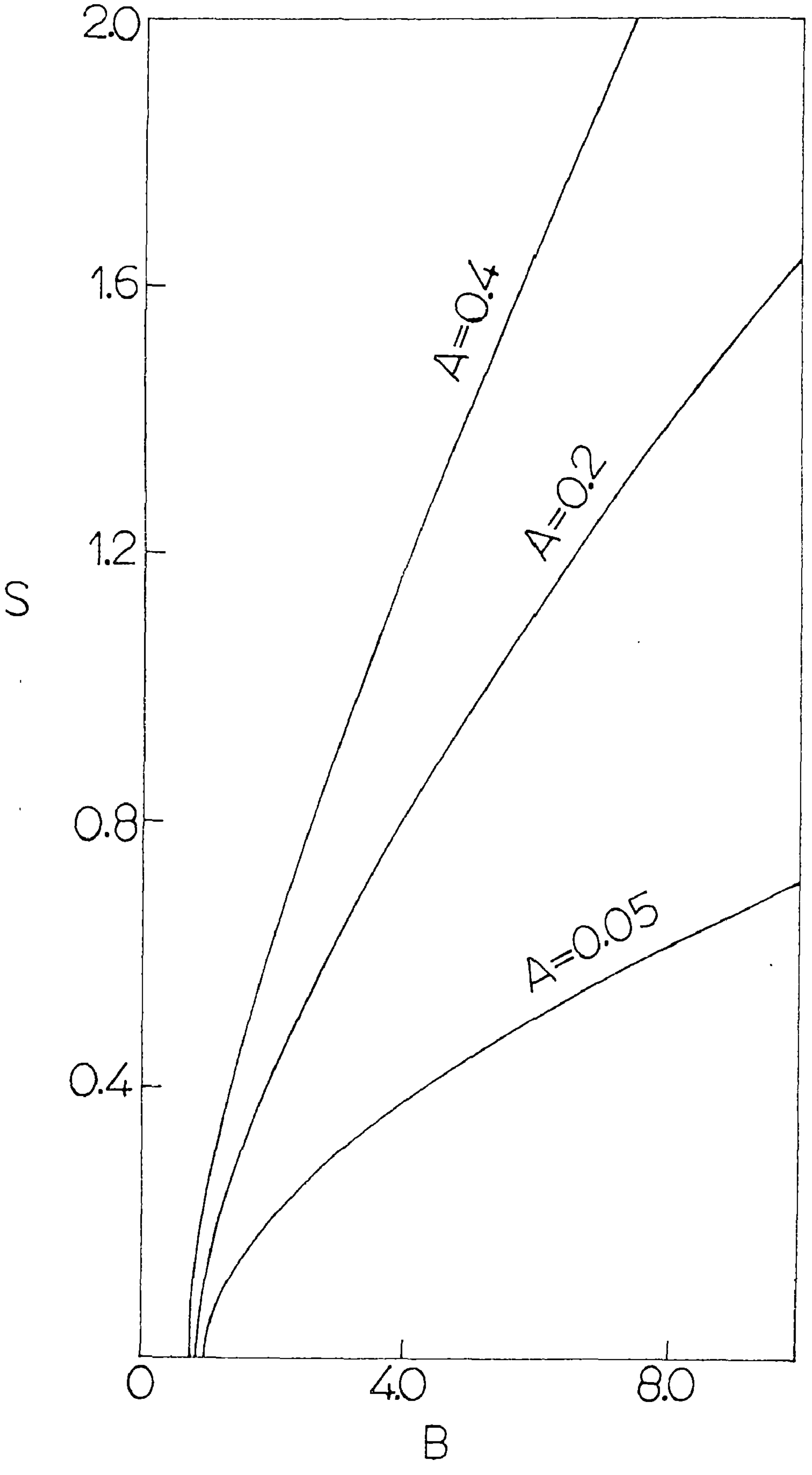

FIG. 5.5 S-B CURVES FOR DIFFERENT VALUES OF A

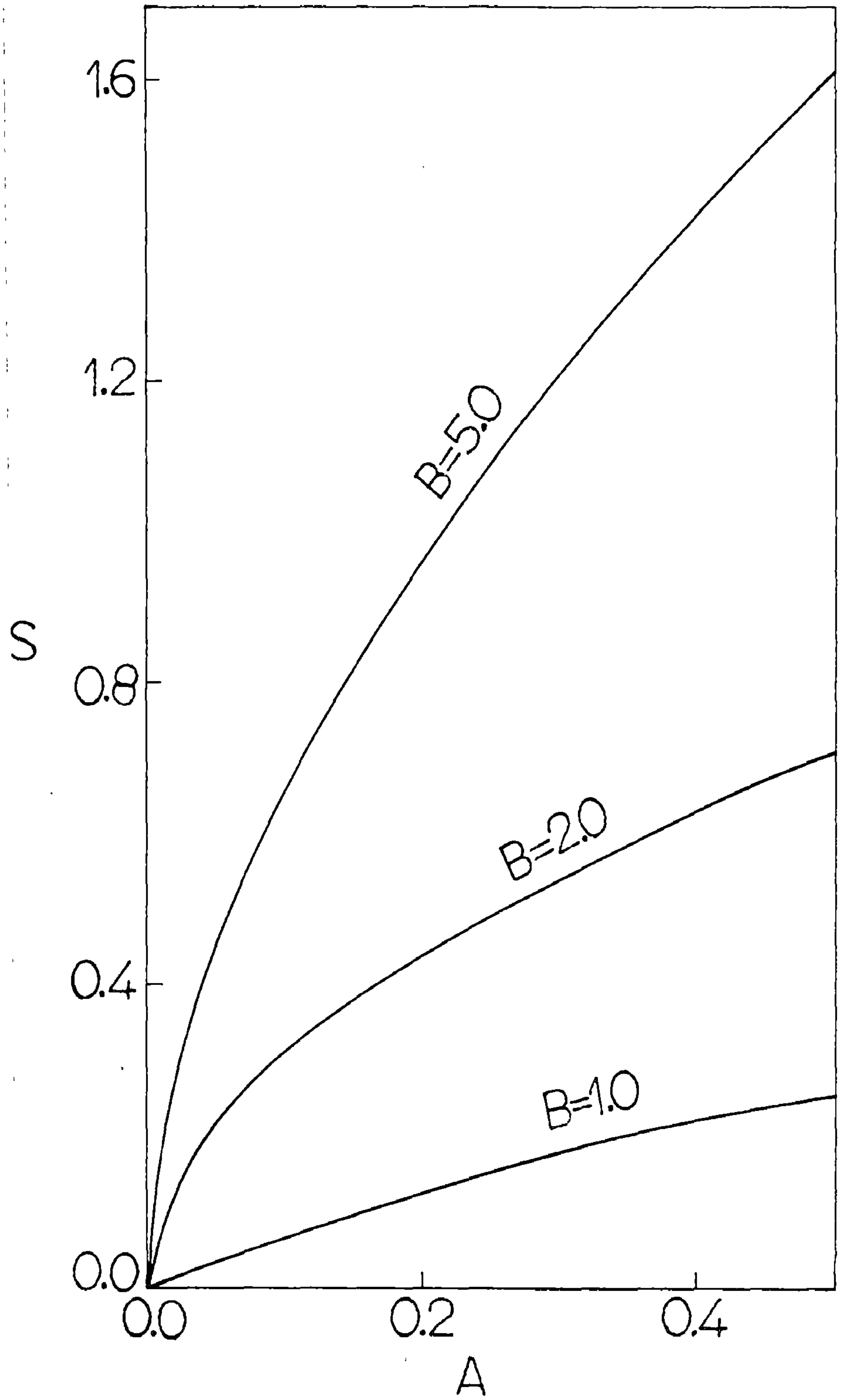

FIG. 5.6 S-A CURVES FOR DIFFERENT VALUES OF B

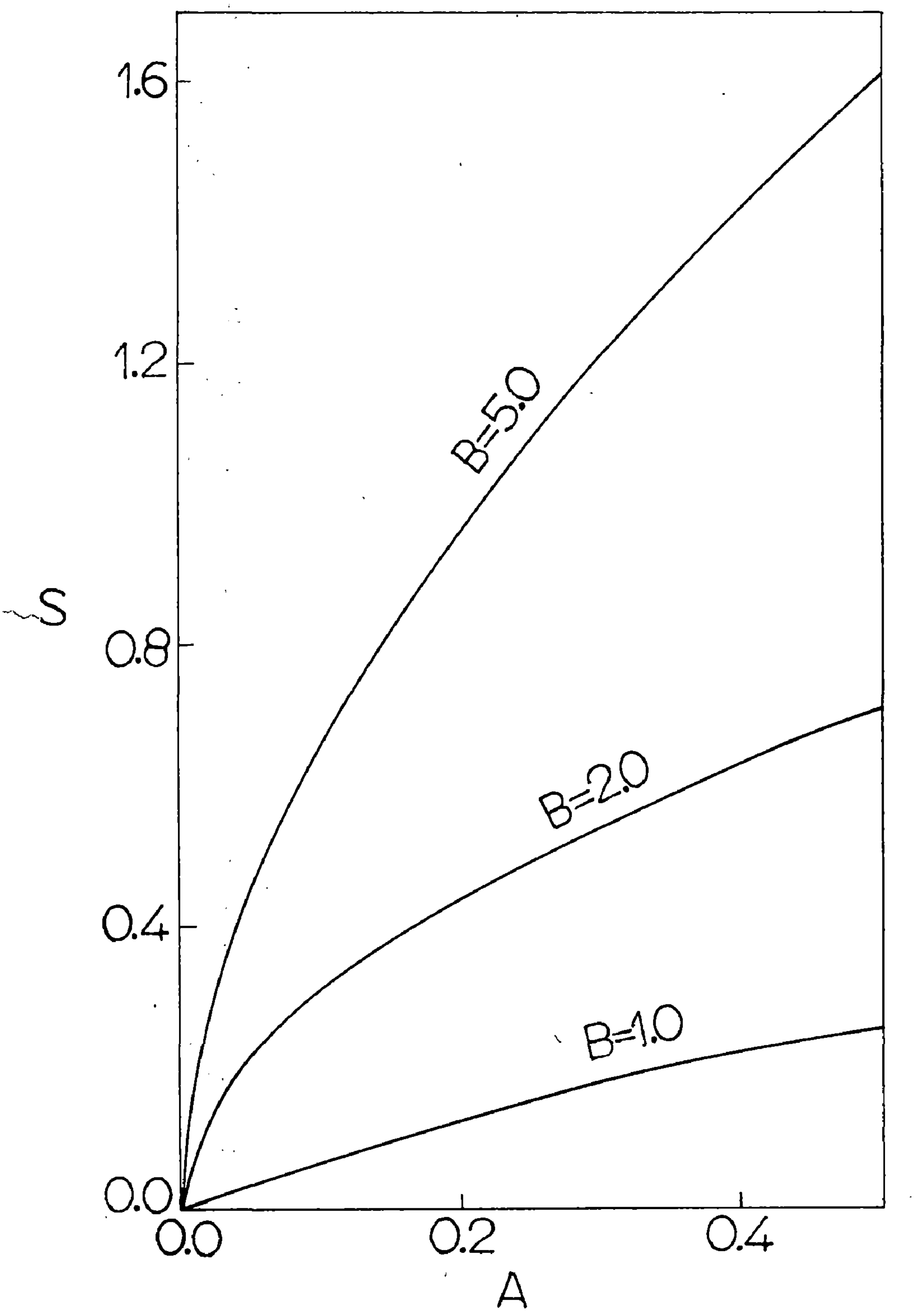

FIG. 5.6 S–A CURVES FOR DIFFERENT VALUES OF B

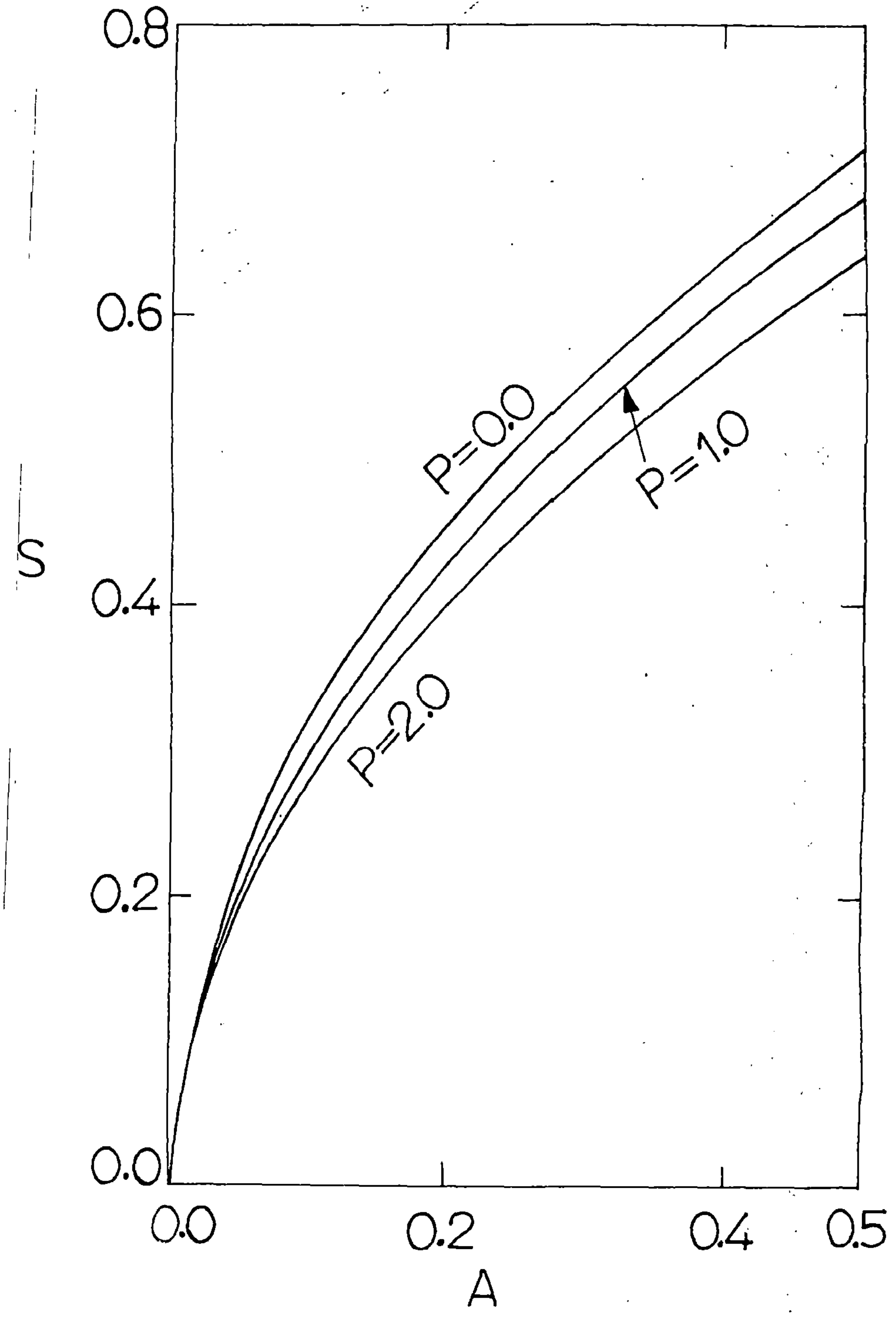

FIG. 5.8 S-A CURVES FOR DIFFERENT VALUES OF P AND B = 2.0

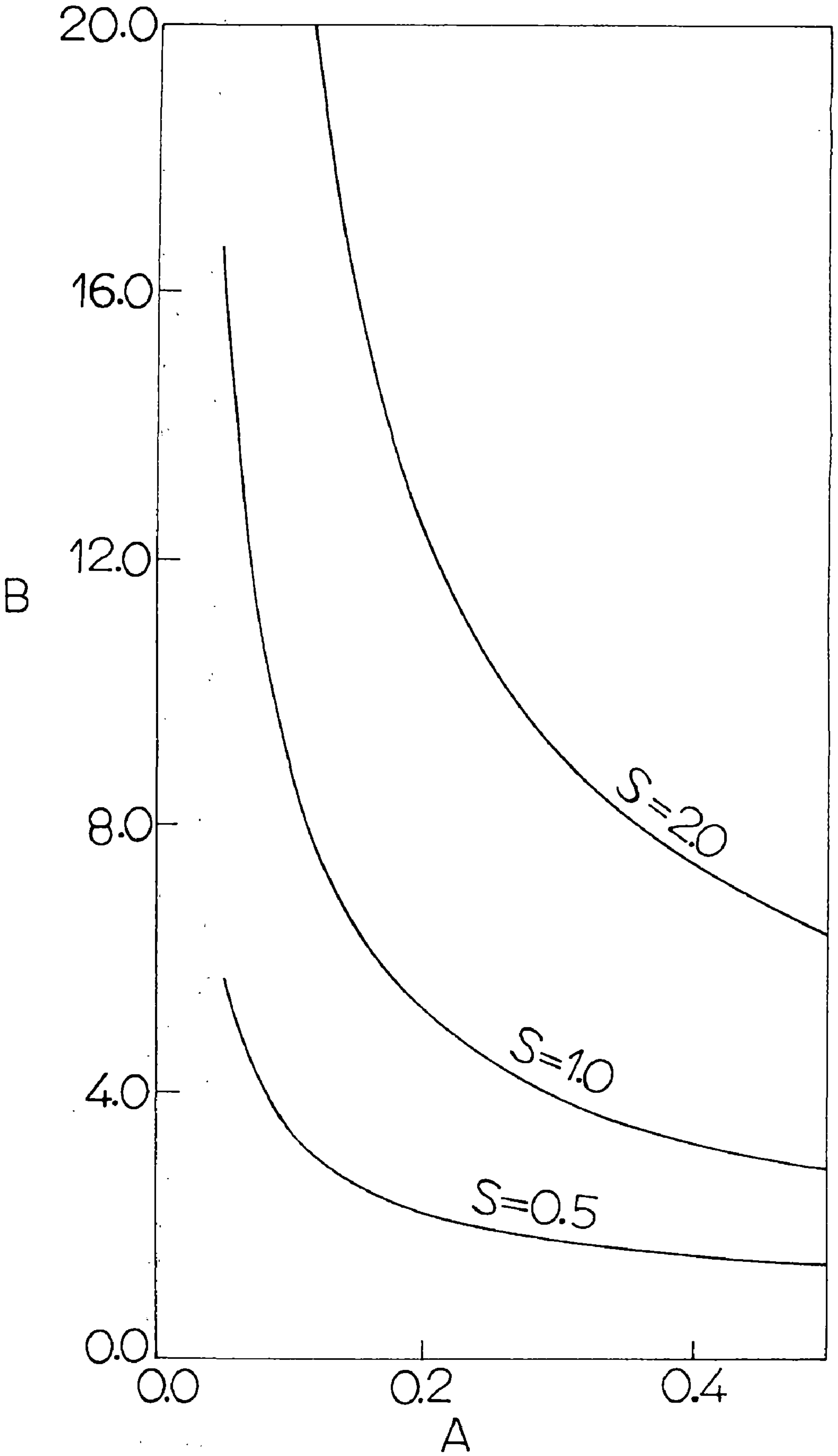

FIG. 5.7 B-A CURVES FOR DIFFERENT VALUES OF S

EPILOGUE

The present work is qualitative in nature. The which have been studied, do not represent the actual situa in the transition metals. To deal with the reality one must take into account the degeneracy of the d bands, the electrostatic interactions between s and d electrons and among themselves, the interaction of s and d electrons with the lattice vibrations, and the relativistic effects (i.e. spin orbit coupling etc.). However the present work may help in finding the ways to deal with the more complex situation in the transition metals. Extension of the present work in the theory of magnetism and metal-nonmetal transitions, within the framework of the models considered here, can be made in several directions.

For a system described by the Hamiltonian (2.1) we have discussed the spatially uniform magnetic solutions at absolute zero although the formulation is valid for all temperatures. A natural extension is to study the spatially nonuniform magnetic solutions (spin density waves) and their relative stability at absolute zero. This will give a qualitative understanding of the effect of s-d hybridization on the ground state stability of spin density waves described by the Hubbard Hamiltonian. The second extension is the investigation of the collective excitations for a system having spin density wave as its ground state. The third extension is to develope the finite temperature

$$\langle\langle a^{\dagger}_{i-\sigma}\, a_{\ell-\sigma}\, a_{i\sigma} ; a^{\dagger}_{j\sigma'} \rangle\rangle_{\omega} \simeq \langle a^{\dagger}_{i-\sigma}\, a_{\ell-\sigma} \rangle G^{\sigma\sigma'}_{ij}(\omega) - \langle a^{\dagger}_{i-\sigma}\, a_{i\sigma} \rangle G^{-\sigma\sigma}_{\ell j}(\omega)$$

$$\langle\langle a^{\dagger}_{\ell-\sigma}\, a_{i-\sigma}\, a_{i\sigma} , a^{\dagger}_{j\sigma} \rangle\rangle_{\omega} \simeq \langle a^{\dagger}_{\ell-\sigma}\, a_{i-\sigma} \rangle G^{\sigma\sigma'}_{ij}(\omega) - \langle a^{\dagger}_{\ell-\sigma}\, a_{i\sigma} \rangle G^{-\sigma\sigma'}_{ij}(\omega)$$

(A.3)

These approximations differ from that of Hubbard's approximations in the sense that they include the terms like $\langle a^{\dagger}_{i-\sigma} a_{\ell\sigma} \rangle$ which represent the correlation between an electron and a hole of opposite spin. Similar approximations were made in Sec.V where such correlation functions play an important role in the theory of metal-nonmetal transitions. Further we shall assume that the correlations between an electron and a hole at different lattice sites are small so that we may take $\langle a^{\dagger}_{i\sigma}\, a_{\ell\sigma} \rangle = 0$ if $i \neq \ell$.

Substituting the approximations (A.3) in (A.2) one obtains

$$(\omega+\mu-I-T_0) \langle\langle n_{i-\sigma}\, a_{i\sigma} , a^{\dagger}_{j\sigma'} \rangle\rangle_{\omega}$$

$$= (\langle n_{i-\sigma} \rangle \delta_{\sigma\sigma'} - \langle a^{\dagger}_{i-\sigma}\, a_{i\sigma} \rangle \delta_{-\sigma\sigma'})\, \delta_{ij}/2\pi$$

$$+ \langle n_{i-\sigma} \rangle \sum_{\ell \neq i} T_{i\ell}\, G^{\sigma\sigma'}_{\ell j}(\omega) - \langle a^{\dagger}_{i-\sigma}\, a_{i\sigma} \rangle \sum_{\ell \neq i} T_{i\ell}\, G^{-\sigma\sigma'}_{\ell j}(\omega)$$

(A.4)

whence

$$\langle\langle n_{i-\sigma}\, a_{i\sigma} , a^{\dagger}_{j\sigma'} \rangle\rangle_{\omega} = \frac{1}{\omega+\mu-I-T_0} \Big[\langle n_{i-\sigma} \rangle \Big\{ \frac{\delta_{ij}\delta_{\sigma\sigma'}}{2\pi} + \sum_{\ell \neq i} T_{i\ell}\, G^{\sigma\sigma'}_{\ell j}(\omega) \Big\}$$

$$- \langle a^{\dagger}_{i-\sigma}\, a_{i\sigma} \rangle \Big\{ \frac{\delta_{ij}\delta_{-\sigma\sigma'}}{2\pi} + \sum_{\ell \neq i} T_{i\ell}\, G^{-\sigma\sigma'}_{\ell j}(\omega) \Big\} \Big]$$

(A.5)

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The electron spin polarization can be written in terms of the Green's function $G^{\sigma}_{\vec{k}\vec{k}'}(\omega)$ as

$$p(\vec{r}) = -\frac{1}{N} \lim_{\epsilon \to 0^+} \sum_{\vec{k}\vec{k}'\sigma} \sigma \, e^{i(\vec{k}-\vec{k}').\vec{r}} \int_{\infty}^{\infty} \mathrm{Im} \left\{ G^{\sigma}_{\vec{k}'\vec{k}}(\omega + i\epsilon) \right\} f(\omega) d\omega \tag{C.12}$$

where $f(\omega) = (e^{\beta\omega} + 1)^{-1}$. By substituting the value of $G^{\sigma}_{\vec{k}'\vec{k}}$ from Eq.(C.11) in Eq.(C.12) we get

$$p(\vec{r}) = -\frac{J(\langle n_{d+}\rangle - \langle n_{d-}\rangle)}{N^2} \sum_{\vec{k}\vec{k}'} \frac{e^{i(\vec{k}-\vec{k}').\vec{r}}}{(\epsilon_{\vec{k}} - \epsilon_{\vec{k}'})} \int_{\infty}^{\infty} \frac{\delta(\omega + \mu - \epsilon_{\vec{k}}) f(\omega) d\omega}{1 + \frac{J^2 \pi^2}{4} \rho(\omega + \mu)} \tag{C.13}$$

where we have assumed that $\epsilon_{\vec{k}} = \epsilon_{-\vec{k}}$ and $F(\omega) = i\pi\rho(\omega)$, $\rho(\omega) = \frac{1}{N} \sum_{\vec{k}} \delta(\omega - \epsilon_{\vec{k}})$ is the density of states per atom for the conduction band. By assuming the energies of the conduction electrons as $\epsilon_{\vec{k}} = k^2/2m^*$, where m^* is the effective mass of the electron, the electronspin polarization in the ground state is given by

$$p(\vec{r}) = \frac{J m^* v^2 (\langle n_{d+}\rangle - \langle n_{d-}\rangle)}{8\pi^3 r^2} \int_0^{\mu} \frac{\mathrm{Sin}\, 2r\sqrt{(2m^*\omega)} \quad d\omega}{1 + \frac{J^2 v^2 m^{*3}}{8\pi^2} \omega} \tag{C.14}$$

where v is the atomic volume. Eq.(C.14) can be rewritten as

$$p(\vec{r}) = \frac{2(\langle n_{d+}\rangle - \langle n_{d-}\rangle)}{\pi\ J\ m^*\ r^2} \int_0^{\frac{|J|v(2m^*)^{3/2}}{8\pi} r} \frac{x \sin\left(\frac{8\pi\ x}{J v m^*}\right)}{r^2 + x^2}\, dx \tag{C.15}$$

For large r, the upper limit of the integration can be taken as ∞. A straight forward integration then gives

$$p(\vec{r}) = \frac{(\langle n_{d+}\rangle - \langle n_{d-}\rangle)}{J m^*\ r^2}\ e^{-\frac{8\pi\ r}{|J| v\ m^*}} \tag{C.16}$$

Thus the electron spin polarization shows exponentially damped behavior similar to that obtained by Bose, et al., although the numerical factor in the power of exponential and the r dependence of the factor multiplying the exponential are different. These differences are due to the differences in the approximations used by us and by Bose et al.

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$$G^{\sigma\sigma'}_{\vec{k}\vec{k}'}(\omega)=\frac{\left\{\omega+\mu-T_o-(\epsilon_{\vec{k}}-T_o)(1-n_o/2)\right\}\left\{(1-n_o/2)\delta_{\sigma\sigma'}\delta_{\vec{k}\vec{k}'}+\Delta_{\vec{q}}\delta_{-\sigma\sigma'}\delta_{\vec{k}+\vec{q},\vec{k}'}\right\}\frac{1}{2\pi}+\Delta_{\vec{q}}\left\{(1-n_o/2)\delta_{-\sigma\sigma'}\delta_{\vec{k}+\vec{q},\vec{k}'}\pm\Delta_{\vec{q}}\delta_{\sigma\sigma'}\delta_{\vec{k}\vec{k}'}\right\}(\epsilon_{\vec{k}+\vec{q}}-T_o)/2\pi}{\left[\left\{\omega+\mu-T_o-(\epsilon_{\vec{k}}-T_o)(1-n_o/2)\right\}\left\{\omega+\mu-T_o-(\epsilon_{\vec{k}+\vec{q}}-T_o)(1-n_o/2)\right\}-\Delta^2_{\vec{q}}(\epsilon_{\vec{k}}-T_o)(\epsilon_{\vec{k}+\vec{q}}-T_o)\right]}$$

(A.18)

III. ENERGY OF THE SYSTEM

As shown in chapter V, the ground state energy per atom of the system described by the Hamiltonian (1.9) is given by

$$E=\frac{i}{2N}\lim_{\epsilon\to 0^+}\sum_{\vec{k}\sigma}\int_{-\infty}^{0}(\omega+\mu+\epsilon_{\vec{k}})\left[G^{\sigma\sigma}_{\vec{k}\vec{k}}(\omega+i\epsilon)-G^{\sigma\sigma}_{\vec{k}\vec{k}}(\omega-i\epsilon)\right]d\epsilon\,.$$

(A.19)

From Eq.(A.18) the Green's function $G^{\sigma\sigma}_{\vec{k}\vec{k}}(\omega)$ is given by

$$G^{\sigma\sigma}_{\vec{k}\vec{k}}(\omega)=\frac{\left[\left\{\omega+\mu-\epsilon_{\vec{k}}(1-n_o/2)\right\}(1-n_o/2)+\Delta^2_{\vec{q}}\,\epsilon_{\vec{k}+\vec{q}}\right]/2\pi}{\left\{\omega+\mu-\epsilon_{\vec{k}}(1-n_o/2)\right\}\left\{\omega+\mu-\epsilon_{\vec{k}+\vec{q}}(1-n_o/2)\right\}-\Delta^2_{\vec{q}}\,\epsilon_{\vec{k}}\,\epsilon_{\vec{k}+\vec{q}}}\,.$$

(A.20)

Here we have assumed that $T_o = 0$ i.e. we measure the energy from the middle of the band $\epsilon_{\vec{k}}$. Eq.(A.20) can be rewritten as

$$G^{\sigma\sigma}_{\vec{k}\vec{k}}(\omega)=\frac{1}{2\pi}\left[\frac{f_{\vec{k}}(\overset{+}{\omega}_{\vec{k}})}{\overset{+}{\omega}_{\vec{k}}-\overset{-}{\omega}_{\vec{k}}}\;\frac{1}{\omega-\overset{+}{\omega}_{\vec{k}}}+\frac{f_{\vec{k}}(\overset{-}{\omega}_{\vec{k}})}{\overset{-}{\omega}_{\vec{k}}-\overset{+}{\omega}_{\vec{k}}}\;\frac{1}{\omega-\overset{-}{\omega}_{\vec{k}}}\right],$$

(A.21)

where

$$\omega^{\pm}_{\vec{k}} = -\mu + \frac{1}{2}\left[(1-n_o/2)(\epsilon_{\vec{k}} + \epsilon_{\vec{k}+\vec{q}}) \pm \sqrt{\left\{(1-n_o/2)^2(\epsilon_{\vec{k}} - \epsilon_{\vec{k}+\vec{q}})^2 + 4\epsilon_{\vec{k}}\epsilon_{\vec{k}+\vec{q}}\Delta^2_{\vec{q}}\right\}}\right],$$

(A.22)

and $f_{\vec{k}}(\omega) = \{\omega+\mu - \epsilon_{\vec{k}}(1-n_o/2)\}(1-n_o/2) + \Delta^2_{\vec{q}}\,\epsilon_{\vec{k}+\vec{q}}$. (A.23)

It is easy to see that $\{f_{\vec{k}}(\omega^{+}_{\vec{k}}) - f_{\vec{k}}(\omega^{-}_{\vec{k}})\}/\{\omega^{+}_{\vec{k}} - \omega^{-}_{\vec{k}}\} = (1-n_o/2)$. Therefore number of states per atom for each spin is equal to $(1-n_o/2)$ and hence for a system with one electron per atom ($n_o = 1$) both the bands ($\omega^{\pm}_{\vec{k}}$) are completely filled and the Fermi level lies at the top of the band $\omega^{+}_{\vec{k}}$.

When we substitute the value of the Green's function $G^{\sigma\sigma}_{\vec{k}\vec{k}}(\omega)$ from Eq.(A.21) in Eq.(A.19), the energy of the system per atom is given by

$$E = \frac{1}{N}\sum_{\vec{k}}\int_{-\infty}^{0} \frac{(\omega+\mu+\epsilon_{\vec{k}})}{\omega^{+}_{\vec{k}} - \omega^{-}_{\vec{k}}}\left[f_{\vec{k}}(\omega^{+}_{\vec{k}})\delta(\omega-\omega^{+}_{\vec{k}}) - f_{\vec{k}}(\omega^{-}_{\vec{k}})\delta(\omega-\omega^{-}_{\vec{k}})\right]d\omega$$

(A.24)

For $n_o = 1$ and square density of states it can easily be shown that for all magnetic phases we have $E = 0$, which shows that all the states (paramagnetic, ferromagnetic and antiferromagnetic) are degenerate. This result is independent of the dimensionality of the system and agrees with the one dimensional result of Lieb and Wu[49] and that of Kemeny[46] mentioned in the begining of this chapter.

IV. CONCLUSIONS

The above treatment reveals that our results agree with the exact results obtained in the limiting cases. We hope our decoupling approximation may be able to give better insight about the general solutions of Hubbard model. It would be illuminating if the solutions are analysed for finite intraatomic interaction I.

APPENDIX B

EXCHANGE SPLITTING OF THE d-BAND IN NICKEL

The exchange splitting of the bands is an important concept for the itinerant model of a ferromagnet[6]. However there is a lot of controversy about this quantity in case of Ni.[113] The earliest estimate of the exchange splitting in Ni is due to Slater[4] who assumed that the splitting is due to the intraatomic exchange between electrons in orthogonal d-orbitals. He found $\Delta E = J\Delta n$, where ΔE is the exchange splitting, Δn is the difference in the mean number of up and down spin d-electrons per atom and J is a suitable average of the exchange integrals with $m \neq m'$, m being the azimuthal quantum number. Using data derived from the atomic spectra, Slater estimated $J = 0.85$ eV which gave $\Delta E = 0.5$ eV for Ni.

It was pointed out by Van Vleck[31] that, because of the quenching of the orbital angular momentum in the metal, J would be more accurately given by a weighted mean of the $J_{mm'}$ including the term $m = m'$. The integral J_{mm} is numerically very large (about 12 eV) and even if the smallest possible weight-factor (1/5 for d-electrons) is associated with it in the average, one obtains J 2.5 eV which is much greater than Slater's estimate.[4] It is known[4,31,113] that the value of J_{mm} is considerably reduced due to shielding effect of 4s and 3d electrons. Van Vleck[31] and Hubbard[113] obtained $I \simeq 7.5$ eV (I is the shielded value of J_{mm}). On the other hand Herring estimated that $I \simeq 0$.[31] Thus according to these estimations

I for Ni may be anywhere in the range from 0 to 7.5 eV. Hubbard[113] pointed out that if Δ is the band width, $\frac{\Delta}{2}$ (2.5 eV for Ni) is a critical value for I. If I is appreciably less than this critical value, the interaction may be regarded as weak and Slater's estimate[4] of the exchange splitting should be good. On the other hand, if I is appreciably greater than the critical value one will be dealing with the strong interaction model. Considering the d-band as five-fold degenerate, Hubbard[113] found that in the strong interaction limit the exchange splitting comes out to be 0.4 eV at the top of the d-band. Thus both limits give almost the same result.

In this note an intermediate situation is considered. Within the Hartree-Fock approximation, the Hubbard model for single nondegenerate band[34] gives the exchange splitting as $\Delta E = I \Delta N$, where ΔN is the difference in the number of up and down spin electrons per atom in the single nondegenerate band. Recently Liu[114] has shown that I = 5 eV gives the right order of the Curie temperature for Ni. Morris[63] also found that for Ni I = 5 eV. This value lies within the range of earlier estimates mentioned above. Ni has a magnetic moment of 0.6 Bohr magneton per atom. If we use I = 5 eV and $\Delta N = 0.6$ for Ni as Liu[114] had done, we get $\Delta E = 3.0$ eV. This value of exchange splitting is six times the value ($\Delta E \simeq 0.5$ eV) given by the energy band calculation. This gives an impression that the Hartree-Fock approximation is not capable of giving the correct exchange splitting. However one should note that for Ni, $\Delta N = 0.6$ and the d band is five fold degenerate. The Hubbard model is developed for single nondegenerate band. One should therefore use the value of Δ N for a single nondegenerate band. This means $\Delta N = (0.6/5) = 0.12$. If we use this value of ΔN, we get exchange splitting $\Delta E = 0.6$ eV which is in close agreement with the result of the band calculations.[115] Thus for a situation where I is not very large or very small, Hubbard model is capable of giving the correct exchange splitting within the Hartree-Fock approximations. When I is quite large the Hartree-Fock approximation fails and one should take into account the correlation effects.

APPENDIX C

ELECTRON SPIN POLARIZATION DUE TO s-d EXCHANGE INTERACTION

The ground state of a dilute magnetic alloy has been studied by many authors [116-119] by using the s-d exchange Hamiltonian. In general in the ground state the localized magnetic impurity moment is found to interact antiferromagnetically with the conduction electron spin and bound state is formed between them. The localized magnetic moment is supposed to be almost quenched as a result of its spin correlations with the conduction electrons. Therefore it is of interest to study the behavior of this spin compensated state in space in particular to calculate the electron spin polarization. Recently Bose et al.[12 have calculated magnetic impurity spin-conduction electron spin correlation function which is directly related to electron spin polarization.[121] By using the method of cluster variation of the co-operative phenomena they obtained an exponentially damped behavior of impurity-spin-conduction-electron-spin correlation function. In this paper we consider a system having a localized magnetic impurity of spin 1/2 and show that the exponentially damped behavior of electron spin polarization can also be obtained by one particle Green's function approach.

The Hamiltonian for the system incorporating the s-d exchange interaction between the conduction electrons and the localized magnetic impurity of spin 1/2 is given by

$$H = \sum_{\vec{k}\sigma} \epsilon_{\vec{k}}\, a^{\dagger}_{\vec{k}\sigma} a_{\vec{k}\sigma} - \frac{J}{N} \sum_{\substack{\vec{k}\vec{k}' \\ \sigma}} \Big\{ \frac{1}{2} \left(a^{\dagger}_{\vec{k}\sigma} a_{\vec{k}'\sigma} - a^{\dagger}_{\vec{k}-\sigma}\, a_{\vec{k}'-\sigma} \right) n_{d\sigma}$$

$$+\, a^{\dagger}_{\vec{k}\sigma}\, a_{\vec{k}'-\sigma}\, a^{\dagger}_{d-\sigma}\, a_{d\sigma} \Big\} \qquad (C.1)$$

where $\epsilon_{\vec{k}}$ is the energy of the conduction electrons of wave vector $\vec{k}$, $a^{\dagger}_{\vec{k}\sigma}$, $a_{\vec{k}\sigma}$ are the creation and annihilation operators for the conduction electrons of wave vector $\vec{k}$ and spin σ ; $a^{\dagger}_{d\sigma}$, $a_{d\sigma}$ are the same for the impurity electrons and $n_{d\sigma} = a^{\dagger}_{d\sigma}\, a_{d\sigma}$. J is the coupling constant of the s-d exchange interaction and N is the total number of atoms in the crystal.

In order to calculate the electron spin polarization

$$p(\vec{r}) = \frac{1}{2N} \sum_{\vec{k}\vec{k}'\sigma} \sigma\, e^{i(\vec{k}-\vec{k}').\vec{r}} \langle a^{\dagger}_{\vec{k}\sigma}\, a_{\vec{k}'\sigma} \rangle, \qquad (C.2)$$

One requires the knowledge of the correlation function $\langle a^{\dagger}_{\vec{k}\sigma} a_{\vec{k}'\sigma} \rangle$ which can be obtained from the one particle Green's function[103]

$$G^{\sigma}_{\vec{k}\vec{k}'}(\omega) = \langle\langle\, a_{\vec{k}\sigma}\, ,\, a^{\dagger}_{\vec{k}'\sigma} \,\rangle\rangle_{\omega}. \qquad (C.3)$$

The Green's function $G^{\sigma}_{\vec{k}\vec{k}'}(\omega)$ can be found by writing its equation of motion[103]

$$\omega\, G^{\sigma}_{\vec{k}\vec{k}'}(\omega) = \frac{\delta_{\vec{k}\vec{k}'}}{2\pi} + \langle\langle \left[a_{\vec{k}\sigma}\, ,\, H \right]_{-},\, a^{\dagger}_{\vec{k}'\sigma} \,\rangle\rangle_{\omega} \qquad (C.4)$$

For the Hamiltonian (C.1) the commutator $\left[a_{\vec{k}\sigma}\, ,\, H \right]_{-}$ is given by

$$[a_{\vec{k}\sigma}, H']_- = (-\mu+\epsilon_{\vec{k}})a_{\vec{k}\sigma} - \frac{J}{N}\sum_{\vec{k}}\left\{\frac{1}{2}a_{\vec{k}\sigma}(n_{d\sigma}-n_{d-\sigma}) + a_{\vec{k}-\sigma}a^{\dagger}_{d-\sigma}a_{d\sigma}\right\} \qquad (C.5)$$

When this is substituted in Eq.(C.4) we get the higher order Green's functions $\sum_{\vec{k}} \langle\langle a_{\vec{k}\sigma}(n_{d\sigma}-n_{d-\sigma}), a^{\dagger}_{\vec{k}'\sigma}\rangle\rangle_{\omega}$ and $\sum_{\vec{k}} \langle\langle a_{\vec{k}-\sigma}a^{\dagger}_{d-\sigma}a_{d\sigma}, a^{\dagger}_{\vec{k}'\sigma}\rangle\rangle_{\omega}$. To evaluate these Green's functions we consider the following equations of motion

$$(\omega+\mu-\epsilon_{\vec{k}})\langle\langle a_{\vec{k}\sigma}(n_{d\sigma}-n_{d-\sigma}), a^{\dagger}_{\vec{k}'\sigma}\rangle\rangle_{\omega}$$

$$= (\langle n_{d\sigma}\rangle - \langle n_{d-\sigma}\rangle)\frac{\delta_{\vec{k}\vec{k}'}}{2\pi}$$

$$-\frac{J}{N}\sum_{\vec{k}}\left\{\frac{1}{2}\langle\langle a_{\vec{k}\sigma}(n_{d\sigma}-n_{d-\sigma})^2, a^{\dagger}_{\vec{k}\sigma}\rangle\rangle_{\omega} + \langle\langle a_{\vec{k}-\sigma}a^{\dagger}_{d-\sigma}a_{d\sigma}, a^{\dagger}_{\vec{k}'\sigma}\rangle\rangle_{\omega}\right\}$$

$$-\frac{2J\sigma}{N}\sum_{\vec{k}_1\vec{k}_2\sigma'}\sigma'\langle\langle a_{\vec{k}\sigma}a^{\dagger}_{\vec{k}_1-\sigma'}a_{\vec{k}_2\sigma'}a^{\dagger}_{d\sigma'}a_{d-\sigma'}, a^{\dagger}_{\vec{k}'\sigma}\rangle\rangle_{\omega} \qquad (C.6)$$

$$(\omega+\mu-\epsilon_{\vec{k}})\langle\langle a_{\vec{k}\sigma}(n_{d\sigma}-n_{d-\sigma})^2, a^{\dagger}_{\vec{k}\sigma}\rangle\rangle_{\omega}$$

$$= \langle(n_{d\sigma}-n_{d-\sigma})^2\rangle\,\delta_{\vec{k}\vec{k}'}/2\pi$$

$$-\frac{J}{N}\sum_{\vec{k}}\left\{\frac{1}{2}\langle\langle a_{\vec{k}\sigma}(n_{d\sigma}-n_{d-\sigma}), a^{\dagger}_{\vec{k}'\sigma}\rangle\rangle_{\omega} + \langle\langle a_{\vec{k}-\sigma}a^{\dagger}_{d-\sigma}a_{d\sigma}, a^{\dagger}_{\vec{k}'\sigma}\rangle\rangle \qquad (C.7)$$

$$(\omega-\epsilon_{\vec{k}}+\mu)\langle\langle a_{\vec{k}-\sigma}\, a^{\dagger}_{d-\sigma}\, a_{d\sigma}\,,\, a^{\dagger}_{\vec{k}'\sigma}\rangle\rangle_{\omega}$$

$$= \frac{J}{N}\sum_{\vec{k}}\Big\{-\frac{1}{2}\langle\langle a_{\vec{k}-\sigma}\, a^{\dagger}_{d-\sigma}\, a_{d\sigma}\,,\, a^{\dagger}_{\vec{k}'\sigma}\rangle\rangle_{\omega}$$

$$-\langle\langle a_{\vec{k}\sigma}\, a^{\dagger}_{d\sigma}\, a_{d-\sigma}\, a^{\dagger}_{d-\sigma}\, a_{d\sigma}\,,\, a^{\dagger}_{\vec{k}'\sigma}\rangle\rangle_{\omega}\Big\}$$

$$+\frac{J}{N}\sum_{\vec{k}_1\vec{k}_2}\Big\{\frac{1}{2}\langle\langle a_{\vec{k}-\sigma}(a^{\dagger}_{\vec{k}_1-\sigma}\, a_{\vec{k}_2-\sigma} - a^{\dagger}_{\vec{k}_1\sigma}\, a_{\vec{k}_2\sigma})a^{\dagger}_{d-\sigma}\, a_{d\sigma}\,,\, a^{\dagger}_{\vec{k}'\sigma}\rangle\rangle_{\omega}$$

$$+\langle\langle a_{\vec{k}-\sigma}\, a^{\dagger}_{\vec{k}_1-\sigma}\, a_{\vec{k}_2\sigma}\, a^{\dagger}_{d\sigma}\, a_{d\sigma}\,,\, a^{\dagger}_{\vec{k}'\sigma}\rangle\rangle_{\omega}\Big\}$$

$$-\frac{J}{N}\sum_{\vec{k}_1\vec{k}_2}\Big\{\frac{1}{2}\langle\langle a_{\vec{k}-\sigma}\, a^{\dagger}_{d-\sigma}(a^{\dagger}_{\vec{k}_1\sigma}\, a_{\vec{k}_2\sigma} - a^{\dagger}_{\vec{k}_1-\sigma}\, a_{\vec{k}_2-\sigma})a_{d\sigma}\,,\, a^{\dagger}_{\vec{k}'\sigma}\rangle\rangle_{\omega}$$

$$+\langle\langle a_{\vec{k}-\sigma}\, a^{\dagger}_{d-\sigma}\, a^{\dagger}_{k_1-\sigma}\, a_{\vec{k}_2\sigma}\, a_{d-\sigma}\,,\, a^{\dagger}_{\vec{k}'\sigma}\rangle\rangle_{\omega}\Big\}$$

$$(C.8)$$

In these equations of motion we have used the identity $(n_{d\sigma})^2 = n_{d\sigma}$. Eqs. (C.6), (C.7) and (C.8) are solved to obtain the Green's functions $\sum_{\vec{k}}\langle\langle a_{\vec{k}\sigma}(n_{d\sigma} - n_{d-\sigma});\, a^{\dagger}_{\vec{k}\sigma}\rangle\rangle_{\omega}$ and $\sum_{\vec{k}}\langle\langle a_{\vec{k}-\sigma}\, a^{\dagger}_{d-\sigma}\, a_{d\sigma}\,,\, a^{\dagger}_{\vec{k}'\sigma}\rangle\rangle_{\omega}$ in terms of higher order Green's functions. By substituting the values of these Green's functions in Eq.(C.4) we get

$$G^{\sigma}_{\vec{k}\vec{k}'}(\omega) = \frac{\delta_{\vec{k}\vec{k}'}}{2\pi(\omega+\mu-\epsilon_{\vec{k}})} - \frac{J\,(\langle n_{d\sigma}\rangle-\langle n_{d-\sigma}\rangle) - \frac{J}{2}F(\omega)\langle(n_{d\sigma} - n_{d-\sigma})^2\rangle}{4\pi N(\omega+\mu-\epsilon_{\vec{k}})(\omega+\mu-\epsilon_{\vec{k}})\left\{1-(\frac{J}{2}F(\omega))^2\right\}}$$

$$+\frac{J^2}{N(\omega+\mu-\epsilon_{\vec{k}})(1+\frac{J}{2}F(\omega))^2}\Big[F(\omega)\sum_{\vec{k}}\langle\langle a_{\vec{k}\sigma}\,a^{\dagger}_{d\sigma}\,a_{d-\sigma}\,a^{\dagger}_{d-\sigma}\,a_{d\sigma}\,,\;a^{\dagger}_{\vec{k}'\sigma}\rangle\rangle_{\omega}$$

$$-\frac{1}{N}\sum_{\vec{k},\vec{k}_1,\vec{k}_2}\frac{1}{(\omega+\mu-\epsilon_{\vec{k}})}\Big\{\langle\langle a_{\vec{k}-\sigma}\,(a^{\dagger}_{\vec{k}_1-\sigma}\,a_{\vec{k}_2-\sigma}-a^{\dagger}_{\vec{k}\sigma}\,a_{\vec{k}_2\sigma})a^{\dagger}_{d-\sigma}a_{d\sigma},\,a^{\dagger}_{\vec{k}'\sigma}\rangle\rangle_{\omega}$$

$$+\langle\langle a_{\vec{k}-\sigma}\;a^{\dagger}_{\vec{k}_1-\sigma}\,a_{\vec{k}_2\sigma}\,(n_{d\sigma}-n_{d-\sigma}),\;a^{\dagger}_{\vec{k}'\sigma}\rangle\rangle_{\omega}\Big\}\Big]$$

$$+\frac{J^2\sigma}{N^2(\omega+\mu-\epsilon_{\vec{k}})\left\{1-(\frac{J}{2}F(\omega))^2\right\}}\sum_{\vec{k},\vec{k}_1,\vec{k}_2,\sigma'}\Big\{\frac{\sigma'}{\omega+\mu-\epsilon_{\vec{k}}}$$

$$\times\langle\langle a_{\vec{k}\sigma}\;a^{\dagger}_{\vec{k}_1-\sigma'}a_{\vec{k}_2\sigma'}\;a^{\dagger}_{d\sigma'}a_{d-\sigma'},a^{\dagger}_{\vec{k}'\sigma}\rangle\rangle_{\omega}\Big\}$$

(C.9)

where $$F(\omega)=\frac{1}{N}\sum_{\vec{k}}\frac{1}{\omega+\mu-\epsilon_{\vec{k}}}\qquad\text{(C.10)}$$

To evaluate $G^{\sigma}_{\vec{k}\vec{k}'}(\omega)$ one has to evaluate the higher order Green's functions appearing in (C.9). However if we assume that J is small and neglect all the terms containing the power of J greater than unity, we get an expression for $G^{\sigma}_{\vec{k}\vec{k}'}(\omega)$ which is exact upto the first power in J. This is given by

$$G^{\sigma}_{\vec{k}\vec{k}'}(\omega)=\frac{\delta_{\vec{k}\vec{k}'}}{2\pi(\omega+\mu-\epsilon_{\vec{k}})}-\frac{J(\langle n_{d\sigma}\rangle-\langle n_{d-\sigma}\rangle)}{4\pi N(\omega+\mu-\epsilon_{\vec{k}})(\omega+\mu-\epsilon_{\vec{k}})\left\{1-(\frac{J}{2}F(\omega))^2\right\}}$$

(C.11)

$$= \left\{\delta_{\sigma\sigma'} + \frac{I\, n_0(-\sigma,-\sigma)\delta_{\sigma\sigma'} - I\, n_0(-\sigma,\sigma)\delta_{-\sigma\sigma'}}{\omega+\mu-T_0-I}\right\}\frac{\delta_{\vec{k}\vec{k}'}}{2\pi}$$

$$+ \frac{I}{\omega+\mu-T_0-I}\left\{n_{\vec{Q}}(-\sigma,-\sigma)\delta_{\sigma\sigma'} - n_{\vec{Q}}(-\sigma,\sigma)\delta_{-\sigma\sigma'}\right\}\frac{\delta_{\vec{k}+\vec{Q},\vec{k}'}}{2\pi}$$

$$(A,7)$$

where the spin density operators $n_{\vec{q}}(\sigma\sigma')$ are defined by the Eqs. (5.11), (5.12) and (5.16). Now we assume that the system is magnetized in the x direction instead of conventional z axis. Such a system has been considered in chapter V. For this case there it is shown that

$$n_{\vec{q}}(\sigma,-\sigma) = n_{\vec{q}}(-\sigma,\sigma) = \Delta_{\vec{q}};\ n_{\vec{q}}(\sigma,\sigma) = n_{\vec{q}}(-\sigma,-\sigma) = n_{\vec{q}}/2$$

Using these relations in Eq.(A.7), we get

$$\left\{\omega+\mu-T_0-(\epsilon_{\vec{k}}-T_0)\left(1+\frac{I\, n_0/2}{\omega+\mu-T_0-I}\right)\right\} G^{\sigma\sigma'}_{\vec{k}\vec{k}'}(\omega)$$

$$+ \frac{I\,\Delta_0}{\omega+\mu-T_0-I}(\epsilon_{\vec{k}}-T_0)\, G^{-\sigma\sigma'}_{\vec{k}\vec{k}'}(\omega)$$

$$+ \frac{I\,\Delta_{\vec{Q}}}{\omega+\mu-T_0-I}(\epsilon_{\vec{k}+\vec{Q}}-T_0)\, G^{-\sigma\sigma'}_{\vec{k}+\vec{Q},\vec{k}'}(\omega)$$

$$- \frac{I\, n_Q/2}{\omega+\mu-T_0-I}(\epsilon_{\vec{k}+\vec{Q}}-T_0)\, G^{\sigma\sigma'}_{\vec{k}+\vec{Q},\vec{k}'}(\omega)$$

$$= \left\{ \delta_{\sigma\sigma'} + \frac{I\, n_0/2\; \delta_{\sigma\sigma'} - I\, \Delta_0\, \delta_{-\sigma\sigma'}}{\omega + \mu - T_0 - I} \right\} \frac{\delta_{\vec{k}\vec{k}'}}{2\pi}$$

$$+ \frac{I}{\omega + \mu - T_0 - I} \left\{ \frac{n_{\vec{Q}}}{2} \delta_{\sigma\sigma'} - \Delta_{\vec{Q}}\, \delta_{-\sigma\sigma'} \right\} \frac{\delta_{\vec{k}+\vec{Q},\vec{k}'}}{2\pi} \qquad (A.8)$$

From this equation we can obtain the Green's function $G^{\sigma\sigma'}_{\vec{k}\vec{k}'}(\omega)$ for para, ferro and antiferromagnetic states.

For paramagnetic state $\Delta_0 = \Delta_{\vec{Q}} = n_{\vec{Q}} = 0$. Therefore from (A.8) we have

$$G^{\sigma\sigma'}_{\vec{k}\vec{k}'}(\omega)_P = \frac{\left\{ \omega + \mu - T_0 - I\,(1 - n_0/2) \right\} \delta_{\sigma\sigma'} \delta_{\vec{k}\vec{k}'} / 2\pi}{(\omega + \mu - T_0)(\omega + \mu - T_0 - I) - (\epsilon_{\vec{k}} - T_0) \left\{ \omega + \mu - T_0 - I(1 - n_0/2) \right\}} \qquad (A.9)$$

This result is the same as that obtained by Hubbard i.e. in paramagnetic case our approximations are equivalent to that of Hubbard.

In ferromagnetic state $\Delta_{\vec{Q}} = n_{\vec{Q}} = 0$, hence from Eq.(A.8) we have

$$\left\{ \omega + \mu - T_0 - (\epsilon_{\vec{k}} - T_0)\left(1 + \frac{I\, n_0/2}{\omega + \mu - T_0 - I}\right) \right\} G^{\sigma\sigma'}_{\vec{k}\vec{k}'}(\omega)$$

$$+ \frac{I}{\omega + \mu - T_0 - I} (\epsilon_{\vec{k}} - T_0)\, G^{-\sigma\sigma'}_{\vec{k}\vec{k}'}(\omega)$$

By solving this equation for $G^{\sigma\sigma'}_{\vec{k}\vec{k}'}(\omega)$ we obtain

$$G^{\sigma\sigma'}_{\vec{k}\vec{k}'}(\omega)_{AF} = \frac{\begin{array}{l} A_{\vec{k}+\vec{Q}}(\omega)\left\{B_o(\omega)\delta_{\sigma\sigma'}\delta_{\vec{k}\vec{k}'} - D_{\vec{Q}}(\omega)\delta_{-\sigma\sigma'}\delta_{\vec{k}+\vec{Q},\vec{k}'}\right\}\frac{1}{2\pi} \\ -D_Q(\omega)\left\{B_o(\omega)\delta_{-\sigma\sigma'}\delta_{\vec{k}+\vec{Q},\vec{k}'} - D_{\vec{Q}}(\omega)\delta_{\sigma\sigma'}\delta_{\vec{k}\vec{k}'}\right\}\frac{(\epsilon_{\vec{k}+\vec{Q}} - T_o)}{2\pi} \end{array}}{A_{\vec{k}}(\omega)\, A_{\vec{k}+\vec{Q}}(\omega) - \left\{D^2_{\vec{Q}}(\omega)\, (\epsilon_{\vec{k}+\vec{Q}} - T_o)(\epsilon_{\vec{k}} - T_o)\right\}} .$$

(A.16)

Eqs. (A.9), (A.11) and (A.16) can be combined into one equation

$$G^{\sigma\sigma'}_{\vec{k}\vec{k}'}(\omega) = \frac{\begin{array}{l} A_{\vec{k}+\vec{q}}(\omega)\left\{B_o(\omega)\delta_{\sigma\sigma'}\delta_{\vec{k}\vec{k}'} - D_{\vec{q}}(\omega)\delta_{-\sigma\sigma'}\delta_{\vec{k}+\vec{q},\vec{k}'}\right\}1/2\pi \\ -D_{\vec{q}}(\omega)\left\{B_o(\omega)\delta_{-\sigma\sigma'}\delta_{\vec{k}+\vec{q},\vec{k}'} - D_{\vec{q}}(\omega)\delta_{\sigma\sigma'}\delta_{\vec{k}\vec{k}'}\right\}(\epsilon_{\vec{k}+\vec{q}} - T_o)/ \end{array}}{A_{\vec{k}}(\omega)\quad A_{\vec{k}+\vec{q}}(\omega) - D^2_{\vec{q}}(\omega)\, (\epsilon_{\vec{k}} - T_o)(\epsilon_{\vec{k}+\vec{q}} - T_o)} .$$

(A.17)

Here paramagnetic state corresponds to $\Delta_{\vec{q}} = 0$, ferromagnetic and antiferromagnetic states correspond to $\vec{q} = 0$ and $\vec{q} = \vec{Q}$ respectively. We shall restrict our study to the strongly correlated systems so that $I \rightarrow \infty$. In this case Eq.(A.17) becomes theory. At present most of the theories of magnetic phase transitions are developed on the localized electron models-Ising and Heisenberg models. The mathematical progress on the critical behavior of nonlocalized magnetic models is lacking.[112] The extension of our study to finite temperatures may help in the study of the critical behavior of the transition metals where magnetic electrons are itinerant. The phenomenon of metal-nonmetal transitions discussed in chapter V on the basis of the Hamiltonian (2.1) may also be extended to finite temperatures The fourth extension is to develop a more refined theory of correlation for finite intraatomic interaction. This can be done by writing down the equations of motion for the higher order Green's functions and using a decoupling scheme so that one can take the correlation between s and d electrons and the correlation between the d electrons at different lattice sites, which have been neglected in the present study.

The study of the Hamiltonians (3.2) and (4.1) can be extended onlthe similar lines. In chapter IV we have shown that for zero bandwidth, both in weak and strong intraatomic interaction theories, the dynamical susceptibility of a system described by the Hamiltonian (4.1) reduces to an expression obtained in the Heisenberg model within the random phase approximation. Thus the model Hamiltonian (4.1) may serve as a bridge between the itinerant model and localized one. And in this respect an improved analysis of the model may be of value because it has long been realized that the properties of the transition metals can be explained by a model which is a compromise between the itinerant model and the Heisenberg one.

APPENDIX A

MAGNETISM IN A STRONGLY CORRELATED NARROW ENERGY BAND

I. INTRODUCTION

As pointed out in chapter I, the Hubbard model has been analysed by many authors using different approaches and approximations. But so far it has not been possible to solve it exactly. However in some limiting cases exact results of this model have been found out. For example for zero bandwidth, for zero intraatomic interaction, and in one dimension exact solutions are now known. In addition to this Kemeny[46] has given an exact proof that for half filled band the ferromagnetic state with maximum spin is never, by itself, the ground state but for $I \to \infty$ it must at best be degenerate with a manifold of other states with one electron on each lattice site and arbitrary spin projection. These exact results can be used to check the particular aspects of approximation schemes to see if these results are found to be true for such approximate solutions. Keeping this view in mind we have tried to improve the Hubbard's decoupling scheme and find that in some limiting cases the results of our theory reduce to the exact results.

In Sec. II we have obtained the one particle Green's functions for para, ferro and antiferromagnetic states using improved decoupling scheme. In Sec. III the energies of the magnetic phases are obtained for the half filled band and $I \to \infty$ using the square density of states. In Sec. IV we summarize our results.

II. GREEN'S FUNCTIONS

We consider the Green's function (5.1). The equation of motion (1.13) for this Green's function, for a system described by the Hubbard Hamiltonian (1.9), is given by

$$(\omega+\mu)\, G_{ij}^{\sigma\sigma'}(\omega) = \frac{\delta_{ij}\delta_{\sigma\sigma'}}{2\pi} + \sum_{\ell} T_{i\ell}\, G_{\ell j}^{\sigma\sigma'}(\omega) + I\langle\langle n_{i-\sigma}\, a_{i\sigma}, a_{j\sigma'}^{\dagger}\rangle\rangle_{\omega} \tag{A.1}$$

The Green's function $\langle\langle n_{i-\sigma}\, a_{i\sigma}, a_{j\sigma'}^{\dagger}\rangle\rangle_{\omega}$ satisfies the equation of motion

$$\begin{aligned}(\omega+\mu-I-T_0)\,&\langle\langle n_{i-\sigma}\, a_{i\sigma}, a_{j\sigma'}^{\dagger}\rangle\rangle_{\omega}\\ &= \langle n_{i-\sigma}\rangle\, \delta_{ij}\,\delta_{\sigma\sigma'} - \langle a_{i-\sigma}^{\dagger}\, a_{i\sigma}\rangle\, \delta_{ij}\,\delta_{-\sigma\sigma'}\\ &+ \sum_{\ell\neq i} T_{i\ell}\,\langle\langle (a_{i-\sigma}^{\dagger}\, a_{i-\sigma} - a_{\ell-\sigma}^{\dagger}\, a_{i-\sigma})a_{i\sigma}, a_{j\sigma'}^{\dagger}\rangle\rangle_{\omega}\\ &+ \sum_{\ell\neq i} T_{i\ell}\,\langle\langle n_{i-\sigma}\, a_{\ell\sigma}, a_{j\sigma'}^{\dagger}\rangle\rangle_{\omega}\end{aligned} \tag{A.2}$$

In order to break off the sequence of Green's function equations, the Green's functions on the right hand side of (A.2) are decoupled as

$$\langle\langle n_{i-\sigma}\, a_{\ell\sigma}, a_{j\sigma'}^{\dagger}\rangle\rangle_{\omega} \simeq \langle n_{i-\sigma}\rangle\, G_{\ell j}^{\sigma\sigma'}(\omega) - \langle a_{i-\sigma}^{\dagger}\, a_{\ell\sigma}\rangle\, G_{ij}^{-\sigma\sigma'}(\omega)$$

which when substituted in (A.1) gives

$$(\omega+\mu-T_o)G_{ij}^{\sigma\sigma'}(\omega) = \left[\left(1+\frac{I\langle n_{i-\sigma}\rangle}{\omega+\mu-T_o-I}\right)\delta_{\sigma\sigma'}-\frac{I\langle a_{i-\sigma}^{\dagger}a_{i\sigma}\rangle}{\omega+\mu-T_o-I}\delta_{-\sigma\sigma'}\right]\frac{\delta_{ij}}{2\pi}$$

$$+\left(1+\frac{I\langle n_{i-\sigma}\rangle}{\omega+\mu-T_o-I}\right)\sum_{\ell\neq i}T_{i\ell}G_{\ell j}^{\sigma\sigma'}(\omega)$$

$$-\frac{I\langle a_{i-\sigma}^{\dagger}a_{i\sigma}\rangle}{\omega+\mu-T_o-I}\sum_{\ell\neq i}T_{i\ell}G_{\ell j}^{-\sigma\sigma'}(\omega)$$

(A.6)

It is easy to see that in both the zero bandwidth limit ($T_{ij} = T_o\delta_{ij}$) and for $I = 0$, the above expression reduces to the exact solutions. By taking the Fourier transform (5.5) of the Green's function $G_{ij}^{\sigma\sigma'}(\omega)$ and using the ansatz (5.7), Eq.(A.6) becomes

$$\left\{\omega+\mu-T_o-(\epsilon_{\vec{k}}-T_o)\left(1+\frac{I\,n_o(-\sigma,-\sigma)}{\omega+\mu-T_o-I}\right)\right\}G_{\vec{k}\vec{k}'}^{\sigma\sigma'}(\omega)$$

$$+\frac{I\,n_o(-\sigma,\sigma)}{\omega+\mu-T_o-I}(\epsilon_{\vec{k}}-T_o)\,G_{\vec{k}\vec{k}'}^{-\sigma\sigma'}(\omega)$$

$$+\frac{I\,n_Q(-\sigma,\sigma)}{\omega+\mu-T_o-I}(\epsilon_{\vec{k}+\vec{Q}}-T_o)\,G_{\vec{k}+\vec{Q},\vec{k}'}^{-\sigma\sigma'}(\omega)$$

$$-\frac{I\,n_{\vec{Q}}(-\sigma,-\sigma)}{\omega+\mu-T_o-I}(\epsilon_{\vec{k}+\vec{Q}}-T_o)\,G_{\vec{k}+\vec{Q},\vec{k}'}^{\sigma\sigma'}(\omega)$$

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Green Function Theory of Transport Properties of Anharmonic Metals

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General expressions for the electron and phonon energy shift and widths are derived with the help of the double time temperature dependent Green's function by using a Hamiltonian which includes both anharmonicity and electron–phonon interaction. The expression for the phonon width shows that Green's function technique provides an understanding of Matthiessen's rule. Well known temperature dependence of the electron and the phonon relaxation times is reproduced by a simple calculation of the elctron and the phonon widths at low and high temperature limits. It is found that the effect of anharmonicity on the electronic transport properties of metals is negligible. Its effect on the lattice transport properties is predominant at high temperature and at low temperature the effect of electron–phonon interaction is predominant.

Allgemeine Ausdrücke für die Energieverschiebung der Elektronen und Phononen und für die Elektron- und Phononenbreite werden mit der zweizeitigen, temperaturabhängigen Greenschen Funktion durch einen Hamiltonian abgeleitet, der sowohl Anharmonizitätseffekte als auch Elektron–Phononwechselwirkung berücksichtigt. Der Ausdruck für die Phononenbreite zeigt, daß die Technik der Greenschen Funktion das Verständnis der Matthiessenschen Regel ermöglicht. Die gut bekannte Temperaturabhängigkeit der Elektronen- und Phononenrelaxationszeiten wird durch eine einfache Berechnung der Elektronen- und Phononenbreiten bei niedrigen und hohen Grenztemperaturen reproduziert. Es wird gefunden, daß der Anharmonizitätseinfluß auf die Elektronentransporteigenschaften von Metallen vernachlässigbar ist. Sein Einfluß auf die Gittertransporteigenschaften ist bei hohen Temperaturen vorherrschend, bei niedrigen Temperaturen ist der Einfluß der Elektron–Phononwechselwirkung vorherrschend.

1. Introduction

The metals are different from insulators in that they have conduction electron which are free to move about the crystal. These electrons interact with the lattice vibrations. The lattice vibrations cause a change in the potential energy of the crystal. The change in potential energy is usually expanded in a power series of ionic displacements from equilibrium positions. In the harmonic approximation one retains only the quadratic terms and then the problem is solved exactly in terms of the normal modes of vibration of the crystal. The system can be quantized and each quantum of normal mode is known as 'phonon'. All the terms beyond the quadratic ones are known as anharmonic terms. These terms contain phonon–phonon interactions which can be used to explain some of the properties of the crystal which harmonic approximation fails to explain.

Recently the theory of anharmonic insulators [1, 2] and effect of electron–phonon interaction on the properties of metals [3, 4] are discussed by a number of authors, but so far we have not come across any published work where simultaneously both anharmonicity and electron–phonon interaction are taken into account to explain the transport properties of metals. For the evaluation the transport coefficients the central quantity which we require is the relaxation time. In the present work we have evaluated one electron and one phonon Green's function for a Bravais crystal whose Hamiltonian contains both anharmonicity and electron–phonon interaction. When we examine the Green's function in the complex energy plane, it is found that there are poles that lie above and below the real axis. The real part of the pole in the positive half plane is identified as the perturbed mode and the imaginary part as the half width of the mode [3]. The electron and phonon width obtained respectively from one electron and one phonon Green's function are the inverse of respective relaxation times. To explain the transport properties one generally assumes the total inverse of relaxation time as the sum of the inverse of relaxation times due to different scattering mechanisms [5]. Here we show that Green's function technique gives an insight into the nature of this assumption which is called Matthiessen's rule. A simple calculation of the electron and the phonon widths reproduces the well known temperature dependence of the electron and the phonon relaxation times at low and high temperature limits.

2. Hamiltonian

We consider our system as an assembly of electrons and phonons interacting with each other. The Hamiltonian for such a system can be written as

$$H = \sum_{\boldsymbol{q}} \omega_{\boldsymbol{q}} \left(b_{\boldsymbol{q}}^{+} b_{\boldsymbol{q}} + \frac{1}{2} \right) + \sum_{\boldsymbol{k}} \varepsilon_{k} a_{\boldsymbol{k}}^{+} a_{\boldsymbol{k}} + \sum_{\boldsymbol{q}_1, \boldsymbol{q}_2, \boldsymbol{q}_3} V^{(3)}(\boldsymbol{q}_1, \boldsymbol{q}_2, \boldsymbol{q}_3) A_{\boldsymbol{q}_1} A_{\boldsymbol{q}_2} A_{\boldsymbol{q}_3} + \\ + \sum_{\boldsymbol{q}_1, \boldsymbol{q}_2, \boldsymbol{q}_3, \boldsymbol{q}_4} V^{(4)}(\boldsymbol{q}_1, \boldsymbol{q}_2, \boldsymbol{q}_3, \boldsymbol{q}_4) A_{\boldsymbol{q}_1} A_{\boldsymbol{q}_2} A_{\boldsymbol{q}_3} A_{\boldsymbol{q}_4} + \sum_{\boldsymbol{k}, \boldsymbol{q}} F_{\boldsymbol{q}} a_{\boldsymbol{k}}^{+} a_{\boldsymbol{k}-\boldsymbol{q}} A_{\boldsymbol{q}} . \tag{1}$$

Here first term is due to phonons under harmonic approximation, second term represents the kinetic energy of electrons, third and fourth terms are due to anharmonicity and correspond to cubic and quartic terms in the expansion of potential energy in powers of ionic displacements from their equilibrium positions and fifth term represents the electron–phonon interaction. We confine overselves only to quadratic, cubic and quartic term in the potential energy. $\omega_{\boldsymbol{q}}$, $b_{\boldsymbol{q}}$, and $b_{\boldsymbol{q}}^{+}$ are the frequency, annihilation, and creation operators for phonon of wave vector $\boldsymbol{q}$; $a_{\boldsymbol{k}}$ and $a_{\boldsymbol{k}}^{+}$ are the annihilation and creation operator for electrons of wave vector $\boldsymbol{k}$, $\varepsilon_{k} = (k^2/2\,m) - \mu$ where m is the mass of electron and μ is the chemical potential; $V^{(3)}$ and $V^{(4)}$ are the Fourier transform of the third and fourth order atomic force constants respectively; $F_{\boldsymbol{q}}$ describes the coupling of the electron to the phonon field and $A_{\boldsymbol{q}} = b_{\boldsymbol{q}} + b_{\boldsymbol{q}}^{+}$. The explicit expressions for the coefficients $V^{(3)}$ and $V^{(4)}$ are given by Maradudin and Fein [1]. $F_{\boldsymbol{q}}$ is given as [6]

$$F_{\boldsymbol{q}} = F \sqrt{\frac{\omega_{\boldsymbol{q}}}{V}} , \tag{2}$$

where F is a constant and V is the volume of the crystal. For simplicity here and in what follows we omit the polarization index for phonons and spin index for electrons and take $\hbar = 1$.

3. Green's Functions

We define the one-electron Green's function $G_{\boldsymbol{k}\boldsymbol{k}'}(t, t')$ and the one phonon Green's function $D_{\boldsymbol{q}\boldsymbol{q}'}(t, t')$ as [3]

$$G_{\boldsymbol{k}\boldsymbol{k}'}(t, t') = \langle\langle a_{\boldsymbol{k}}(t);\, a^+_{\boldsymbol{k}'}(t')\rangle\rangle = -i\,\theta\,(t - t')\,\langle[a_{\boldsymbol{k}}(t),\, a^+_{\boldsymbol{k}'}(t')]_+\rangle\,, \tag{3}$$

$$D_{\boldsymbol{q}\boldsymbol{q}'}(t, t') = \langle\langle b_{\boldsymbol{q}}(t);\, b^+_{\boldsymbol{q}'}(t')\rangle\rangle = -i\,\theta\,(t - t')\,\langle[b_{\boldsymbol{q}}(t),\, b^+_{\boldsymbol{q}'}(t')_-\rangle\,, \tag{4}$$

where

$$[A, B]_\pm = A\,B \pm B\,A\,,$$

$$\theta(\varkappa) = \begin{cases} 1 & \text{for} \quad \varkappa > 0 \\ 0 & \text{for} \quad \varkappa < 0\,, \end{cases}$$

and angular brackets $\langle\ \rangle$ denote the average over canonical or grand canonical ensemble. The Fourier transforms $G_{\boldsymbol{k}\boldsymbol{k}'}(\omega)$ and $D_{\boldsymbol{q}\boldsymbol{q}'}(\omega)$ of one-electron and one-phonon Green's functions are defined as

$$G_{\boldsymbol{k}\boldsymbol{k}'}(t, t') = \int_{-\infty}^{\infty} G_{\boldsymbol{k}\boldsymbol{k}'}(\omega)\, \mathrm{e}^{-i\omega(t-t')}\, \mathrm{d}\omega\,, \tag{5}$$

$$D_{\boldsymbol{q}\boldsymbol{q}'}(t, t') = \int_{-\infty}^{\infty} D_{\boldsymbol{q}\boldsymbol{q}'}(\omega)\, \mathrm{e}^{-i\omega(t-t')}\, \mathrm{d}\omega\,. \tag{6}$$

For convenience we also define the operator $B_{\boldsymbol{q}} = b_{\boldsymbol{q}} - b^+_{\boldsymbol{q}}$.

In evaluating the Green's function we shall need the equations of motion for the operators $a_{\boldsymbol{k}}$, $a^+_{\boldsymbol{k}}$, $b_{\boldsymbol{q}}$, and $b^+_{\boldsymbol{q}}$. These equations of motion are given as

$$i\,\frac{\mathrm{d}a_{\boldsymbol{k}}}{\mathrm{d}t} = [a_{\boldsymbol{k}}, H]_- = \varepsilon_{\boldsymbol{k}}\, a_{\boldsymbol{k}} + \sum_{\boldsymbol{q}} F_{\boldsymbol{q}}\, a_{\boldsymbol{k}-\boldsymbol{q}}\, A_{\boldsymbol{q}}\,, \tag{7}$$

$$i\,\frac{\mathrm{d}a^+_{\boldsymbol{k}}}{\mathrm{d}t} = [a^+_{\boldsymbol{k}}, H]_- = -\,\varepsilon_{\boldsymbol{k}}\, a^+_{\boldsymbol{k}} - \sum_{\boldsymbol{q}} F_{\boldsymbol{q}}\, a^+_{\boldsymbol{k}+\boldsymbol{q}}\, A_{\boldsymbol{q}}\,, \tag{8}$$

$$\begin{aligned} i\,\frac{\mathrm{d}b_{\boldsymbol{q}}}{\mathrm{d}t} = [b_{\boldsymbol{q}}, H]_- = \omega_{\boldsymbol{q}}\, b_{\boldsymbol{q}} &+ \sum_{\boldsymbol{k}} F_{\boldsymbol{q}}\, a^+_{\boldsymbol{k}}\, a_{\boldsymbol{k}+\boldsymbol{q}} + 3 \sum_{\boldsymbol{q}_1, \boldsymbol{q}_2,} V^{(3)}(-\boldsymbol{q}, \boldsymbol{q}_1, \boldsymbol{q}_2)\, A_{\boldsymbol{q}_1} A_{\boldsymbol{q}_2} + \\ &+ 4 \sum_{\boldsymbol{q}_1, \boldsymbol{q}_2, \boldsymbol{q}_3} V^{(4)}(-\boldsymbol{q}, \boldsymbol{q}_1, \boldsymbol{q}_2, \boldsymbol{q}_3)\, A_{\boldsymbol{q}_1} A_{\boldsymbol{q}_2} A_{\boldsymbol{q}_3}\,, \end{aligned} \tag{9}$$

$$\begin{aligned} i\,\frac{\mathrm{d}b^+_{\boldsymbol{q}}}{\mathrm{d}t} = [b^+_{\boldsymbol{q}}, H]_- = -\,\omega_{\boldsymbol{q}}\, b^+_{\boldsymbol{q}} &- \sum_{\boldsymbol{k}} F_{\boldsymbol{q}}\, a^+_{\boldsymbol{k}}\, a_{\boldsymbol{k}-\boldsymbol{q}} - 3 \sum_{\boldsymbol{q}_1, \boldsymbol{q}_2} V^{(3)}(-\boldsymbol{q}, \boldsymbol{q}_1, \boldsymbol{q}_2)\, A_{\boldsymbol{q}_1} A_{\boldsymbol{q}_2} - \\ &- 4 \sum_{\boldsymbol{q}_1, \boldsymbol{q}_2, \boldsymbol{q}_3} V^{(4)}(-\boldsymbol{q}, \boldsymbol{q}_1, \boldsymbol{q}_2, \boldsymbol{q}_3)\, A_{\boldsymbol{q}_1} A_{\boldsymbol{q}_2} A_{\boldsymbol{q}_3}\,. \end{aligned} \tag{10}$$

3.1 Electron Green's function

The equation of motion for the Green's function $G_{\boldsymbol{k}\boldsymbol{k}'}$ is

$$i\,\frac{\mathrm{d}G_{\boldsymbol{k}\boldsymbol{k}'}}{\mathrm{d}t} = \delta_{\boldsymbol{k}\boldsymbol{k}'}\, \delta\,(t - t') + \varepsilon_{\boldsymbol{k}}\, G_{\boldsymbol{k}\boldsymbol{k}'} + \sum_{\boldsymbol{q}} F_{\boldsymbol{q}} \langle\langle a_{\boldsymbol{k}-\boldsymbol{q}}\, A_{\boldsymbol{q}};\, a^+_{\boldsymbol{k}'}(t')\rangle\rangle\,. \tag{11}$$

To evaluate the higher order Green's function $G_1 = \langle\langle a_{\boldsymbol{k}-\boldsymbol{q}}\, A_{\boldsymbol{q}};\, a^+_{\boldsymbol{k}'}(t')\rangle\rangle$ we shall need the Green's function $G_2 = \langle\langle a_{\boldsymbol{k}-\boldsymbol{q}}\, B_{\boldsymbol{q}};\, a^+_{\boldsymbol{k}'}\,(t')\rangle\rangle$. The equations of motion for G_1 and G_2 are

$$i\frac{\mathrm{d}G_1}{\mathrm{d}t} = \varepsilon_{\boldsymbol{k}-\boldsymbol{q}}\, G_1 + \omega_{\boldsymbol{q}}\, G_2 + \sum_{\boldsymbol{q}_1} F_{\boldsymbol{q}_1} \langle\langle a_{\boldsymbol{k}-\boldsymbol{q}-\boldsymbol{q}_1} A_{\boldsymbol{q}_1} A_{\boldsymbol{q}};\, a^+_{\boldsymbol{k}'}(t')\rangle\rangle\,, \tag{12}$$

$$\begin{aligned} i\frac{\mathrm{d}G_2}{\mathrm{d}t} = {} & \varepsilon_{\boldsymbol{k}-\boldsymbol{q}}\, G_2 + \omega_{\boldsymbol{q}}\, G_1 + \sum_{\boldsymbol{q}_1} F_{\boldsymbol{q}_1} \langle\langle a_{\boldsymbol{k}-\boldsymbol{q}-\boldsymbol{q}_1} A_{\boldsymbol{q}_1} B_{\boldsymbol{q}};\, a^+_{\boldsymbol{k}'}(t')\rangle\rangle + \\ & + 2 \sum_{\boldsymbol{k}_1} F_{\boldsymbol{q}} \langle\langle a_{\boldsymbol{k}-\boldsymbol{q}}\, a^+_{\boldsymbol{k}'}\, a_{\boldsymbol{k}_1+\boldsymbol{q}};\, a^+_{\boldsymbol{k}'}(t')\rangle\rangle + \\ & + 6 \sum_{\boldsymbol{q}_1, \boldsymbol{q}_2} V^{(3)}(-\boldsymbol{q}, \boldsymbol{q}_1, \boldsymbol{q}_2)\, \langle\langle a_{\boldsymbol{k}-\boldsymbol{q}} A_{\boldsymbol{q}_1} A_{\boldsymbol{q}_2};\, a^+_{\boldsymbol{k}'}(t')\rangle\rangle + \\ & + 8 \sum_{\boldsymbol{q}_1, \boldsymbol{q}_2 \boldsymbol{q}_3} V^{(4)}(-\boldsymbol{q}, \boldsymbol{q}_1, \boldsymbol{q}_2, \boldsymbol{q}_3)\, \langle\langle a_{\boldsymbol{k}-\boldsymbol{q}} A_{\boldsymbol{q}_1} A_{\boldsymbol{q}_2} A_{\boldsymbol{q}_3};\, a^+_{\boldsymbol{k}'}(t')\rangle\rangle\,. \qquad (13 \end{aligned}$$

Apart from Green's functions G_1 and G_2 (12) and (13) contain also higher order Green's functions for which we should in turn construct equations of motion and continue the process further. In this way we shall get infinite number of equations of motion for the Green's functions. We can break this chain of equations and decouple the higher order Green's functions into lower order Green's functions by making some kind of approximations. Here we decouple the higher order Green's function containing four and five operator according to the following scheme [3, 7]

$$\langle\langle a\, b\, c;\, d\rangle\rangle = \langle a\, b\rangle \langle\langle c;\, d\rangle\rangle \pm \langle a\, c\rangle \langle\langle b;\, d\rangle\rangle + \langle b\, c\rangle \langle\langle a;\, d\rangle\rangle\,, \tag{14}$$

$$\begin{aligned} \langle\langle a\, b\, c\, d;\, e\rangle\rangle = {} & \langle a\, b\rangle \langle\langle c\, d;\, e\rangle\rangle \pm \langle a\, c\rangle \langle\langle b\, d;\, e\rangle\rangle + \\ & + \langle a\, d\rangle \langle\langle b\, c;\, e\rangle\rangle + \langle b\, c\rangle \langle\langle a\, d;\, e\rangle\rangle \pm \\ & \pm \langle b\, d\rangle \langle\langle a\, c;\, e\rangle\rangle + \langle c\, a\rangle \langle\langle a\, b;\, e\rangle\rangle\,, \end{aligned} \tag{15}$$

where plus sign is for the case when the two operators inside the angular brackets $\langle\,\rangle$ are either bosons or the combination of bosons and fermions and minus sign is for the case when these two operators are fermions. In addition to this decoupling scheme we also assume that

$$\left.\begin{aligned} \langle b^+_{\boldsymbol{q}}\, b_{\boldsymbol{q}'}\rangle = \nu_{\boldsymbol{q}}\, \delta_{\boldsymbol{q}\,\boldsymbol{q}'}\,, \quad & \langle a^+_{\boldsymbol{k}}\, a_{\boldsymbol{k}'}\rangle = n_{\boldsymbol{k}}\, \delta_{\boldsymbol{k}\,\boldsymbol{k}'}\,, \\ \langle b^+_{\boldsymbol{q}}\, b^+_{\boldsymbol{q}'}\rangle = \langle b_{\boldsymbol{q}}\, b_{\boldsymbol{q}'}\rangle = {} & \langle a^+_{\boldsymbol{k}}\, a^+_{\boldsymbol{k}'}\rangle = \langle a_{\boldsymbol{k}}\, a_{\boldsymbol{k}'}\rangle = 0\,, \\ \langle b^+_{\boldsymbol{q}}\, a_{\boldsymbol{k}}\rangle = \langle b^+_{\boldsymbol{q}}\, a^+_{\boldsymbol{k}}\rangle = {} & \langle b_{\boldsymbol{q}}\, a_{\boldsymbol{k}}\rangle = \langle b_{\boldsymbol{q}}\, a^+_{\boldsymbol{k}}\rangle = 0\,, \end{aligned}\right\} \tag{16}$$

where

$$\nu_{\boldsymbol{q}} = \langle b^+_{\boldsymbol{q}}\, b_{\boldsymbol{q}}\rangle \quad \text{and} \quad n_{\boldsymbol{k}} = \langle a^+_{\boldsymbol{k}}\, a_{\boldsymbol{k}}\rangle\,.$$

With the help of these decoupling approximations, and from (11), (12), and (13) we get the following set of equations for the Fourier transform of Green's function

$$(\omega - \varepsilon_{\boldsymbol{k}})\, G_{\boldsymbol{k}\boldsymbol{k}'}(\omega) = \frac{\delta_{\boldsymbol{k}\,\boldsymbol{k}'}}{2\,\pi} + \sum_{\boldsymbol{q}} F_{\boldsymbol{q}}\, G_1(\omega)\,, \tag{17}$$

$$(\omega - \varepsilon_{\boldsymbol{k}-\boldsymbol{q}})\, G_1(\omega) = \omega_{\boldsymbol{q}}\, G_2(\omega) + F_{\boldsymbol{q}}\, N_{\boldsymbol{q}}\, G_{\boldsymbol{k}\boldsymbol{k}'}(\omega)\,, \tag{18}$$

$$\begin{aligned} (\omega - \varepsilon_{\boldsymbol{k}-\boldsymbol{q}})\, G_2(\omega) = {} & [N'_{\boldsymbol{q}} + 2\,(1 - n_{\boldsymbol{k}-\boldsymbol{q}})]\, F_{\boldsymbol{q}}\, G_{\boldsymbol{k}\boldsymbol{k}'}(\omega) + \\ & + \left[\omega_{\boldsymbol{q}} + 24 \sum_{\boldsymbol{q}_1} V^{(4)}(-\boldsymbol{q}, \boldsymbol{q}, -\boldsymbol{q}_1, \boldsymbol{q}_1) N_{\boldsymbol{q}}\right] G_1(\omega)\,, \end{aligned} \tag{19}$$

where $N_{\boldsymbol{q}} = \langle A_{\boldsymbol{q}}^{+} A_{\boldsymbol{q}} \rangle, \quad N'_{\boldsymbol{q}} = \langle A_{\boldsymbol{q}}^{+} B_{\boldsymbol{q}} \rangle$.

We solve these equations for $G_{\boldsymbol{k}\boldsymbol{k}'}(\omega)$ and get

$$G_{\boldsymbol{k}\boldsymbol{k}'}(\omega) = \frac{\delta_{\boldsymbol{k}\boldsymbol{k}'}/2\pi}{\omega - \varepsilon_{\boldsymbol{k}} - M_{\boldsymbol{k}}(\omega)}, \tag{20}$$

where

$$M_{\boldsymbol{k}}(\omega) = \sum_{\boldsymbol{q}} F_{\boldsymbol{q}}^{2} \frac{[N'_{\boldsymbol{q}} + 2(1 - n_{\boldsymbol{k}-\boldsymbol{q}})]\, \omega_{\boldsymbol{q}} + N_{\boldsymbol{q}}(\omega - \varepsilon_{\boldsymbol{k}-\boldsymbol{q}})}{(\omega - \varepsilon_{\boldsymbol{k}-\boldsymbol{q}})^{2} - \omega_{\boldsymbol{q}}^{2} \left\{1 + \frac{24}{\omega_{\boldsymbol{q}}} \sum_{\boldsymbol{q}_1} V^{(4)}(-\boldsymbol{q}, \boldsymbol{q}, -\boldsymbol{q}_1, \boldsymbol{q}_1)\, N\, \boldsymbol{q}_1\right\}}. \tag{21}$$

It is shown by Klemens [8] that $V^{(4)}(-\boldsymbol{q}, \boldsymbol{q}, -\boldsymbol{q}_1, \boldsymbol{q}_1) = \frac{\eta\, \omega_{\boldsymbol{q}}\, \omega_{\boldsymbol{q}_1}}{96\, \omega_{\mathrm{L}}\, N}$ where η is a dimensionless parameter. N is the number of atoms in the crystal and ω_{L} is the maximum phonon frequency. Therefore the quantity inside the curly bracket in (21) is independent of $\boldsymbol{q}$. We denote it by A^2. Now let us define

$$M_{\boldsymbol{k}}(\omega \pm i\varepsilon) = \Delta_{\boldsymbol{k}}(\omega) \mp i\, \Gamma_{\boldsymbol{k}}(\omega), \tag{22}$$

where $\Delta_{\boldsymbol{k}}(\omega)$ and $\Gamma_{\boldsymbol{k}}(\omega)$ are the energy shift and half width of the electron of wave vector $\boldsymbol{k}$. The explicit expressions for $\Delta_{\boldsymbol{k}}(\omega)$ and $\Gamma_{\boldsymbol{k}}(\omega)$ are given as

$$\Delta_{\boldsymbol{k}}(\omega) = \mathrm{p} \sum_{\boldsymbol{q}} F_{\boldsymbol{q}}^{2} \frac{[N'_{\boldsymbol{q}} + 2(1 - n_{\boldsymbol{k}-\boldsymbol{q}})]\, \omega_{\boldsymbol{q}} + N_{\boldsymbol{q}}(\omega - \varepsilon_{\boldsymbol{k}-\boldsymbol{q}})}{(\omega - \varepsilon_{\boldsymbol{k}-\boldsymbol{q}})^{2} - A^{2} \omega_{\boldsymbol{q}}^{2}}, \tag{23}$$

$$\begin{aligned} \Gamma_{\boldsymbol{k}}(\omega) = \frac{\pi}{2A} \sum_{\boldsymbol{q}} F_{\boldsymbol{q}}^{2} [&\{N'_{\boldsymbol{q}} + 2(1 - n_{\boldsymbol{k}-\boldsymbol{q}}) + A\, N_{\boldsymbol{q}}\}\, \delta(\omega - \varepsilon_{\boldsymbol{k}-\boldsymbol{q}} - A\, \omega_{\boldsymbol{q}}) - \\ &- \{N'_{\boldsymbol{q}} + 2(1 - n_{\boldsymbol{k}-\boldsymbol{q}}) - A\, N_{\boldsymbol{q}}\}\, \delta(\omega - \varepsilon_{\boldsymbol{k}-\boldsymbol{q}} + A\, \omega_{\boldsymbol{q}})], \end{aligned} \tag{24}$$

where P denotes the principal value.

The above expressions reduce to that obtained by Zubarev [3] if the effect of anharmonicity is neglected. It should be noted that in these expressions the effect of anharmonicity comes only through $V^{(4)}$ coefficient which is smaller than $V^{(3)}$ coefficient in the expansion of potential energy. Hence the anharmonicity does not contribute noticeably to the electronic properties of metals and therefore for qualitative discussions one may neglect its effect.

3.2 Phonon Green's function

The equation of motion for the phonon Green's function $D_{\boldsymbol{q}\boldsymbol{q}'}$ is

$$\begin{aligned} i \frac{\mathrm{d}}{\mathrm{d}t} D_{\boldsymbol{q}\boldsymbol{q}'} = \delta_{\boldsymbol{q}\boldsymbol{q}'}\, \delta(t - t') + \omega_{\boldsymbol{q}} D_{\boldsymbol{q}\boldsymbol{q}'} + \sum_{\boldsymbol{k}} F_{\boldsymbol{q}} \langle\langle a_{\boldsymbol{k}}^{+} a_{\boldsymbol{k}+\boldsymbol{q}};\ b_{\boldsymbol{q}'}^{+}(t') \rangle\rangle + \\ + 3 \sum_{\boldsymbol{q}_1, \boldsymbol{q}_2} V^{(3)}(-\boldsymbol{q}, \boldsymbol{q}_1, \boldsymbol{q}_2) \langle\langle A_{\boldsymbol{q}_1} A_{\boldsymbol{q}_2};\ b_{\boldsymbol{q}'}^{+}(t') \rangle\rangle + \\ + 4 \sum_{\boldsymbol{q}_1, \boldsymbol{q}_2, \boldsymbol{q}_3} V^{(4)}(-\boldsymbol{q}, \boldsymbol{q}_1, \boldsymbol{q}_2, \boldsymbol{q}_3) \langle\langle A_{\boldsymbol{q}_1} A_{\boldsymbol{q}_2} A_{\boldsymbol{q}_3};\ b_{\boldsymbol{q}'}^{+}(t') \rangle\rangle . \end{aligned} \tag{25}$$

The Green's function of last term can be decoupled according to equations (14), (15), and (16). To evaluate the Green's functions $D_1 = \langle\langle a_{\boldsymbol{k}}^{+} a_{\boldsymbol{k}+\boldsymbol{q}}; b_{\boldsymbol{q}'}^{+}(t') \rangle\rangle$ and $D_2 = \langle\langle A_{\boldsymbol{q}_1} A_{\boldsymbol{q}_2}; b_{\boldsymbol{q}'}^{+}(t') \rangle\rangle$ contained in third and fourth terms, we need the Green's functions $D_3 = \langle\langle B_{\boldsymbol{q}_1} A_{\boldsymbol{q}_2}; b_{\boldsymbol{q}'}^{+}(t') \rangle\rangle$, $D_4 = \langle\langle A_{\boldsymbol{q}_1} B_{\boldsymbol{q}_2}; b_{\boldsymbol{q}'}^{+}(t') \rangle\rangle$, and $D_5 = \langle\langle B_{\boldsymbol{q}_1} B_{\boldsymbol{q}_2}; b_{\boldsymbol{q}'}^{+}(t') \rangle\rangle$

as can be seen from the equations of motion given below

$$i\frac{\mathrm{d}D_1}{\mathrm{d}t} = (\varepsilon_{k-q} - \varepsilon_k)\, D_1 + \sum_{q_1} F_{q_1} \{\langle\langle a_k^+ a_{k-q_1+q} A_{q_1};\ b_{q'}^+(t')\rangle\rangle - \\ - \langle\langle a_{k+q_1}^+ a_{k+q} A_{q_1};\ b_{q'}^+(t')\rangle\rangle\}\,, \tag{26}$$

$$i\frac{\mathrm{d}D_2}{\mathrm{d}t} = \omega_{q_1} D_3 + \omega_{q_2} D_4\,, \tag{27}$$

$$i\frac{\mathrm{d}D_3}{\mathrm{d}t} = \omega_{q_1} D_2 + \omega_{q_2} D_5 + 2 \sum_k F_{q_1} \langle\langle a_k^+ a_{k+q_1} A_{q_2};\ b_{q'}^+(t')\rangle\rangle + \\ + 6 \sum_{q_3, q_4} V^{(3)}(-q_1, q_3, q_4)\, \langle\langle A_{q_3} A_{q_4} A_{q_2};\ b_{q'}^+(t')\rangle\rangle + \\ + 8 \sum_{q_3, q_4, q_5} V^{(4)}(-q_1, q_3, q_4, q_5)\, \langle\langle A_{q_3} A_{q_4} A_{q_5} A_{q_2};\ b_{q'}^+(t')\rangle\rangle\,, \tag{28}$$

$$i\frac{\mathrm{d}D_4}{\mathrm{d}t} = \omega_{q_2} D_2 + \omega_{q_1} D_5 + 2 \sum_k F_{q_2} \langle\langle A_{q_1} a_k^+ a_{k+q_2};\ b_{q'}^+(t')\rangle\rangle + \\ + 6 \sum_{q_3, q_4} V^{(3)}(-q_2, q_3, q_4)\, \langle\langle A_{q_1} A_{q_3} A_{q_4};\ b_{q'}^+(t')\rangle\rangle + \\ + 8 \sum_{q_3, q_4, q_5} V^{(4)}(-q_2, q_3, q_4, q_5)\, \langle\langle A_{q_1} A_{q_3} A_{q_4} A_{q_5};\ b_{q'}^+(t')\rangle\rangle\,, \tag{29}$$

$$i\frac{\mathrm{d}D_5}{\mathrm{d}t} = \omega_{q_2} D_3 + \omega_{q_1} D_4 + 2 \sum_k F_{q_1} \langle\langle a_k^+ a_{k+q_1} B_{q_2};\ b_{q'}^+(t')\rangle\rangle + \\ + 2 \sum_k F_{q_2} \langle\langle B_{q_1} a_k^+ a_{k+q_2};\ b_{q'}^+(t')\rangle\rangle + \\ + 6 \sum_{q_3, q_4} \{V^{(3)}(-q_1, q_3, q_4)\, \langle\langle A_{q_3} A_{q_4} B_{q_2};\ b_{q'}^+(t')\rangle\rangle + \\ + V^{(3)}(-q_2, q_3, q_4)\, \langle\langle B_{q_1} A_{q_3} A_{q_4};\ b_{q'}^+(t')\rangle\rangle\} + \\ + 8 \sum_{q_3, q_4, q_5} \{V^{(4)}(-q_1, q_3, q_4, q_5)\, \langle\langle A_{q_3} A_{q_4} A_{q_5} B_{q_2};\ b_{q'}^+(t')\rangle\rangle + \\ + V^{(4)}(-q_2, q_3, q_4, q_5)\, \langle\langle B_{q_1} A_{q_3} A_{q_4} A_{q_5};\ b_{q'}^+(t')\rangle\rangle\,. \tag{30}$$

After decoupling all the higher order Green's functions appearing in equations from (25) to (30) according to equations (14), (15), and (16) and taking the Fourier transform one can proceed to solve these equations of motion for $D_{qq'}(\omega)$. It is easily noticed that the contributions from the terms obtained from decoupling the five operator Green's functions are small, being of the order of the product of cubic and quartic coupling parameters. We neglect them because such terms are comparable to the contributions that can arise from the higher order expansion of the potential energy of the crystal beyond the quartic anharmonic term. We obtain following equation for $D_{\boldsymbol{q}\boldsymbol{q}'}(\omega)$.

$$D_{\boldsymbol{q}\boldsymbol{q}'}(\omega) = \frac{\delta_{\boldsymbol{q}\boldsymbol{q}'}/2\pi}{\omega - \omega_{\boldsymbol{q}} - P_{\boldsymbol{q}}(\omega)}, \tag{31}$$

where

$$P_{\boldsymbol{q}}(\omega) = \sum_{\boldsymbol{k}} F_{\boldsymbol{q}}^2 \frac{n_{\boldsymbol{k}} - n_{\boldsymbol{k}+\boldsymbol{q}}}{\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}}} + 3 \sum_{\boldsymbol{q}_1, \boldsymbol{q}_2} |V^{(3)}(-\boldsymbol{q}, \boldsymbol{q}_1, \boldsymbol{q}_2)|^2 \, \Psi(\boldsymbol{q}_1, \boldsymbol{q}_2, \omega) + $$

$$+ 12 \sum_{\boldsymbol{q}_1} V^{(4)}(\boldsymbol{q}_1, -\boldsymbol{q}_1, \boldsymbol{q}, -\boldsymbol{q}) \, N_{\boldsymbol{q}_1} \tag{32}$$

and

$$\Psi(\boldsymbol{q}_1, \boldsymbol{q}_2, \omega) = 6\,(N_{\boldsymbol{q}_1} + N_{\boldsymbol{q}_2}) \frac{\omega_{\boldsymbol{q}_1} + \omega_{\boldsymbol{q}_2}}{\omega^2 - (\omega_{\boldsymbol{q}_1} + \omega_{\boldsymbol{q}_2})^2} + 6\,(N_{\boldsymbol{q}_2} - N_{\boldsymbol{q}_1}) \frac{\omega_{\boldsymbol{q}_1} - \omega_{\boldsymbol{q}_2}}{\omega^2 - (\omega_{\boldsymbol{q}_1} - \omega_{\boldsymbol{q}_2})^2}. \tag{33}$$

Now we define

$$P_{\boldsymbol{q}}\,(\omega \pm i\,\varepsilon) = \Delta_{\boldsymbol{q}}(\omega) \mp i\,\Gamma_{\boldsymbol{q}}(\omega)\,,$$

where phonon frequency shift $\Delta_{\boldsymbol{q}}(\omega)$ and half-width $\Gamma_{\boldsymbol{q}}(\omega)$ are given as

$$\Delta_{\boldsymbol{q}}(\omega) = \Delta_{\boldsymbol{q}}^{\text{e.p.}}(\omega) + \Delta_{\boldsymbol{q}}^{\text{anh}}(\omega)\,, \tag{34}$$

$$\Gamma_{\boldsymbol{q}}(\omega) = \Gamma_{\boldsymbol{q}}^{\text{e.p.}}(\omega) + \Gamma_{\boldsymbol{q}}^{\text{anh}}(\omega)\,, \tag{35}$$

where superscripts e.p. and anh. denote the contributions due to electron–phonon interaction and anharmonicity respectively. $\Delta_{\boldsymbol{q}}^{\text{e.p.}}$, $\Delta_{\boldsymbol{q}}^{\text{anh}}$, $\Gamma_{\boldsymbol{q}}^{\text{e.p.}}$, and $\Gamma_{\boldsymbol{q}}^{\text{anh}}$ are given by

$$\Delta_{\boldsymbol{q}}^{\text{e.p.}}(\omega) = \mathrm{P} \sum_{\boldsymbol{k}} F_{\boldsymbol{q}}^2 \frac{n_{\boldsymbol{k}} - n_{\boldsymbol{k}+\boldsymbol{q}}}{\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}}}\,, \tag{36}$$

$$\Delta_{\boldsymbol{q}}^{\text{anh.}}(\omega) = 18\,\mathrm{P} \sum_{\boldsymbol{q}_1, \boldsymbol{q}_2} |V^{(3)}(-\boldsymbol{q}, \boldsymbol{q}_1, \boldsymbol{q}_2)|^2 \Big[(N_{\boldsymbol{q}_1} + N_{\boldsymbol{q}_2}) \frac{\omega_{\boldsymbol{q}_1} + \omega_{\boldsymbol{q}_2}}{\omega^2 - (\omega_{\boldsymbol{q}_1} + \omega_{\boldsymbol{q}_2})^2} + $$

$$+ (N_{\boldsymbol{q}_2} - N_{\boldsymbol{q}_1}) \frac{\omega_{\boldsymbol{q}_1} - \omega_{\boldsymbol{q}_2}}{\omega^2 - (\omega_{\boldsymbol{q}_1} - \omega_{\boldsymbol{q}_2})^2} \Big] + $$

$$+ 12 \sum_{\boldsymbol{q}_1} V^{(4)}(-\boldsymbol{q}, \boldsymbol{q}, -\boldsymbol{q}_1, \boldsymbol{q}_1) \, N_{\boldsymbol{q}_1}\,, \tag{37}$$

$$\Gamma_{\boldsymbol{q}}^{\text{e.p.}}(\omega) = \pi \sum_{\boldsymbol{k}} F_{\boldsymbol{q}}^2 \, (n_{\boldsymbol{k}} - n_{\boldsymbol{k}+\boldsymbol{q}}) \, \delta\,(\omega - \varepsilon_{\boldsymbol{k}+\boldsymbol{q}} + \varepsilon_{\boldsymbol{k}})\,, \tag{38}$$

$$\Gamma_{\boldsymbol{q}}^{\text{anh.}}(\omega) = 18\,\pi\,\varepsilon(\omega) \sum_{\boldsymbol{q}_1, \boldsymbol{q}_2} |V^{(3)}(-\boldsymbol{q}, \boldsymbol{q}_1, \boldsymbol{q}_2)|^2 \times$$

$$\times \big[(N_{\boldsymbol{q}_1} + N_{\boldsymbol{q}_2}) (\omega_{\boldsymbol{q}_1} + \omega_{\boldsymbol{q}_2}) \, \delta\,\{\omega^2 - (\omega_{\boldsymbol{q}_1} + \omega_{\boldsymbol{q}_2})^2\} + $$

$$+ (N_{\boldsymbol{q}_2} - N_{\boldsymbol{q}_1}) (\omega_{\boldsymbol{q}_1} - \omega_{\boldsymbol{q}_2}) \, \delta\,\{\omega^2 - (\omega_{\boldsymbol{q}_1} - \omega_{\boldsymbol{q}_2})^2\} \big]\,, \tag{39}$$

where

$$\varepsilon(\omega) = \begin{cases} 1 & \text{for} \quad \omega > 0 \\ -1 & \text{for} \quad \omega < 0\,. \end{cases}$$

The equations (34) and (35) reduce to the equations obtained by Zubarev [3] if effect of anharmonicity is neglected. Also one obtains the expressions obtained by Pathak [2] if effect of electron phonon interaction is neglected. In the theory of transport properties it is generally assumed that the total inverse of relaxation time is the sum of the inverse of relaxation times due to different scattering mechanisms. From (35) it is clear that Green's function theory gives an insight about the nature of this assumption.

4. Electron Width

To evaluate electron width we substitute the value of F_q from (2) in (24) and replace summation over wave vector $\boldsymbol{q}$ by integration. After performing the angular integration with the help of delta function we get

$$\begin{aligned}\Gamma_k(\varepsilon_k) = \frac{F^2\, m\, c}{8\,\pi\, A\, k} \Bigg[& \int\limits_0^{2k-2mAc} q^2 \left\{ 1 + A - \frac{2}{e^{\beta(\varepsilon_k - A\,\omega_q)} + 1} + \frac{2\,A}{e^{\beta\,\omega_q} - 1} \right\} dq \, - \\ & - \int\limits_0^{2k+2mAc} q^2 \left\{ 1 - A - \frac{2}{e^{\beta(\varepsilon_k + A\,\omega_q)} + 1} - \frac{2\,A}{e^{\beta\,\omega_q} - 1} \right\} dq \Bigg] . \end{aligned} \tag{40}$$

Since $k \gg m\,A\,c$, the upper limit of integration in both the integrals of (40) can be taken as $2\,k$. Also since $\varepsilon_k \gg A\,\omega_q$, the Fermi distribution functions $1/(\exp\{\beta\,(\varepsilon_k - A\,\omega_q)\} + 1)$ and $1/(\exp\{\beta\,(\varepsilon_k + A\,\omega_q)\} + 1)$ can be replaced by $1/(\exp(\beta\,\varepsilon_k) + 1)$. Within these approximation (40) reduces to

$$\Gamma_k(\varepsilon_k) = \frac{F^2\, m\, c}{4\,\pi\, k} \int\limits_0^{2k} \left(1 + \frac{2}{e^{\beta\,\omega_q} - 1} \right) q^2 \, dq \, . \tag{41}$$

At low temperature ($k_B T \ll \omega_q$) we get

$$\Gamma_k(\varepsilon_k) = \frac{F^2\, m\, I}{4\,\pi\, c\, \beta^3\, k} \, , \tag{42}$$

where

$$I = \int\limits_0^{\infty} \varkappa^2 \coth \frac{\varkappa}{2} \, d\varkappa \, . \tag{43}$$

In (43) the upper limit $2\,k\,\beta\,c$ is replaced by ∞ which is perfectly justified in this range of temperature. At high temperature ($\omega_q \ll k_B T \ll \mu$) we replace phonon distribution function $1/(\exp(\beta\,\omega_q) - 1)$ by $1/\beta\,\omega_q$ and get [9]

$$\Gamma_k(\varepsilon_k) = \frac{F^2\, m\, k}{\pi\, c\, \beta} \, . \tag{44}$$

The expressions (42) and (44) give the well known temperature dependence of electron relaxation time at low and high temperature respectively [5]. These expressions are independent of anharmonic parameter A and thus one can safely neglect the effect of anharmonicity on the electronic transport properties of metals.

5. Phonon Width

To evaluate $\Gamma_{\boldsymbol{q}}(\omega)$ we note from (35) that it is a sum of two terms $\Gamma_{\boldsymbol{q}}^{\text{e.p.}}$ and $\Gamma_{\boldsymbol{q}}^{\text{anh.}}$. The contribution to $\Gamma_{\boldsymbol{q}}(\omega)$ from $\Gamma_{\boldsymbol{q}}^{\text{anh.}}$ has been evaluated by Pathak [2] and is given by

$$\Gamma_{\boldsymbol{q}}^{\text{anh.}}(\omega_{\boldsymbol{q}}) = \frac{3\,\lambda}{32\,\beta}\,(k\,a)^2\,\theta\,(k_{\text{m}} - k)\,, \tag{45}$$

where λ is a dimensionless parameter and a is a lattice constant. We evaluate $\Gamma_{\boldsymbol{q}}^{\text{e.p.}}$ at low and high temperature as follows.

At low temperature ($T \to 0$) the electron distribution functions n_k and n_{k-q} can be replaced by $\theta\,(k_{\text{F}}^2 - k^2)$ and $\theta\,(k_{\text{F}}^2 - \overline{\boldsymbol{k} - \boldsymbol{q}}^2)$ respectively. Here k_{F} is the electron wave vector at the Fermi surface. After replacing the summation over $\boldsymbol{k}$ by integration and summing over spin index (38) reduces to

$$\Gamma_{\boldsymbol{q}}(\omega) = \frac{F\,\boldsymbol{q}^2}{2\,\pi}\int\limits_0^\infty k^2\,\mathrm{d}k\int\limits_{-\infty}^\infty \theta\,(1-\varkappa)\,\theta\,(1+\varkappa)\,\{\theta\,(k_{\text{F}}^2 - k^2) -$$
$$- \theta\,(k_{\text{F}}^2 - k^2 - q^2 + 2\,k\,q\,\varkappa)\}\;\delta\left(\omega - \frac{q^2}{2\,m} - \frac{k\,q\,\varkappa}{m}\right)\mathrm{d}\varkappa\,. \tag{46}$$

After performing the integration over x and k we get

$$\Gamma_{\boldsymbol{q}}^{\text{e.p.}}(\omega) = \begin{cases} \dfrac{F^2\,c\,m^2\,\omega}{2\,\pi} & \text{when} \quad q < 2\,k_{\text{F}} \qquad (47)\\[2ex] 0 & \text{when} \quad q > 2\,k_{\text{F}}\,. \qquad (48)\end{cases}$$

At high temperature ($T \to \infty$) we replace Fermi distribution function by Boltzmann distribution function and get

$$\Gamma_{\boldsymbol{q}}^{\text{e.p.}}(\omega) = \frac{F^2\,m\,c}{2\,\pi\,\beta}\,\mathrm{e}^{\beta\mu}\,(1 - \mathrm{e}^{-\beta\omega})\,\mathrm{e}^{-\frac{\beta}{2\,m}\left(\frac{m\,\omega}{q} - \frac{q}{2}\right)^2}\,. \tag{49}$$

If we examine (45), (47), (48), and (49) we come to the conclusion that the effect of anharmonicity is predominant only at high temperature ($T \to \infty$) and at low temperature ($T \to 0$) the effect of electron–phonon interaction is predominant. When we consider these points, we find that these expressions give the well known temperature dependence of phonon width at low and high temperature limit.

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Electrical Conductivity of Metals

By

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With the help of Kubo formula an expression for the electrical conductivity of metals is obtained within the Hartree-Fock approximation using the method of double time temperature dependent Green's function. A simple calculation of the relevant relaxation time appearing in the expression is presented. This gives a reasonably good estimate of the electrical conductivity of metals.

Mittels der Formel von Kubo wird ein Ausdruck für die elektrische Leitfähigkeit der Metalle gewonnen, wobei in der Hartree-Fock-Näherung die Methode der doppelt zeit-temperaturabhängigen Greenschen Funktion benutzt wird. Eine einfache Berechnung wird für die in dem Ausdruck erscheinende Relaxationszeit angegeben. Damit ergibt sich eine ziemlich gute Abschätzung der elektrischen Leitfähigkeit von Metallen.

We start with the Kubo formula [1] of the electrical conductivity

$$\sigma_{\mu\nu} = \lim_{\varepsilon \to 0} \int_0^\infty \mathrm{e}^{-\varepsilon t}\, \mathrm{d}t \int_0^\beta \mathrm{d}\lambda\, \langle J_\nu\, J_\mu\, (t + i\,\lambda)\rangle\,, \tag{1}$$

where $\beta = 1/k_\mathrm{B} T$; J_ν is the ν-th cartesian component of the electron current density operator and is given by

$$J_\nu = -\, e \sum_{\boldsymbol{k}\sigma} \frac{\partial \varepsilon_{\boldsymbol{k}}}{\partial \boldsymbol{k}_\nu}\, n_{\boldsymbol{k}\sigma}\,, \tag{2}$$

where $\varepsilon_{\boldsymbol{k}} = (k^2/2\,m) - \mu$ and $n_{\boldsymbol{k}\sigma} = a^+_{\boldsymbol{k}\sigma}\, a_{\boldsymbol{k}\sigma}$. $\boldsymbol{k}$, m and μ are the wave vector, mass and the chemical potential of the electron respectively. $a^+_{\boldsymbol{k}\sigma}$ and $a_{\boldsymbol{k}\sigma}$ are the creation and annihilation operators of the electron of wave vector $\boldsymbol{k}$ and spin σ. Here and in what follows we take $\hbar = 1$. The angular brackets in equation (1) denote an ensemble average, namely for any operator O

$$\langle O\rangle = \frac{\operatorname{tr} \mathrm{e}^{-\beta H} O}{\operatorname{tr} \mathrm{e}^{-\beta H}}\,, \tag{3}$$

where H is the Hamiltonian of the system.

For our particular problem of electrons in a crystal, the system is described by the Hamiltonian [2]

$$H = \sum_{\boldsymbol{q}} \omega_{\boldsymbol{q}}\, b^+_{\boldsymbol{q}}\, b_{\boldsymbol{q}} + \sum_{\boldsymbol{k}} \varepsilon_{\boldsymbol{k}}\, a^+_{\boldsymbol{k}}\, a_{\boldsymbol{k}} + \sum_{\boldsymbol{k}\boldsymbol{q}} A_{\boldsymbol{q}}\, a^+_{\boldsymbol{k}+\boldsymbol{q}}\, a_{\boldsymbol{k}}\, (b_{\boldsymbol{q}} + b^+_{-\boldsymbol{q}}) + \\ + \frac{1}{2} \sum_{\boldsymbol{p},\boldsymbol{q},\boldsymbol{k}} V_{\boldsymbol{k}}\, a^+_{\boldsymbol{p}+\boldsymbol{k}}\, a^+_{\boldsymbol{q}-\boldsymbol{k}}\, a_{\boldsymbol{q}}\, a_{\boldsymbol{p}}\,, \tag{4}$$

where $\omega_{\boldsymbol{q}}$, $b^+_{\boldsymbol{q}}$ and $b_{\boldsymbol{q}}$ are the energy, creation and annihilation operators of the phonon of wave vector $\boldsymbol{q}$ respectively. $A_{\boldsymbol{q}}$ is the coupling constant for the

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electron–phonon interaction. V_k is the Fourier transform of the Coulomb interaction between the electrons and is given by

$$V_k = \frac{4\pi e^2}{k^2}.$$

For simplicity here and in what follows we have omitted the spins and polarizations of electrons and phonons respectively.

In fact taking the equation of motion of the density fluctuation of the electron in the random phase approximation (R.P.A.) one gets [2]

$$\sum_q a^+_{q-k}\, a_q = -\frac{A_k}{V_k}\,\frac{\varepsilon(\boldsymbol{k},\omega)-1}{\varepsilon(\boldsymbol{k},\omega)}\,(b_k + b^+_{-k}), \tag{5}$$

where the frequency dependent dielectric constant is given as

$$\varepsilon(\boldsymbol{k},\omega) = 1 + V_k \sum_p \frac{n_p - n_{p+k}}{\omega - \varepsilon_p + \varepsilon_{p+k} + i\,\delta}.$$

After substituting the value of $\sum_q a^+_{q-k}\, a_q$ from equation (5) in equation (4), the Hamiltonian of the system reduces to

$$H = \sum_q \omega_q\, b^+_q\, b_q + \sum_k \varepsilon_k\, a^+_k\, a_k + \sum_{k,q} A^{\mathrm{eff}}_q\, a^+_{k+q}\, a_k\, (b_q + b^+_{-q}), \tag{6}$$

where

$$A^{\mathrm{eff}}_q = \frac{A_q}{\varepsilon(\boldsymbol{k},\omega)}. \tag{7}$$

For d.c. electrical conductivity the energy of the applied field $\omega = 0$ and so in this case $A^{\mathrm{eff}}_q = A_q/\varepsilon(\boldsymbol{k},0)$. To evaluate A^{eff}_q we take the simplified 'Jellium' model in which all effects associated with periodicity of the ions are neglected. In this model after applying R.P.A. one obtains [2]

$$A^{\mathrm{eff}}_q = -i\left(\frac{2}{3}\,\frac{Z\mu}{n}\,q\right)\left(\frac{n}{M\nu}\right)^{1/2}\frac{1}{(2\,\omega_q)^{1/2}}, \tag{8}$$

where n is the number of electrons per unit volume, ν is the number of electrons per atom, Z is the number of charges of an ion and M is the mass of an ion. For phonon frequency ω_q we take the Debye model and obtain from equation (8)

$$A^{\mathrm{eff}}_q = -i\,\frac{2}{3}\,\frac{Z\mu}{n}\left(\frac{n\,q}{2\,M\,\nu\,c}\right)^{1/2}. \tag{9}$$

For an isotropic solid the expression for the electrical conductivity can be written as

$$\sigma = \lim_{\varepsilon\to 0}\frac{e^2}{3}\sum_{k,k'}\frac{\partial\varepsilon_k}{\partial k}\,\frac{\partial\varepsilon_{k'}}{\partial k'}\int_0^\infty \mathrm{e}^{-\varepsilon t}\,\mathrm{d}t\int_0^\beta \mathrm{d}\lambda\,\langle n_k\, n_{k'}\,(t + i\,\lambda)\rangle. \tag{10}$$

It is evident from equation (10) that the evaluation of electrical conductivity essentially involves the evaluation of the correlation function of two electron number density operators at different times. This correlation function can be expressed in terms of the Fourier transform $G_{k,k'}(\omega)$ of the one-particle Green's function [3]

$$G_{k,k'}(t) = -i\,\theta(t)\,\langle\{a_k(t), a^+_{k'}(0)\}\rangle, \tag{11}$$

where $\theta(t)$ is the Heaveside unit step function and curly brackets denote the anticommutator

$$\{A, B\} = A\,B + B\,A\,.$$

Now within the Hartree Fock approximation and neglecting the correlation between two creation and the annihilation operators the electrical conductivity can easily be shown to be (4)

$$\sigma = \frac{\pi e^2}{3} \lim_{\varepsilon \to 0} \sum_{\boldsymbol{k}, \boldsymbol{k}'} \frac{\partial \varepsilon_{\boldsymbol{k}}}{\partial \boldsymbol{k}} \frac{\partial \varepsilon_{\boldsymbol{k}'}}{\partial \boldsymbol{k}'} \int\limits_{-\infty}^{\infty} \mathrm{d}\omega \frac{\mathrm{e}^{\beta\omega}}{(\mathrm{e}^{\beta\omega}+1)^2} \times$$
$$\times \{G_{\boldsymbol{k},\boldsymbol{k}'}(\omega + i\varepsilon) - G_{\boldsymbol{k},\boldsymbol{k}'}(\omega - i\varepsilon)\}\,\{G_{\boldsymbol{k}'\boldsymbol{k}}(\omega + i\varepsilon) - G_{\boldsymbol{k}'\boldsymbol{k}}(\omega - i\varepsilon)\}\,. \quad (12)$$

For our system of electrons in a crystal described by the Hamiltonian (6) one can obtain the expression for the Fourier transform of the Green's function [3] as

$$G_{\boldsymbol{k},\boldsymbol{k}'}(\omega) = \frac{1}{2\pi} \frac{\delta_{\boldsymbol{k},\boldsymbol{k}'}}{\omega - \varepsilon_{\boldsymbol{k}} - M_{\boldsymbol{k}}(\omega)}\,, \quad (13)$$

where $M_{\boldsymbol{k}}(\omega)$ gives the effect of electron–phonon and electron–electron interaction on the single-particle energy and is explicitly given as

$$M_{\boldsymbol{k}}(\omega) = \sum_{\boldsymbol{q}} (A_{\boldsymbol{q}}^{\mathrm{eff}})^2 \frac{\langle \nu_{\boldsymbol{q}} \rangle - \langle n_{\boldsymbol{k}-\boldsymbol{q}} \rangle}{\omega - \varepsilon_{\boldsymbol{k}-\boldsymbol{q}} - \omega_{\boldsymbol{q}}} + \frac{\langle n_{\boldsymbol{k}-\boldsymbol{q}} \rangle + \langle \nu_{\boldsymbol{q}} \rangle}{\omega - \varepsilon_{\boldsymbol{k}-\boldsymbol{q}} + \omega_{\boldsymbol{q}}}\,, \quad (14)$$

where

$$\nu_{\boldsymbol{q}} = b_{\boldsymbol{q}}^{+}\, b_{\boldsymbol{q}}\,.$$

Now we substitute the Green's function $G_{\boldsymbol{k},\boldsymbol{k}'}(\omega)$ from equation (13) in equation (12) and obtain the expression for the electrical conductivity as

$$\sigma = \frac{\beta e^2}{3} \sum_{\boldsymbol{k}} \left(\frac{\partial \varepsilon_{\boldsymbol{k}}}{\partial \boldsymbol{k}}\right)^2 \frac{\mathrm{e}^{\beta E_{\boldsymbol{k}}}}{(\mathrm{e}^{\beta E_{\boldsymbol{k}}}+1)^2} \cdot \frac{1}{2\,\Gamma_{\boldsymbol{k}}(E_{\boldsymbol{k}})}\,, \quad (15)$$

where the renormalized electron energy $E_{\boldsymbol{k}}$ is

$$E_{\boldsymbol{k}} = \varepsilon_{\boldsymbol{k}} + \Delta_{\boldsymbol{k}}(E_{\boldsymbol{k}})\;;$$

$\Delta_{\boldsymbol{k}}$ and $\Gamma_{\boldsymbol{k}}$ are the real and imaginary part of $M_{\boldsymbol{k}}(\omega)$ which can be obtained from equation (14).

In general the shift in energy $\Delta_{\boldsymbol{k}}(E_{\boldsymbol{k}})$ is very small and therefore we assume $E_{\boldsymbol{k}} \approx \varepsilon_{\boldsymbol{k}}$. In this case equation (15) for the electrical conductivity reduces to

$$\sigma = \frac{e^2}{6\pi^2 m} \int\limits_{0}^{\infty} (2\,m\,\varepsilon)^{3/2} \left(-\frac{\partial f}{\partial \varepsilon}\right) \frac{\partial \varepsilon}{\Gamma(\varepsilon - \mu)}\,, \quad (16)$$

where $f = 1/(\mathrm{e}^{\beta\varepsilon_{\boldsymbol{k}}} + 1)$ and $\varepsilon = k^2/2\,m$.

For temperatures well below the Fermi temperature ($k_{\mathrm{B}}T \ll \mu$) equation (16) reduces to the usual relaxation time expression of electrical conductivity

$$\sigma = \frac{n\,e^2\,\tau}{m}\,, \quad (17)$$

where the relaxation time $\tau = 1/2\,\Gamma(0)$; $\Gamma(0)$ is the half-width of the electron distribution function at the Fermi surface.

The expression for the electron width $\Gamma_k(\omega)$ can easily be obtained from equation (14) and one gets (3)

$$\Gamma_k(\omega) = \pi \sum_{q} (A_q^{\text{eff}})^2 (\nu_q + 1 - n_{k-q})\, \delta(\omega - \varepsilon_{k-q} - \omega_q) + \\ + (n_{k-q} + \nu_q)\, \delta(\omega - \varepsilon_{k-q} + \omega_q)\,. \tag{18}$$

Now we evaluate the electron width $\Gamma_k(\omega)$ in the temperature range $\omega_q \ll k_{\mathrm{B}} T \ll \ll \mu$. In this range of temperature the phonon distribution function ν_q can be approximated by $1/\beta\, \omega_q$ and the Fermi distribution function n_{k-q} by unity. Within these approximations and with the help of equation (9) the expression for the electron width can be written as

$$\Gamma_k(\omega) = \frac{\mu^2 Z^2}{18\, \pi\, n\, M\, c^2\, \nu\, \beta} \int q^2\, \mathrm{d}q \int_0^{\pi} \sin\theta\, \mathrm{d}\theta \left\{\delta\left(\omega + \mu + c\, q - \right.\right. \\ \left.\left. - \frac{k^2 + q^2 - 2\, k\, q \cos\theta}{2\, m}\right) + \delta\left(\omega + \mu - c\, q - \frac{k^2 + q^2 - 2\, k\, q \cos\theta}{2\, m}\right)\right\} + \\ + \frac{\mu^2 Z^2}{18\, \pi\, n\, M\, c\, \nu} \int q^3\, \mathrm{d}q \int_0^{\pi} \sin\theta\, \mathrm{d}\theta\, \delta\left(\omega + \mu + c\, q - \frac{k^2 + q^2 - 2\, k\, q \cos\theta}{2\, m}\right), \tag{19}$$

where we have replaced the summation over the phonon wave vector $\boldsymbol{q}$ by integration over a Debye sphere. The evaluation of integrals in equation (19) is discussed in the Appendix where finally we get

$$\Gamma(0) = \frac{2\, Z^2 \mu^2\, m\, k_{\mathrm{f}}}{9\, \pi\, n\, M\, c^2\, \nu\, \beta} + \left\{\frac{m^3\, c^2\, \mu^2\, Z^2}{3\, \pi\, n\, M\, c^2\, \nu\, \beta\, k_{\mathrm{f}}} + \frac{m\, \mu^2\, Z^2}{54\, \pi\, n\, M\, c\, \nu\, k_{\mathrm{f}}} \times \right. \\ \left. \times \left[8\, k_{\mathrm{f}}^3 + 14\, m^3\, c^3 + 24\, k_{\mathrm{f}}^2\, m\, c + 30\, m^2\, c^2\, k_f + \frac{15\, m^4\, c^4}{2\, k_{\mathrm{f}}} + \frac{3\, m^3\, c^5}{2\, k_{\mathrm{f}}^3}\right]\right\}, \tag{20}$$

where k_{f} is the wave vector at the Fermi surface. In this equation all terms inside the curly bracket are small in comparison to the first term, so after neglecting them we get

$$\Gamma(0) = \frac{2\, m\, \mu^2\, Z^2\, k_{\mathrm{f}}}{9\, \pi\, n\, M\, c^2\, \nu\, \beta}\,. \tag{21}$$

Now after substituting the value of $\Gamma(0)$ from equation (21) in equation (17) we get an expression for the electrical conductivity as

$$\sigma = \frac{e^2\, M\, c^2\, \nu}{\pi^3\, Z^2\, k_{\mathrm{B}} T} (2\, m\, \mu)^{1/2}\,. \tag{22}$$

After substituting the values of different quantities and taking $\nu = 1$ in equation (22) we have calculated the electrical conductivity for Li, K, Na, Cu, Ag, and Au at 0 °C. The calculated and experimental values in e.s.u. are given in the following table:

	Li	K	Na	Cu	Ag	Au
$\sigma_{\text{cal}} \times 10^{-17}$	0.82	1.4	1.02	10.2	4.8	8.8
$\sigma_{\text{exp}} \times 10^{-17}$	1.06	1.47	2.09	5.76	6.12	4.37

From the above table it is clear that the calculated values of electrical conductivity of Li, K, and Ag are in reasonably good agreement with the experimental values, but in case of Na, Cu, and Au the agreement is somewhat poor. This discrepancy may be due to two reasons: Firstly our model for the coupling constant A_q^{eff} is not very realistic and secondly the value of ν may not be equal to unity for all elements. To get a better agreement with experimental results we must know more accurate value of ν and use a more realistic model for the calculation of coupling constant. To our knowledge, this type of first principle estimates of the electrical conductivity is not available at present.

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Appendix

In equation (19) putting $\cos\theta = x$ we get

$$\begin{aligned}\Gamma_k(\omega) = {} & \frac{\mu^2 Z^2}{18\,\pi\, n\, M\, c^2\, \nu\, \beta} \int q^2\, \mathrm{d}q \int\limits_{-\infty}^{\infty} \theta\,(1-x)\,\theta\,(1+x)\, \times \\ & \times \left\{\delta\left(\omega - \frac{k^2+q^2-2\,k\,q\,x}{2\,m} + \mu - c\,q\right) + \right. \\ & \left. + \,\delta\left(\omega - \frac{k^2+q^2-2\,k\,q\,x}{2\,m} + \mu + c\,q\right)\right\} \mathrm{d}x\, + \\ & + \frac{\mu^2 Z^2}{18\,\pi\, n\, M\, c} \int q^3\, \mathrm{d}q \int\limits_{-\infty}^{\infty} \theta\,(1-x)\,\theta\,(1+x)\, \times \\ & \times\, \delta\left(\omega - \frac{k^2+q^2-2\,k\,q\,x}{2\,m} + \mu + c\,q\right) \mathrm{d}x\,. \end{aligned} \tag{23}$$

After performing the integration over x we obtain

$$\begin{aligned}\Gamma_k(\omega) = {} & \frac{\mu^2 Z^2 m}{18\,\pi\, n\, M\, c^2\, \nu\, \beta\, k} \int q\, \mathrm{d}q \left\{\theta\,(1-x_1)\,\theta\,(1+x_1) + \theta\,(1-x_2)\,\theta\,(1+x_2)\right\} + \\ & + \frac{\mu^2 Z^2 m}{18\,\pi\, n\, M\, c\, \nu\, k} \int q^2\, \mathrm{d}q\, \theta\,(1-x_2)\,\theta\,(1+x_2)\,, \end{aligned} \tag{24}$$

where

$$x_1 = \frac{k^2+q^2}{2\,k\,q} - \frac{(\omega+\mu-c\,q)\,m}{k\,q}\,, \tag{25a}$$

$$x_2 = \frac{k^2+q^2}{2\,k\,q} - \frac{(\omega+\mu+c\,q)\,m}{k\,q}\,. \tag{25b}$$

The limits of integration in equation (24) are determined by θ functions. For example the limits of integration $\int q\, \mathrm{d}q\, \theta\,(1-x_1)\, \theta(1+x_1)$ are obtained by the conditions

$$1 - x_1 > 0 \tag{26a}$$

and

$$1 + x_1 > 0\,. \tag{26b}$$

Substituting the value of x_1 from equation (25a) into the inequalities (26) we get

$$(q - a)(q - b) < 0 \tag{27a}$$

and

$$(q - a')(q - b') > 0\,, \tag{27b}$$

where

$$a = k - m\,c + \sqrt{[m^2 c^2 + 2\,m\,(\omega + \mu - c\,k)]}\,,$$

$$b = k - m\,c - \sqrt{[m^2 c^2 + 2\,m\,(\omega + \mu - c\,k)]}\,,$$

$$a' = -(k + m\,c) + \sqrt{[m^2 c^2 + 2\,m\,(\omega + \mu + c\,k)]}\,,$$

and

$$b' = -(k + m\,c) - \sqrt{[m^2 c^2 + 2\,m\,(\omega + \mu + c\,k)]}\,.$$

It is easy to see that both the inequalities (27a) and (27b) will be satisfied simultaneously only when $a' < q < a$. Similarly the limits of other integrals can be determined. Integrating the equations (24) under these limits and retaining only the first two terms in the expression of the quantities under the square root sign, we get the expression (20).

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On Transverse Electrical Conductivity of Metals

By

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With the help of the Kubo formula an expression for the transverse electrical conductivity of metals is obtained within the Hartree-Fock approximation using the method of the double-time temperature-dependent Green's function. It is observed that the expression is the same as that obtained by Leribaux with the help of perturbation theory using the Feynman diagram technique if the change in the energy of the electrons due to electron–phonon interaction is neglected.

Mit Hilfe der Formel von Kubo wird in der Hartree-Fock-Näherung ein Ausdruck für die transversale elektrische Leitfähigkeit von Metallen erhalten, wobei die Methode der zweizeitigen, temperaturabhängigen Greenschen Funktion benutzt wird. Es wird gefunden, daß der Ausdruck mit dem von Leribaux mit Hilfe der Störungstheorie unter Benutzung der Feynmanschen Diagrammtechnik erhaltenen übereinstimmt, wenn die Energieänderung der Elektronen durch Elektron-Phonon-Wechselwirkung vernachlässigt wird.

The problem of electrical conductivity is usually treated by two quantum mechanical approaches. These are Boltzmann transport equation [1] and Kubo [2] approaches. Instead of using the Boltzmannn equation or solving in a particular representation the density matrix equation of motion, we shall start from an exact expression (within the linear approximation in the electric field) for the conductivity (the so-called Kubo formula). The advantage of this formalism is its independence of the particular representation. The explicit evaluation of the conductivity from the Kubo formula has been done by many authors [3 to 7] using the thermodynamics Green's function technique. In the conductivity problem however, efforts have been directed mostly towards obtaining the diagonal elements of the doncuctivity tensor. In some cases such as in the evaluation of the Hall coefficient we need transverse (or off diagonal) components of the tensor [7].

In this paper we present the calculation of the transverse electrical conductivity of metals from the Kubo formula within the Hartree-Fock approximation using the method of double-time temperature dependent Green's function. Here the electron transport is assumed to be limited by electron–phonon interaction. It is found that the final expression for the conductivity is the same as that obtained by Leribaux [7] with the help of perturbation theory using diagram technique if the change in energy of the electrons due to electron–phonon interaction is neglected.

The Kubo formula for the electrical conductivity is

$$\sigma_{\mu\nu} = \lim_{\varepsilon \to 0} V \int_0^\infty \mathrm{e}^{-\varepsilon t} \,\mathrm{d}t \int_0^\beta \mathrm{d}\lambda \,\langle J_\nu \, J_\mu \,(t + i\,\lambda)\rangle\,, \tag{1}$$

where $\beta = (k_\mathrm{B} T)^{-1}$; V the volume of the system, J_ν is the νth cartesian component of electron current density operator and angular brackets denote the grand canonical ensemble average, namely for any operator

$$\langle O \rangle = \frac{\mathrm{Tr}\, \mathrm{e}^{-\beta(H-\mu N)}\, O}{\mathrm{Tr}\, \mathrm{e}^{-\beta(H-\mu N)}}, \tag{2}$$

where H is the Hamiltonian of the system, N is the number of particles in the system and μ is the chemical potential. Here and in the following we take $\hbar = 1$.

In the second quantized representation, the Hamiltonian of the system of electron interacting with the system of phonon is [8]

$$H = \sum_{\boldsymbol{q}} \omega_{\boldsymbol{q}}\, b_{\boldsymbol{q}}^{+} b_{\boldsymbol{q}} + \sum_{l} E_l\, a_l^{+} a_l + \sum_{l_1 l_2 \boldsymbol{q}} A_{\boldsymbol{q}}\, a_{l_1}^{+} a_{l_2} (b_{\boldsymbol{q}} + b_{\boldsymbol{q}}^{+}), \quad (\boldsymbol{k}_1 - \boldsymbol{k}_2 = \boldsymbol{q}), \tag{3}$$

where a_l^{+}, a_l are respectively the creation and annihilation operators of an electron in state l; $b_{\boldsymbol{q}}^{+}$, $b_{\boldsymbol{q}}$ are the same for a phonon with wave-vector $\boldsymbol{q}$, $\omega_{\boldsymbol{q}}$ is the energy of the phonon with wave vector $\boldsymbol{q}$; $l \equiv (n, \boldsymbol{k})$, where n stands both for the band level and the spin quantum number and $\boldsymbol{k}$ is the wave vector of the electron; $E_l = \varepsilon_l - \mu$, where ε_l are the eigenvalues of any suitable chosen one-electron Hamiltonian, $A_{\boldsymbol{q}}$ describes the coupling of the electrons to the phonon field. The second quantized form of current density operator is

$$J_\mu = -\frac{e}{V} \sum_{ll'} (v_\mu)_{ll'}\, a_l^{+} a_l\,. \tag{4}$$

Here e is the charge of the electron and v_μ is the μth cartesian component of electron velocity. The diagonal matrix elements are

$$(v_\mu)_l = \frac{\partial \varepsilon_l}{\partial k_\mu}. \tag{5}$$

The off diagonal matrix elements may be written in the form [9]

$$(v_\mu)_{ll'} = i\, \omega_{ll'} (\varkappa_\mu)_{ll'} = -\omega_{ll'}\, J_\mu^{nn'}(\boldsymbol{k})\, \delta(\boldsymbol{k}, \boldsymbol{k}'), \quad l \neq l' \tag{6}$$

with

$$\omega_{ll'} = \varepsilon_l - \varepsilon_{l'}$$

and

$$\tau_\mu^{nn'}(\boldsymbol{k}) = \int_V w_{n\boldsymbol{k}}(\boldsymbol{r})\, \frac{\partial}{\partial R_\mu}\, w_{n'\boldsymbol{k}}(\boldsymbol{r})\, \mathrm{d}^3 r, \tag{7}$$

where $w_{n\boldsymbol{k}}$ are the periodic parts of the Bloch eigenfunction of one electron Hamiltonian.

When we combine equation (4) and (1), the expression for the electrical conductivity reduces to

$$\sigma_{\mu\nu} = \lim_{\varepsilon \to 0} \frac{e^2}{V} \int_0^\infty \mathrm{e}^{-\varepsilon t}\, \mathrm{d}t \int_0^\beta \mathrm{d}\lambda \sum_{l_1 l_1'} \sum_{l_2 l_2'} (v_\nu)_{l_1 l_1'} (v_\mu)_{l_2 l_2'} \times \\ \times \langle a_{l_1}^{+} a_{l_1'}\, a_{l_2}^{+}(t + i\lambda)\, a_{l_2'}(t + i\lambda) \rangle \tag{8}$$

within the Hartree-Fock approximation and neglecting the correlation between creation and annihilation operator, the conductivity is given by [10]

$$\sigma_{\mu\nu} = -\frac{e^2}{V}\lim_{\varepsilon\to 0}\int_0^\infty \mathrm{e}^{-\varepsilon t}\,\mathrm{d}t\int_0^\beta \mathrm{d}\lambda \sum_{l_1 l_1'}\sum_{l_2 l_2'} (v_\nu)_{l_1 l_1'}\,(v_\mu)_{l_2 l_2'}\,\times$$
$$\times \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{d}\omega_1\,\mathrm{d}\omega_2\,\frac{\mathrm{e}^{\beta\omega_2}}{(\mathrm{e}^{\beta\omega_1}+1)\,(\mathrm{e}^{\beta\omega_2}+1)}\,\mathrm{e}^{-i(\omega_1-\omega_2)\,(t+i\lambda)}\,\times$$
$$\times \left\{G_{l_2' l_1}(\omega_1+i\,\varepsilon) - G_{l_2' l_1}(\omega_1-i\,\varepsilon)\right\}\left\{G_{l_1' l_2}(\omega_2+i\,\varepsilon) - G_{l_1' l_2}(\omega_2-i\,\varepsilon)\right\}, \tag{9}$$

where $G_{l_1 l_2}(\omega)$ is the Fourier transform of the Green's function

$$G_{l_1 l_2}(t, t') = -i\,\theta\,(t-t')\,\langle\{a_{l_1}(t),\, a^{+}_{l_2}(t')\}\rangle\,, \tag{10}$$

where $\theta(t)$ is the Heaviside unit step function and curly brackets denote the anticommutator. In the present case when the electron in a crystal is described by the Hamiltonian (3), the expression for the Fourier transform of the Green's function is [8]

$$G_{l_1 l_2}(\omega) = \frac{1}{2\pi}\,\frac{\delta_{l_1 l_2}}{\omega - E_{l_1} - M_{l_1}(\omega)}\,, \tag{11}$$

where $M_{l_1}(\omega)$ gives the effect of electron–phonon interaction on the single particle energy.

If we substitute $G(\omega)$ from (11) in (9) and perform the integration over t and λ, we get

$$\sigma_{\mu\nu} = -\frac{i\,e^2}{\pi^2\,V}\left\{\sum_l (v_\nu)_{ll}\,(v_\mu)_{ll} - \sum_{\substack{l_1 l_2\\ l_1 \neq l_2}} (v_\nu)_{l_1 l_2}\,(v_\mu)_{l_2 l_1}\right\}\times$$
$$\times \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{d}\omega_1\,\mathrm{d}\omega_2\,\frac{\mathrm{e}^{\beta\omega_1}-\mathrm{e}^{\beta\omega_2}}{(\omega_1-\omega_2)^2}\,\frac{1}{(\mathrm{e}^{\beta\omega_1}+1)\,(\mathrm{e}^{\beta\omega_2}+1)}\,\times$$
$$\times \frac{\Gamma_{l_1}(\omega_1)\,\Gamma_{l_2}(\omega_2)}{\left\{(\omega_1 - E'_{l_1})^2 + \Gamma^2_{l_1}(\omega_1)\right\}\left\{(\omega_2 - E'_{l_2})^2 + \Gamma^2_{l_2}(\omega_2)\right\}}\,, \tag{12}$$

where $E_l' = E_l + \Delta_l(E_l')$; Δ_l and Γ_l are the real and imaginary parts of the $M_l(\omega)$, it can be shown that for $\nu \neq \mu$, the first term on the right hand side of equation (12) vanishes. After substituting the values of the matrix elements of the components of velocity from equation (6) in equation (12); integrating over ω_1 and ω_2 and assuming $\Gamma_l(\omega)$ a small quantity we get

$$\sigma_{\mu\nu} = -\frac{i\,e^2}{V}\sum_{l_1 l_2}\frac{\omega_{l_1 l_2}\,\omega_{l_2 l_1}}{(E'_{l_1} - E'_{l_2})^2}\,\delta(\boldsymbol{k}_1, \boldsymbol{k}_2)\,\times$$
$$\times\left[\tau_\nu^{n_2 n_1}(\boldsymbol{k}_1)\,\tau_\mu^{n_1 n_2}(\boldsymbol{k}_1) - \tau_\nu^{n_1 n_2}(\boldsymbol{k}_1)\,\tau_\mu^{n_2 n_1}(\boldsymbol{k}_1)\right] f_{l_1}\,(1 - f_{l_2})\,, \tag{13}$$

where

$$f_l = \frac{1}{\mathrm{e}^{\beta E'_l}+1}\,.$$

The expression (13) gives the transverse electrical conductivity under electron–phonon interaction. If we neglect the effect of electron–phonon interaction i.e. if we take $E_l' \approx E_l = \varepsilon_l - \mu$ we get the same expression as obtained by

Leribaux [7] in Zeroth order in electron–phonon interaction. Leribaux used the perturbation theory and diagram technique. We feel this derivation more satisfactory because it considers the contribution of electron–phonon interaction on the transverse electrical conductivity in a more complete manner. Leribaux study becomes a special case of our investigations.

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for viscosity tensor becomes

$$\eta_{ijlm}=\frac{4\pi\beta^2Mc^4}{3\omega_L\gamma^2a^2}\int_0^{k_m}dk\frac{k^2e^{\beta ck}}{(e^{\beta ck}-1)^2}(I_{ijlm}-\gamma^{ij}\gamma^{lm}),\tag{22}$$

where

$$I_{ijlm}=\frac{1}{12\pi}\int dr\sum_s\gamma_{\mathbf{k}s}{}^{ij}\gamma_{\mathbf{k}s}{}^{ml}.\tag{23}$$

For the crystals having cubic symmetry there are three independent coefficients of viscosity. For the calculation of the longitudinal and transverse attenuation we shall require only two of them. Using abbreviated notation[17] for the coefficients of viscosity and elasticity, we write

$$\eta_{11}=\frac{4\pi\beta^2Mc^4}{3\omega_L\gamma^2a^2}(I_{11}-\gamma^2)\int_0^{k_m}dk\frac{k^2e^{\beta ck}}{(e^{\beta ck}-1)^2}\tag{24}$$

and

$$\eta_{44}=\frac{4\pi\beta^2Mc^4}{3\omega_L\gamma^2a^2}I_{44}\int_0^{k_m}dk\frac{k^2e^{\beta ck}}{(e^{\beta ck}-1)^2}.\tag{25}$$

At low temperature, Eqs. (24) and (25) reduce to

$$\eta_{11}=\frac{16\pi Mk_BT}{3\gamma^2a}(I_{11}-\gamma^2),\tag{26}$$

$$\eta_{44}=\frac{16\pi Mk_BT}{3\gamma^2a}I_{44}.\tag{27}$$

ATTENUATION

The longitudinal and transverse attenuations of sound waves in a crystal having cubic symmetry are given as[18]

$$a_l=\frac{\omega^2}{2\rho c_l^3}\left(\eta_{11}+\frac{\lambda T\gamma^2}{c_l^2}\right),\tag{28}$$

$$a_t=\frac{\omega^2}{2\rho c_t^3}\eta_{44},\tag{29}$$

where ω is the frequency of the sound waves, ρ is the density of the system, λ is the thermal conductivity, and c_l, c_t are the longitudinal and transverse velocities of sound waves in the system. Now by using the calculated values of I_{11}, I_{44}, and γ obtained by Devault[9] and experimental values of the thermal conductivity, we calculate the longitudinal- and transverse-wave attenuation for Ge and Si at room temperature (300°K) from the above expressions. The results of these calculations are compared with the experimental results of Mason and Bateman[11] and the theoretical results of Devault[9] in Table I.

TABLE I. Theoretical and experimental attenuations. The numbers in parentheses are the frequencies of the sound waves in Mc/sec.

	a_l(dB/cm)	a_t(dB/cm)
Ge (calc)	2.92 (306)	0.54 (306)
Ge (Devault)	1.34 (306)	0.42 (306)
Ge (expt)	2.75 (306)	0.73 (306)
Si (calc)	2.20 (480)	0.42 (495)
Si (Devault)	1.18 (480)	0.33 (495)
Si (expt)	2.20 (480)	0.62 (495)

CONCLUSIONS

From Table I it is clear that our calculations are in very good agreement with the experimental values of the longitudinal attenuation, and that for the transverse attenuation the agreement is somewhat poorer, but still better than that of Devault's calculation. In this calculation we have not assumed that the relaxation time for longitudinal attenuation is twice that for transverse attenuation. We therefore feel that the conjecture that the relaxation time for longitudinal attenuation should be about twice that for transverse attenuation derives no support from the data considered.

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after substituting the values of H_0, J_{ij}, and $\partial\langle J_{ij}\rangle/\partial\langle H_0\rangle$ from Eqs. (5), (7), and (9), respectively, we get

$$\hat{J}_{ij}=\frac{1}{V}\sum_{ks}\omega_{ks}\gamma_{\mathbf{k}s}{}^{ij}(\langle n_{\mathbf{k}s}\rangle+\tfrac{1}{2})+\frac{\gamma^{ij}}{V}\sum_{\mathbf{k}s}\omega_{\mathbf{k}s}(n_{\mathbf{k}s}-\langle n_{\mathbf{k}s}\rangle)\cdots. \tag{11}$$

Now we use the values of J_{ij} and $\hat{J}_{ij}$ from Eqs. (7) and (11) in Eqs. (1) and get the expression for the viscosity tensor as

$$\eta_{ijlm}=\frac{\beta}{V}\lim_{\epsilon\to 0}\int_0^\infty dt\, e^{-\epsilon t}\sum_{\mathbf{k}s,\mathbf{k}'s'}\omega_{\mathbf{k}s}\omega_{k's'}\gamma_{\mathbf{k}s}{}^{ij}\times(\gamma_{k's'}{}^{lm}-\gamma^{lm})\langle n_{\mathbf{k}s}(t)(n_{\mathbf{k}'s'}-\langle n_{k's'}\rangle)\rangle\cdots. \tag{12}$$

It is evident from Eq. (12) that the evaluation of the viscosity tensor essentially involves the evaluation of the correlation function of two phonon number operators. Within the Hartree-Fock approximation this correlation function can be decoupled as[15]

$$\langle n_{ks}(t)(n_{k's'}-\langle n_{k's'}\rangle)\rangle=\langle a_{\mathbf{k}s}{}^\dagger(t)a_{\mathbf{k}'s'}\rangle\langle a_{\mathbf{k}s}(t)a_{\mathbf{k}'s'}{}^\dagger\rangle+\langle a_{ks}{}^\dagger(t)a_{k's'}{}^\dagger\rangle\langle a_{\mathbf{k}s}(t)a_{k's'}\rangle\cdots. \tag{13}$$

In most normal processes the functions $\langle a_{ks}{}^\dagger(t)a_{k's'}{}^\dagger\rangle$ and $\langle a_{ks}(t)a_{k's'}\rangle$ which depend on the correlation between two creation and two annihilation operators are negligibly small (in superconductivity[16] or superfluidity, they are no longer so negligible). Confining ourselves to the normal case and expressing the correlation functions $\langle a_{\mathbf{k}s}{}^\dagger(t)a_{\mathbf{k}'s'}\rangle$ and $\langle a_{\mathbf{k}s}(t)a_{\mathbf{k}'s'}{}^\dagger\rangle$ in terms of the Fourier transform $G_{\mathbf{k}\mathbf{k}'}{}^{ss'}(\omega)$ of the one-phonon Green function.[15]

$$G_{\mathbf{k}\mathbf{k}'}{}^{ss'}(t)=-i\theta(t)\langle[a_{\mathbf{k}s}(t),a_{\mathbf{k}'s'}{}^\dagger]\rangle, \tag{14}$$

where $\theta(t)$ is the Heaviside step function, we get the expression for the viscosity tensor as

$$\eta_{ijlm}=\frac{\beta}{V}\sum_{\mathbf{k}s,k's'}\omega_{ks}\omega_{k's'}\gamma_{ks}{}^{ij}(\gamma_{k's'}{}^{lm}-\gamma^{lm})\times\lim_{\epsilon\to 0}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_0^\infty dt\,d\omega_1 d\omega_2\frac{e^{\{\beta\omega_2+i(\omega_1-\omega_2+i\epsilon)t\}}}{(e^{\beta\omega_1}-1)(e^{\beta\omega_2}-1)}\times[G_{k'k}{}^{s's}(\omega_1+i\epsilon)-G_{k'k}{}^{s's}(\omega_1-i\epsilon)]\times[G_{kk'}{}^{ss'}(\omega_2+i\epsilon)-G_{kk'}{}^{ss'}(\omega_2-i\epsilon)]\cdots. \tag{15}$$

For the Hamiltonian (4) the expression for the Green's function $G_{\mathbf{k}\mathbf{k}'}{}^{ss'}(\omega)$ can be written as[13]

$$G_{\mathbf{k}\mathbf{k}'}{}^{ss'}(\omega)=\frac{\delta_{\mathbf{k}\mathbf{k}'}\delta_{ss'}/2\pi}{\omega-\omega_{\mathbf{k}s}-M_{\mathbf{k}s}(\omega)}, \tag{16}$$

where $M_{\mathbf{k}s}(\omega)$ gives the effect of perturbation on the self-energy of one particle. Let us define

$$M_{\mathbf{k}s}(\omega\pm i\epsilon)=\Delta_{\mathbf{k}s}(\omega)\mp i\Gamma_{\mathbf{k}s}(\omega), \tag{17}$$

where $\Delta_{\mathbf{k}s}(\omega)$ and $\Gamma_{\mathbf{k}s}(\omega)$ are the frequency shift and half-width of the phonon of wave vector $\mathbf{k}$ and polarization s. After substituting the Green's function from Eq. (16) in the viscosity expression (15), we see that the integrals over t, ω_1, and ω_2 can be easily evaluated.[7] For small values of $\Gamma_{\mathbf{k}s}$ we get

$$\eta_{ijlm}=\frac{\beta}{V}\sum_{\mathbf{k}s}\omega_{\mathbf{k}s}{}^2\gamma_{\mathbf{k}s}{}^{ij}(\gamma_{\mathbf{k}s}{}^{lm}-\gamma^{lm})\frac{e^{\beta\epsilon_{ks}}}{(e^{\beta\epsilon_{ks}}-1)^2}\times\frac{1}{2\Gamma_{\mathbf{k}s}(\epsilon_{\mathbf{k}s})}\cdots, \tag{18}$$

where

$$\epsilon_{\mathbf{k}s}=\omega_{\mathbf{k}s}+\Delta_{\mathbf{k}s}(\epsilon_{\mathbf{k}s}).$$

It can be easily shown that this expression is the same as that obtained by Devault[9] if one neglects the phonon frequency shift and takes the relaxation time as $\tau_{\mathbf{k}s}=1/2\Gamma_{\mathbf{k}s}$. In general the phonon frequency shift is very small, so we assume that $\epsilon_{\mathbf{k}s}\approx\omega_{\mathbf{k}s}$. The expression for the frequency width is given by[13]

$$\Gamma_{\mathbf{k}s}=(3\lambda_s/32\beta)(ka)^2\theta(k_m-k), \tag{19}$$

where a is the lattice constant and λ_s is a dimensionless parameter. We shall introduce one more parameter, called the Grüneisen constant, defined as

$$\gamma=\tfrac{1}{3}\sum_i\gamma^{ii}=\frac{1}{36\pi^2}\int d\Omega\sum_i\sum_s\gamma_{\mathbf{k}s}{}^{ii}. \tag{20}$$

It has been shown by Devault[9] that the Grüneisen constant for Ge and Si obtained by this expression is in quite good agreement with the experimental value obtained by the relation $\gamma=\alpha\kappa/C_v$, where α is the volume thermal expansion coefficient, κ is the bulk modulus, and C_v is the specific heat per unit volume. For this parameter we shall use Klemens's model,[14] according to which

$$\lambda_s=\frac{48\omega_{LS}}{Mc^2}\gamma^2, \tag{21}$$

where M is the mass of the atom on the lattice site and c is a suitably averaged velocity of sound waves. Now using the Debye model and replacing

$$\sum_{\mathbf{k}}\to\frac{N}{\Omega}\int k^2dkd\Omega,$$

where Ω is the volume of the first Brillouin zone and N is the total number of unit cells in the crystal, Eq. (18)

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it is easily noticed that $\langle J_{ij}\rangle=0$ if $i\neq j$. After performing the angular integration, the expression for the shear viscosity ($\eta=\eta_{ijij}$) reduces to

$$\eta=\frac{\beta}{15\pi^2m^2}\int_0^\infty dk\, k^6 e^{\beta\epsilon_k}(e^{\beta\epsilon_k}+1)^{-2}\tau_k, \qquad (14)$$

where we have assumed that $\tilde{\epsilon}_k=\epsilon_k$ and that $\tau_k=(2\Gamma_k)^{-1}$ may be identified as the relaxation time. Equation (12) can be rewritten as

$$\eta=\frac{1}{15\pi^2m^2}\int_0^\infty (2m\epsilon)^{5/2}\left(-\frac{\partial f}{\partial\epsilon}\right)\tau(\epsilon)\, d\epsilon, \qquad (15)$$

where $f=(e^{\beta(\epsilon-\mu)}+1)^{-1}$ and $\epsilon=k^2/2m$. In the low-temperature limit ($k_BT\ll\mu$), the derivative of the Fermi function can be replaced by $\delta(\epsilon-\mu)$, and we obtain

$$\eta=\tfrac{2}{5}n\mu\tau, \qquad (16)$$

where n is the number of electrons per unit volume and the relaxation time is to be evaluated at the Fermi surface. At high temperatures the Fermi function can be replaced by the Boltzman factor, and assuming that the relaxation is independent of the energy, one can obtain from Eq. (15) the usual kinetic-theory expression of the viscosity in the classical limit. The expression (16) is rigorously derived here by an entirely different method. We consider the present derivation more satisfactory.

of the electron subsystem, where $n_{\mathbf{k}}=a_{\mathbf{k}}^{\dagger}a_{\mathbf{k}}$ is the electron number operator. After substituting for the momentum flux operator $\hat{J}_{ij}$ from Eqs. (4) in (1), we obtain the expression for the viscosity tensor as

$$\eta_{ijlm}=\frac{\beta}{mV}\sum_{\mathbf{k},\mathbf{k}'}k_ik_j\left(\frac{1}{m}k_l'k_m'-V\epsilon_{k'}\frac{\partial\langle J_{lm}\rangle}{\partial\langle H_0\rangle}-V\frac{\partial\langle J_{lm}\rangle}{\partial\langle N\langle}\right)$$
$$\times\lim_{\epsilon\to 0}\int_0^{\infty}dt\,e^{-\epsilon t}\langle n_{\mathbf{k}}(t)(n_k'-\langle n_{k'}\rangle)\rangle. \quad (5)$$

It is evident from Eq. (5) that the evaluation of the viscosity tensor essentially involves the evaluation of the correlation function of two electron number operators at different times. Note the similarity of the above expression of the viscosity tensor to that of the electrical conductivity.[8] In the Hartree-Fock approximation the two-particle correlation function can be decoupled as

$$\langle n_k(t)(n_{k'})\rangle\simeq\langle a_k^{\dagger}(t)a_{k'}\rangle\langle a_k(t)a_{k'}^{\dagger}\rangle$$
$$-\langle a_k^{\dagger}(t)a_{k'}^{\dagger}\rangle\langle a_k(t)a_{k'}\rangle. \quad (6)$$

In normal metals the correlations between two annihilation and two creation operators are negligibly small, and therefore we neglect them. The other two correlation functions, $\langle a_k^{\dagger}(t)a_{k'}\rangle$ and $\langle a_k(t)a_{k'}^{\dagger}\rangle$, can be expressed in terms of the Fourier transform $G_{\mathbf{kk}'}(\omega)$ of the one-particle Green's function[9]

$$G_{\mathbf{kk}'}(t)=-i\theta(t)\langle[a_{\mathbf{k}}(t),a_{k'}^{\dagger}]_+\rangle, \quad (7)$$

where $\theta(t)$ is the Heaviside unit step function, and square brackets denote the anticommutator. After these appropriate substitutions, the result for the viscosity tensor can easily be shown to be[10]

$$\eta_{ijlm}=\frac{4\pi\beta}{mV}\sum_{\mathbf{k},\mathbf{k}'}k_ik_j\left(\frac{1}{m}k_l'k_m'-V\epsilon_{\mathbf{k}'}\frac{\partial\langle J_{lm}\rangle}{\partial\langle H_0\rangle}-V\frac{\partial\langle J_{lm}\rangle}{\partial\langle N\rangle}\right)$$
$$\times\lim_{\epsilon\to 0}\int_{-\infty}^{\infty}d\omega\,e^{\beta\omega}(e^{\beta\omega}+1)^{-2}[\mathrm{Im}G_{\mathbf{kk}'}(\omega+i\epsilon)]^2, \quad (8)$$

where Im stands for the imaginary part.

For the system of electrons in a crystal described by the Hamiltonian (3), or even more generally, the expression for the Fourier transform of the one-electron Green's function is given as[9]

$$G_{\mathbf{kk}'}(\omega)=\frac{\delta_{\mathbf{kk}'}/2\pi}{\omega-\epsilon_{\mathbf{k}}-M_{\mathbf{k}}(\omega)}, \quad (9)$$

where $M_{\mathbf{k}}(\omega)$ gives the effect of perturbation on the electron self-energy. For the present problem it is explicitly given as[9]

$$M_{\mathbf{k}}(\omega)=\sum_{\mathbf{q}}A_{\mathbf{q}}^2\left(\frac{1+\langle\nu_{\mathbf{q}}\rangle+\langle n_{\mathbf{k}-\mathbf{q}}\rangle}{\omega-\epsilon_{\mathbf{k}-\mathbf{q}}-\omega_{\mathbf{q}}}+\frac{\langle n_{\mathbf{k}-\mathbf{q}}\rangle+\langle\nu_{\mathbf{q}}\rangle}{\omega-\epsilon_{\mathbf{k}-\mathbf{q}}+\omega_{\mathbf{q}}}\right), \quad (10)$$

where $\nu_{\mathbf{q}}=b_{\mathbf{q}}^{\dagger}b_{\mathbf{q}}$ is the phonon number operator. We define $M_{\mathbf{k}}(\omega+i\epsilon)=\Delta_{\mathbf{k}}(\omega)-i\Gamma_{\mathbf{k}}(\omega)$, where the real part $\Delta_{\mathbf{k}}(\omega)$ will be again given by Eq. (10), except that now the principal value of the summation must be taken, and the imaginary part is

$$\Gamma_{\mathbf{k}}(\omega)=\pi\sum_{\mathbf{q}}A_{\mathbf{q}}^2[(1+\langle\nu_{\mathbf{q}}\rangle-\langle n_{\mathbf{k}-\mathbf{q}}\rangle)\delta(\omega-\epsilon_{\mathbf{k}-\mathbf{q}}-\omega_{\mathbf{q}})$$
$$+(\langle n_{\mathbf{k}-\mathbf{q}}\rangle+\langle\nu_{\mathbf{q}}\rangle)\delta(\omega-\epsilon_{\mathbf{k}-\mathbf{q}}+\omega_{\mathbf{q}})]. \quad (11)$$

Substituting for the imaginary part of the Green's function $G_{\mathbf{kk}'}(\omega+i\epsilon)$ from (9) into Eq. (8), we obtain the expression for the viscosity tensor as

$$\eta_{ijlm}=\frac{\beta}{mV}\sum_{\mathbf{k}}k_ik_j\left(\frac{1}{m}k_lk_m-V\epsilon_{\mathbf{k}}\frac{\partial\langle J_{lm}\rangle}{\partial\langle H_0\rangle}-V\frac{\partial\langle J_{lm}\rangle}{\partial\langle N\rangle}\right)$$
$$\times\frac{1}{\pi}\int_{-\infty}^{\infty}d\omega\,e^{\beta\omega}(e^{\beta\omega}+1)^{-2}$$
$$\times\frac{\Gamma_{\mathbf{k}}^2(\omega)}{\{[\omega-\epsilon_{\mathbf{k}}-\Delta_{\mathbf{k}}(\omega)]^2+\Gamma_{\mathbf{k}}^2(\omega)\}^2}. \quad (12)$$

Note that for small values of $\Gamma_{\mathbf{k}}(\omega)$ the integrand in (12) is peaked around the point where $\omega-\epsilon_{\mathbf{k}}-\Delta_{\mathbf{k}}(\omega)=0$. If the solution of this equation is at $\omega=\bar{\epsilon}_{\mathbf{k}}$ and electron damping $\Gamma_k(\omega)$ is small at this point, then the integral can be easily evaluated and we get

$$\eta_{ijlm}=\frac{\beta}{mV}\sum_{\mathbf{k}}k_ik_j\left(\frac{1}{m}k_lk_m-V\epsilon_{\mathbf{k}}\frac{\partial\langle J_{lm}\rangle}{\partial\langle H_0\rangle}-V\frac{\partial\langle J_{lm}\rangle}{\partial\langle N\rangle}\right)$$
$$\times\frac{\exp(\beta\bar{\epsilon}_{\mathbf{k}})}{[\exp(\beta\bar{\epsilon}_{\mathbf{k}})+1]^2}\frac{1}{2\Gamma_{\mathbf{k}}(\bar{\epsilon}_{\mathbf{k}})}. \quad (13)$$

The expression (13) is believed to be the new result of the viscosity of the electron gas in metals. This is what one would expect in the usual relaxation-time approximation provided we identify $(2\Gamma_{\mathbf{k}}(\bar{\epsilon}_{\mathbf{k}}))^{-1}$ as the relaxation time. The only difference is that here the effect of renormalization of the electron energy is also taken into account. In addition, we have derived Eq. (13) starting from correlation-function formula which is known to be more general than the usual Boltzman transport equation.

As a simple application of our general result (13), we shall now obtain the expression of the shear viscosity of the electron gas in isotropic metals. Introducing the spherical polar coordinates (k,θ,ϕ) for the wave vector $\mathbf{k}$, and replacing summation over $\mathbf{k}$ by integration as

$$\sum_{\mathbf{k}}\to\frac{2V}{(2\pi)^3}\int k^2\,dk\,\sin\theta\,d\theta\,d\phi,$$

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Shear Viscosity of the Electron Gas in Metals

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The correlation-function calculation of the shear viscosity of the electron gas in metals is presented within the Hartree-Fock approximation. The usual expressions of the viscosity obtained by using the Boltzmann transport equation are recovered in the appropriate limits.

THE absorption of ultrasonic waves in solids is attributed to various interaction processes. In the case of insulating crystals, a significant contribution to the attenuation coefficient is due to the lattice viscosity. In recent years, the phonon contributions to the viscosity of a solid have been discussed by several authors[1–4] using the correlation-function formula of McLennan.[5] In metals at low temperatures, the major contribution to the attenuation of ultrasonic waves is due to the scattering of the conduction electrons by phonons. The mechanism proposed by Mason[6] for the attenuation is based on the concept that in the normal state a lattice vibration can communicate energy to the electron gas by transfer of momentum and is damped by the viscosity of the gas. Steinberg[7] has presented the calculation of the shear viscosity of the electron gas by using the Boltzman transport equation.

In this paper, we present the correlation-function calculation of the shear viscosity of the electron gas in metals using the method of double-time temperature-dependent Green's functions. We deduce an expression for the electronic viscosity tensor within the Hartree-Fock approximation. It is found that the relaxation time appears in the expression for the viscosity in a natural way as the reciprocal of the imaginary part of the self-energy of the electrons. This result is valid at all temperatures. The usual kinetic-theory expressions of viscosity are recovered in the appropriate limits. Thus it provides an alternative derivation of the usual kinetic-theory expressions of the viscosity.

We start with the correlation-function expression for the viscosity tensor[5]

$$\eta_{ijlm}=\beta V\lim_{\epsilon\to 0}\int_0^\infty dt\, e^{-\epsilon t}\langle J_{ij}(t)(J_{lm}-\hat{J}_{lm})\rangle\,, \qquad (1)$$

where V is the volume $\beta=(k_BT)^{-1}$, k_B being the Boltzman constant and T the absolute temperature. The angular brackets denote the grand canonical ensemble average appropriate to the Hamiltonian H of the system in equilibrium, $J_{ij}(t)$ is the microscopic momentum flux operator in the Heisenberg representation, and

$$\hat{J}_{ij}=\langle J_{ij}\rangle+\frac{\partial\langle J_{ij}\rangle}{\partial\langle H\rangle}(H-\langle H\rangle)+\frac{\partial\langle J_{ij}\rangle}{\partial\langle N\rangle}(N-\langle N\rangle)\,. \qquad (2)$$

In Eq. (2), the second and third terms arise due to fluctuations in energy and total particle number N in a grand canonical ensemble. The Hamiltonian for our particular problem, that of electrons in a crystal, may be taken as

$$H=\sum_{\mathbf{k}}\epsilon_{\mathbf{k}}a_{\mathbf{k}}^\dagger a_{\mathbf{k}}+\sum_{\mathbf{q}}\omega_{\mathbf{q}}(b_{\mathbf{q}}^\dagger b_{\mathbf{q}}+\tfrac{1}{2})+\sum_{\mathbf{k},\mathbf{q}}A_{\mathbf{q}}a_{\mathbf{k}+\mathbf{q}}^\dagger a_{\mathbf{k}}(b_{\mathbf{q}}+b_{-\mathbf{q}}^\dagger)\,. \qquad (3)$$

In Eq. (3), ϵ_k is the energy of an electron in the crystal with wave vector **k**. In the free-electron approximation $\epsilon_k=k^2/2m-\mu$, where m is the electronic mass and μ is the chemical potential. $a_{\mathbf{k}}^\dagger$, $a_{\mathbf{k}}$ and $b_{\mathbf{q}}^\dagger$, $b_{\mathbf{q}}$ are the creation and annihilation operators for electrons and phonons, respectively. $A_{\mathbf{q}}$ is the electron-phonon coupling constant and $\omega_{\mathbf{q}}$ is the energy of phonon of wave vector **q**. In writing the Hamiltonian (3), we have suppressed the spin and polarization indices for electrons and phonons, respectively, and have put $\hbar=1$. It is to be pointed out that in the random-phase approximation, the electron-electron interaction can also be included in the Hamiltonian (3) simply by replacing $A_{\mathbf{q}}$ with $A_{\mathbf{q}}^{\mathrm{eff}}$. This has been discussed by one of us earlier.[8] One of the effects of electron-electron interaction is to modify the electron-phonon coupling constant. In the representation in which the one-electron Hamiltonian is diagonal, the momentum flux operator and $\hat{J}_{ij}$ are given by

$$J_{ij}=\frac{1}{mV}\sum_{\mathbf{k}}k_ik_ja_{\mathbf{k}}^\dagger a_{\mathbf{k}} \qquad (4a)$$

and

$$\hat{J}_{ij}=\langle J_{ij}\rangle+\frac{\partial\langle J_{ij}\rangle}{\partial\langle H_0\rangle}(H_0-\langle H_0\rangle)+\frac{\partial\langle J_{ij}\rangle}{\partial\langle N\rangle}(N-\langle N\rangle)\,. \qquad (4b)$$

In (4b), $H_0=\sum_{\mathbf{k}}\epsilon_{\mathbf{k}}n_{\mathbf{k}}$ is the unperturbed Hamiltonian

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cubic anharmonic momentum-flux operator and obtained an expression for the lattice viscosity and attenuation of sound waves in Ge and Si. In this calculation he has made two assumptions for the relaxation time: The first assumption is that relaxation time is independent of the phonon wave vector, and the second is that the relaxation time for longitudinal-wave attenuation should be about twice that for transverse-wave attenuation. This second assumption was also suggested by Mason and Bateman[11] and by Klemens.[12] These assumptions are not well understood theoretically. Therefore it is desirable to consider the problem without making these assumptions.

In this paper we present a correlation-function calculation of the lattice viscosity within the Hartree-Fock approximation using the cubic anharmonic momentum-flux operator obtained by Devault.[10] This expression is the same as that obtained by Devault[9] if one neglects the change in frequency due to anharmonicity. For the relaxation time we have used the expression obtained by Pathak.[13] Klemens's[14] model is used for estimating the parameter appearing in that expression. The solutions for the coefficients of viscosity at low temperature are obtained in the Debye approximation for phonons. From these solutions the attenuations of longitudinal and transverse waves for Ge and Si is calculated. In this calculation the assumptions made by Devault[9] concerning relaxation times are not made. It is found that at room temperature (300°K) the longitudinal attenuation is in very good agreement with the experimental value obtained by Mason and Bateman,[11] and the agreement for the transverse attenuation is better than obtained in the calculation of Devault.[9]

COEFFICIENTS OF VISCOSITY

We start with the correlation-function formula for the viscosity tensor[4]:

$$\eta_{ijlm}=\beta V\lim_{\epsilon\to0}\int_0^\infty dl\, e^{-\epsilon l}\langle J_{ij}(l)(J_{lm}-\hat{J}_{lm})\rangle\cdots, \quad (1)$$

where V is the volume of the crystal, $\beta=(k_BT)^{-1}$, J_{ij} denotes the microscopic momentum-flux operator for the lattice, and

$$\hat{J}_{ij}=\langle J_{ij}\rangle+\frac{\partial\langle J_{ij}\rangle}{\partial\langle H\rangle}(H-\langle H\rangle), \quad (2)$$

where H is the Hamiltonian of the system, and the angular brackets denote the canonical ensemble average, namely,

$$\langle O\rangle=\mathrm{Tr}e^{-\beta H}O/\mathrm{Tr}e^{-\beta H}. \quad (3)$$

In second-quantized form the Hamiltonian of the system can be written as

$$H=H_0+H_1, \quad (4)$$

where

$$H_0=\sum_{\mathbf{k}s}\omega_{\mathbf{k}s}(a_{\mathbf{k}s}{}^\dagger a_{\mathbf{k}s}+\tfrac{1}{2}) \quad (5)$$

and

$$H_1=\sum_{\substack{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3\\ s_1,s_2,s_3}}V^{(3)}(\mathbf{k}_1s_1,\mathbf{k}_2s_2,\mathbf{k}_3s_3)A_{\mathbf{k}_1s_1}A_{\mathbf{k}_2s_2}A_{\mathbf{k}_3s_3}+\sum_{\substack{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4\\ s_1,s_2,s_3,s_4}}V^{(4)}(\mathbf{k}_1s_1,\mathbf{k}_2s_2,\mathbf{k}_3s_3,\mathbf{k}_4s_4)\times A_{\mathbf{k}_1s_1}A_{\mathbf{k}_2s_2}A_{\mathbf{k}_3s_3}A_{\mathbf{k}_4s_4}. \quad (6)$$

Here $\omega_{\mathbf{k}s}$, $a_{\mathbf{k}s}\dagger$, $a_{\mathbf{k}s}$ are the frequency and the creation and annihilation operators for a phonon of wave vector $\mathbf{k}$ and polarization s, respectively; $V^{(3)}$ and $V^{(4)}$ are the Fourier transforms of the third- and fourth-order atomic force constants; and $A_{\mathbf{k}s}=a_{\mathbf{k}s}+a_{\mathbf{k}s}\dagger$. We have used a notation where $\hbar=1$.

An expression for cubic anharmonic momentum-flux operator is obtained by Devault[10] and is given by

$$J_{ij}=\frac{1}{V}\sum_{\mathbf{k}s}\omega_{\mathbf{k}s}(n_{\mathbf{k}s}+\tfrac{1}{2})\gamma_{\mathbf{k}s}{}^{ij}, \quad (7)$$

where $n_{\mathbf{k}s}=a_{\mathbf{k}s}{}^+a_{\mathbf{k}s}$ and $\gamma_{\mathbf{k}s}{}^{ij}$ is the generalized Grüneisen parameter, which in the long-wavelength limit is given as

$$\gamma_{ks}{}^{ij}=-e_{ks}{}^ie_{ks}{}^j-\tfrac{1}{2}\sum_{lmp}e_{\mathbf{k}s}{}^le_{\mathbf{k}s}{}^p\left(\frac{k_mk_r}{\rho\omega_{\mathbf{k}s}{}^2}\right)\times[c_{ijlmpr}+c_{ijmr}\delta_{lp}]\cdots, \quad (8)$$

where $c_{\mathbf{k}s}{}^i$ is the ith component of the polarization vector of a phonon of wave vector k and polarization s; c_{ijmr} and c_{ijlmpr} are the second- and third-order elastic constants. If we assume that the polarization vectors do not depend on the magnitude of $\mathbf{k}$, but only on the direction $\hat{k}=\mathbf{k}/k$, and that all polarization for a given $\mathbf{k}$ contribute equally to the thermal energy, then we can approximate the ensemble average of (7) by

$$\langle J_{ij}\rangle=(1/V)\langle H_0\rangle\gamma^{ij}, \quad (9)$$

where

$$\gamma^{ij}=\frac{1}{12\pi}\int d\Omega\sum_s\gamma_{\mathbf{k}s}{}^{ij}. \quad (10)$$

$\langle H_0\rangle$ is the total thermal energy of the solid, and $d\Omega$ is an element of solid angle in $\mathbf{k}$ space. In Eq. (2) for $\hat{J}_{ij}$ we approximate H by its harmonic part H_0, and

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Acoustic Attenuation in Solids

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With the help of the correlation-function formula given by McLennan, an expression for the viscosity tensor is obtained within the Hartree-Fock approximation using the cubic anharmonic momentum-flux operator. In the Debye approximation for phonons and with a simple expression for relaxation time, solutions are obtained for the coefficients of viscosity at low temperature. These solutions are used to calculate the attenuation of longitudinal and transverse sound waves at 300°K. The calculations are compared with experiment for Ge and Si, and good agreement is found.

INTRODUCTION

In solids sound waves are damped by thermal conduction and internal friction or viscosity. The correlation-function expression for the viscosity has been obtained by many authors.[1–4] Here we shall use the expression for the viscosity obtained by McLennan[4] to calculate the attenuation of sound waves in solids. In the case of insulating solids, a significant contribution to the attenuation of sound waves is due to lattice viscosity which arises from the scattering of phonons. Recently the phonon contribution to the viscosity has been discussed by several authors,[5–9] using the correlation-function formula given by McLennan. Some authors[5–8] have derived the expression for the viscosity by using the harmonic part of the momentum-flux operator, which is the central quantity in the calculation of viscosity. Devault[10] has shown that the harmonic part of the momentum-flux operator vanishes, so all the treatments given by these authors are wrong, and it is necessary to reconsider the problem using the anharmonic momentum-flux operator. Devault[9] has used the

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creation and annihilation operator, the conductivity is given by [10]

$$\sigma_{\mu\nu} = -\frac{e^2}{V}\lim_{\varepsilon\to 0}\int_0^\infty \mathrm{e}^{-\varepsilon t}\,\mathrm{d}t\int_0^\beta \mathrm{d}\lambda \sum_{l_1 l_1'}\sum_{l_2 l_2'} (v_\nu)_{l_1 l_1'}(v_\mu)_{l_2 l_2'} \times$$
$$\times \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{d}\omega_1\,\mathrm{d}\omega_2 \frac{\mathrm{e}^{\beta\omega_2}}{(\mathrm{e}^{\beta\omega_1}+1)(\mathrm{e}^{\beta\omega_2}+1)}\,\mathrm{e}^{-i(\omega_1-\omega_2)(t+i\lambda)} \times$$
$$\times \left\{G_{l_2' l_1}(\omega_1+i\varepsilon) - G_{l_2' l_1}(\omega_1-i\varepsilon)\right\}\left\{G_{l_1' l_2}(\omega_2+i\varepsilon) - G_{l_1' l_2}(\omega_2-i\varepsilon)\right\}, \tag{9}$$

where $G_{l_1 l_2}(\omega)$ is the Fourier transform of the Green's function

$$G_{l_1 l_2}(t, t') = -i\,\theta\,(t-t')\,\langle\{a_{l_1}(t), a_{l_2}^{+}(t')\}\rangle\,, \tag{10}$$

where $\theta(t)$ is the Heaviside unit step function and curly brackets denote the anticommutator. In the present case when the electron in a crystal is described by the Hamiltonian (3), the expression for the Fourier transform of the Green's function is [8]

$$G_{l_1 l_2}(\omega) = \frac{1}{2\pi}\,\frac{\delta_{l_1 l_2}}{\omega - E_{l_1} - M_{l_1}(\omega)}\,, \tag{11}$$

where $M_{l_1}(\omega)$ gives the effect of electron–phonon interaction on the single particle energy.

If we substitute $G(\omega)$ from (11) in (9) and perform the integration over t and λ, we get

$$\sigma_{\mu\nu} = -\frac{i\,e^2}{\pi^2 V}\left\{\sum_l (v_\nu)_{ll}(v_\mu)_{ll} - \sum_{\substack{l_1 l_2\\ l_1 \neq l_2}} (v_\nu)_{l_1 l_2}(v_\mu)_{l_2 l_1}\right\} \times$$
$$\times \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{d}\omega_1\,\mathrm{d}\omega_2 \frac{\mathrm{e}^{\beta\omega_1}-\mathrm{e}^{\beta\omega_2}}{(\omega_1-\omega_2)^2}\,\frac{1}{(\mathrm{e}^{\beta\omega_1}+1)(\mathrm{e}^{\beta\omega_2}+1)} \times$$
$$\times \frac{\Gamma_{l_1}(\omega_1)\,\Gamma_{l_2}(\omega_2)}{\left\{(\omega_1-E_{l_1}')^2+\Gamma_{l_1}^2(\omega_1)\right\}\left\{(\omega_2-E_{l_2}')^2+\Gamma_{l_2}^2(\omega_2)\right\}}\,, \tag{12}$$

where $E_l' = E_l + \Delta_l(E_l')$; Δ_l and Γ_l are the real and imaginary parts of the $M_l(\omega)$, it can be shown that for $\nu \neq \mu$, the first term on the right hand side of equation (12) vanishes. After substituting the values of the matrix elements of the components of velocity from equation (6) in equation (12); integrating over ω_1 and ω_2 and assuming $\Gamma_l(\omega)$ a small quantity we get

$$\sigma_{\mu\nu} = -\frac{i\,e^2}{V}\sum_{l_1 l_2}\frac{\omega_{l_1 l_2}\,\omega_{l_2 l_1}}{(E_{l_1}'-E_{l_2}')^2}\,\delta(\boldsymbol{k}_1, \boldsymbol{k}_2) \times$$
$$\times \left[\tau_\nu^{n_2 n_1}(\boldsymbol{k}_1)\,\tau_\mu^{n_1 n_2}(\boldsymbol{k}_1) - \tau_\nu^{n_1 n_2}(\boldsymbol{k}_1)\,\tau_\mu^{n_2 n_1}(\boldsymbol{k}_1)\right] f_{l_1}\,(1-f_{l_2})\,, \tag{13}$$

where

$$f_l = \frac{1}{\mathrm{e}^{\beta E_l'}+1}\,.$$

The expression (13) gives the transverse electrical conductivity under electron–phonon interaction. If we neglect the effect of electron–phonon interaction i.e. if we take $E_l' \approx E_l = \varepsilon_l - \mu$ we get the same expression as obtained by

Leribaux [7] in Zeroth order in electron–phonon interaction. Leribaux used the perturbation theory and diagram technique. We feel this derivation more satisfactory because it considers the contribution of electron–phonon interaction on the transverse electrical conductivity in a more complete manner. Leribaux study becomes a special case of our investigations.

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quite different method. Thus we conclude that the eq. (6) is a very useful expression for estimating the shear viscosity of solids at high temperatures.

Recently Gluck [5] has also used the anharmonic model proposed by one of us [3] to estimate the shear viscosity of rare gas crystals.

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SHEAR VISCOSITY OF INSULATING SOLIDS

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A simple force model calculation of the shear viscosity of insulating solids is presented within the Hartree Fock approximation. It gives a very good estimate of the shear viscosity at high temperatures.

Recently Rice [1] has discussed the shear viscosity of insulating crystals using the correlation function formula of Mclennan. After making some approximations Rice obtained the expression for the viscosity tensor in terms of the correlation function of two number density operators. It is evident from eq. (2.7) of Rice that the evaluation of viscosity tensor essentially involves the evaluation of correlation function of two number density operators. In this respect it is very similar to the calculation of the lattice thermal conductivity.

Following the analysis of Deo and Behera [2] one can express the viscosity tensor in terms of the Fourier transforms of the one phonon Green function

$$\mathrm{G}_{\boldsymbol{kk}'}^{ss'}(t) = -\mathrm{i}\,\theta(t)\,\langle[a_{\boldsymbol{k}s}(t),\ a_{\boldsymbol{k}'s'}(0)]\rangle \tag{1}$$

For the anharmonic crystals [3] the expression for the Green function can easily be obtained and finally one gets the relaxation time expression for the viscosity tensor as

$$\eta_{ijlm} = \frac{(k_\mathrm{B}T)^{-1}}{4\Omega}\sum_{\boldsymbol{k}s}\omega_{\boldsymbol{k}s}^{2}\,e_i(\boldsymbol{k}s)\,e_j(\boldsymbol{k}s)\times \left(e_l(\boldsymbol{k}s)\,e_m(\boldsymbol{k}s)-2\Omega\frac{\partial\langle J_{lm}^{\mathrm{o}}\rangle}{\partial\langle H^{\mathrm{o}}\rangle}\right)\frac{\exp(\epsilon_{\boldsymbol{k}s}/k_\mathrm{B}T)}{\{\exp(\epsilon_{\boldsymbol{k}s}/k_\mathrm{B}T)-1\}^2\,\Gamma_{\boldsymbol{k}s}} \tag{2}$$

where $\epsilon_{\boldsymbol{k}s}$ and $\Gamma_{\boldsymbol{k}s}$ are the renormalized phonon frequency and half width respectively. Here and in what follows we use the notation of Rice.

In ref. 3 we have evaluated the phonon frequency shift and width for a very simple anharmonic model of solids. To relate the viscosity to the interatomic forces in solids and make an explicite calculation, we here choose the anharmonic coupling parameters given by Leibfried and Schlomann [4] for a nearest neighbour central force model. After comparing this model to eq. (56) of ref. 3 we get

$$\lambda_j/\omega_{Lj} = \delta^2/36\gamma^3 \qquad (3$$

where γ and δ are the harmonic and cubic force constants respectively. Substituting this value of λ_j/ω_{Lj} we obtain from eq. (59) of ref. 3

$$\Gamma_{\boldsymbol{k}s} = \delta^2 k_\mathrm{B}T\,(ka)^2\omega_{Ls}\,\theta\,(k_m - k)/384\gamma^3 \tag{4}$$

We now evaluate the viscosity tensor for an isotropic solid using $\epsilon_{ks} = \epsilon_{Ls}\sin\frac{1}{2}\pi ka$ and eq. (4). It is clear from the analysis of ref. 3 that we can write $\epsilon_{Ls} = \omega_{Ls}(1+AT)$, where the coefficient A essentially involves the anharmonic parameters. We thus obtain for the shear viscosity at high temperatures as

$$\eta = \frac{52}{5\pi^2}\,\frac{\gamma^3}{\delta^2 a^2}\,\frac{\omega_L}{\epsilon_L{}^2}\,k_{\mathrm{max}}. \tag{5}$$

This can be written as

$$\eta = \frac{26}{5\pi}\,\frac{\gamma^3}{\delta^2 a^2}\,\frac{1}{v}\,(1 - 2AT) \tag{6}$$

where v is the sound velocity. This is a very important result. It relates the shear viscosity to the atomic force constants. Therefore, experimental study of acoustic attenuation in solids will be useful to understand the interatomic forces in solids. The conclusion of Rice [1] that the shear viscosity is independent of temperature at high temperatures is not quite correct, if one takes into account the effect of phonon frequency shift.

We estimate the values of shear viscosity of solids taking a Morse potential. Using the sublimation energy data to evaluate the Morse parameter, we obtain from eq. (6) for gold the value of the shear viscosity about 2 millipoise. This value is the same as reported by Rice [1] by a