I. STATISTICAL MECHANICS OF THE HALF - FILLED BAND HUBBARD MODEL II. RANDOM EXCHANGE ISING CHAINS

Dissertation for the Degree of Ph. D. MICHIGAN STATE UNIVERSITY DARIO CABIB 1973

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This is to certify that the

thesis entitled I. STATISTICAL MECHANICS OF THE HALF-FILLED BAND HUBBARD MODEL

I, RANDOM EXCHANGE ISING CHAINS

presented by

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has been accepted towards fulfillment of the requirements for

Ph. D. degree in Physics

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Major professor

Date 3/3/1973

O-7639



ABSTRACT

I. STATISTICAL MECHANICS OF THE HALF-FILLED BAND HUBBARD MODEL II. RANDOM EXCHANGE ISING CHAINS

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The two main subjects of this thesis, unrelated as they may seem, can be regarded from a general theoretical point of view as being two different aspects of the same branch of Physics. This branch of Physics studies the properties of systems consisting of interacting particles at finite temperature. Both parts of the thesis are essentially studies of theoretical models for interacting particles, and in both the general methods and concepts of Statistical Mechanics are used.

Part A is a study of the Half-Filled-Band Hubbard model. In the introductory chapter we make comment on the history and derivation of the model, we mention the various exact results existing in the literature and we outline the properties of some organic solids that have been recently related to the Hubbard model. In the following chapter we



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present the exact results obtained for the four-atom ring: these results are interpreted physically, and used to resolve serious discrepancies existing in the literature; furthermore an attempt is made to extrapolate these results to an infinite one-dimensional system and contact is made with recent experiments on the organic solid N-methyl phenazinium tetracyanoquinodimethan (NMP-TCNQ). The results obtained for the susceptibility show that the Half-Filled-Band Hubbard model is deficient as to the explanation of these experiments. We tried to improve the theory in various ways but our efforts were not completely satisfactory: we show that although one can quantitatively fit the experimental paramagnetic susceptibility of NMP-TCNQ using a temperature dependent Hubbard model, there is still a lack of understanding of the physical mechanisms responsible for the behavior of such a system. We then describe a hightemperature expansion of the Half-Filled-Band Hubbard hamiltonian, which is valid in the case of small interaction between the electrons compared to the temperature; we give the result for the susceptibility in first order of the ratio interaction/temperature. In the final chapter of Part A we explain and correct a serious error occurring in the literature involving a calculation of the zero frequency conductivity in the single band Hubbard model. We point out the subtleties involved in the symmetry properties of the



current operator as defined with a model hamiltonian such as the Hubbard hamiltonian, and explain how the lack of understanding of these subtleties were the cause of the above mentioned error.

Part B is a study of the Ising model with random exchange interactions. One strong motivation for this work is to understand the effects of the randomness of the interactions on the critical behavior at finite temperature. Our calculations refer only to one-dimensional systems; from the analysis of the low-temperature behavior of such systems we get some insight on the critical behavior of systems which display phase transitions at finite temperature. We describe extensively this low-temperature behavior, especially as a function of different distributions of the exchange parameters. Finally the effect of a random highly anisotropic Heisenberg interaction at low and high temperature is studied. The results are compared with the periodic Ising chain. I. STATISTICAL MECHANICS OF THE HALF-FILLED BAND HUBBARD MODEL

II. RANDOM EXCHANGE ISING CHAINS

Bу

Dario Cabib

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Physics

ACKNOWLEDGMENTS

It is a great pleasure to express my gratitude to Professor T. A. Kaplan for having given me the opportunity to collaborate closely with him in physics research. This collaboration has been a continuous stimulation for me to learn, especially because of Professor Kaplan's deep insight into the problems of concern and his way of enjoying teaching and doing science. This thesis would not have been possible without his continuous friendship, his time and effort.

I am very grateful to Professor S. D. Mahanti for suggesting the problem discussed in the second part of this thesis and for close collaboration in carrying it through. It has been very exciting to interact with him and to enjoy his friendship throughout my program.

I am greatly indebted to Professor T. O. Woodruff and the Physics Department of Michigan State University for providing me with a research assistantship, and the Commission for Cultural Exchanges between Italy and the U.S.A. for providing me with a Fulbright Travel Grant.

I thank Dr. R. A. Bari for helpful discussions in connection with Section AII.2 and Chapter AIII, and Dr. Jill Bonner for helpful suggestions in connection with Chapter BI.

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PART A



PART A

CHAPTER I

INTRODUCTION

1. <u>Preliminaries and Definition</u> of the Model

One of the fundamental problems in Solid State Physics is to solve the equation of motion for an arbitrary number of electrons and nuclei interacting via Coulomb forces. This problem is so extremely difficult in the general case that it has been solved analytically only in the case of one nucleus interacting with one electron (the hydrogen atom). As the number of particles increases, the difficulties rise rapidly and when the collection of particles is a macroscopic system, a detailed solution to the Schrödinger equation, with all the interactions, is out of the question.

On the other hand much of the information about the behavior of systems of electrons and nuclei can be attained by the use of general theorems and of different approximations, valid in different physical situations. In many cases these approximations or theories (one may regard the development of a theory as being an attempt to understand nature through a simplified, and therefore approximate, picture) give an accurate account of physical phenomena; therefore one is often confronted with the problem of understanding the features of a theory and the phenomena that it predicts, to be able to make contact with experimental findings. The way one usually does this is to choose on semi-qualitative grounds a simplified Hamiltonian, and



study its properties exactly, if possible, or approximately, otherwise; the results are then compared with experiments. It is in this spirit that Hubbard proposed¹ his Hamiltonian in 1963. Similar to other contemporary work.² Hubbard was concerned with the study of correlated electrons in solids; his goal was to account for the effects of correlations in narrow bands and he suggested that his theory be applied to d-electrons in transition metals. As we shall see in Section AI.4, some authors³ proposed that this theory be applied also to some organic solids; furthermore it has been claimed⁴ that this or very similar theories can account for the physics of the benzene ring and of a vast number of magnetic insulators,⁵ usually thought of as being described by the Heisenberg Hamiltonian (at the end of Section AI.3 we will mention the relationship between the Heisenberg and the Hubbard Hamiltonian).

Let us now focus upon the description of Hubbard's model and its properties. It is well known that in a crystal the energy levels of the electrons are grouped in bands. Throughout this work we will restrict ourselves to the case of a crystal of N atoms and an average of N electrons, filling exactly half of one non-degenerate band; we will disregard the presence of all the other bands. (To do so we construct a so called projected Hamiltonian, where part of the full Hamiltonian matrix is completely ignored.) We define an orthonormal complete set of N Wannier functions

for this band; the Wannier functions are localized at the lattice sites i.e. each of them is appreciably different from zero only in the neighborhood of a lattice site, and can be occupied by a maximum number of two electrons, allowing for the spin degeneracy. The theory will not depend on the detailed functional form of the Wannier functions, and we will therefore leave them completely general. We then define operators $c_{i\sigma}^+$ and $c_{i\sigma}$ which respectively create and destroy an electron in the Wannier function at site i with spin projection σ . The $c_{j\sigma}^+$'s and $c_{i\sigma}$'s satisfy the usual fermion anticommutation relations and $n_{i\sigma}=c_{i\sigma}^+c_{i\sigma}$ is the number operator of site i and spin σ . The Hubbard Hamiltonian is written in terms of these operators as

$$H = \sum_{ij\sigma} b_{ij} (c_{i\sigma}^{\dagger} c_{j\sigma}^{\dagger} c_{j\sigma}^{\dagger} c_{i\sigma}) + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$
(1)

The b_{ij} 's and U are constant parameters and have precise physical meanings. For simplicity we will always consider the case b_{ij} =b for i and j nearest neighbors, and zero otherwise. b is often called the transfer or hopping integral. The first summation in (1) is a noninteracting electron term that can be written, in the basis of the Bloch functions, as

$$\frac{\Sigma}{\underline{k}\sigma} \stackrel{\alpha}{\underline{k}} \stackrel{n}{\underline{k}\sigma}$$
(2)

nkg are defined as

$$n_{\underline{k}\sigma} = a_{\underline{k}\sigma}^{\dagger} a_{\underline{k}\sigma}$$
(3)

where $a_{\underline{k}\sigma}^{+}$ and $a_{\underline{k}\sigma}^{-}$ are respectively the creation and annihilation operators for an electron in the Bloch function with crystal momentum \underline{k} and spin σ . $a_{\underline{k}\sigma}^{+}$ is related to the Wannier functions creation operators by

$$a_{\underline{k}\sigma}^{+} = N^{-1/2} \sum_{m} e^{i\underline{k} \cdot \underline{R}}_{m} c_{m\sigma}^{+}$$
(4)

 $\varepsilon_{\underline{k}}$ are the one-electron energies of the band in question, whose width is proportional to b; in general

 $\varepsilon_{\underline{k}} = \sum_{j} b_{ij} e^{i\underline{k}\cdot\underline{R}}ij$ (5)

 $(\underline{R}_{ij}$ is the position vector between sites i and j) . In one dimension, for instance, ε_{ν} = 2bcosk.

The second summation in (1) is the interaction term: when two electrons with opposite spins occupy the same site (the exclusion principle forbids two electrons with the same spin to occupy the same site) they repel each other with an energy U. They do not interact if they are on different sites.

Hubbard gave a derivation of the Hamiltonian that took his name and studied it in different approximations: the Hartree-Fock approximation,¹ a Green function decoupling procedure¹ (Hubbard I), and a second approximate solution⁶ (Hubbard III), which improved Hubbard I.



Since then the Hubbard Hamiltonian has been of great theoretical interest. There are some exact results, 7-12but in the general case $b, U \neq 0$ at finite temperature T $\neq 0$ they refer only to small one-dimensional systems; the ground state and some of the low lying states have been calculated for infinite chains. The approximate calculations are usually based on Green function decoupling schemes 1,6,13,14 which do not give criteria for the estimates of the errors involved and sometimes¹⁴ are wrong in the limiting case $b_{ii}/U \rightarrow 0$; these difficulties were overcome in part by T. A. Kaplan and R. A. Bari¹⁵ with the TSDA. (The TSDA is a variational approximation due to T. A. Kaplan¹⁶ and discussed in some detail by Kaplan and Argyres.¹⁷) Finally the derivation of the Hamiltonian itself given by Hubbard has been recently criticized¹⁸ and an attempt is being made to improve that derivation.

The fundamental question which arises is: why study such a model, since it appears to be only a crude approximation to reality. This is so because, as we explained before, we take into account only one band and the intrasite Coulomb repulsion: the presence of other bands and the long range of the Coulomb interaction may be nonnegligible. To try to answer this question let us briefly examine the two cases b/U<<1. U/b<<1.



Originally equation (1) was derived in the case of narrow band electrons; in this case the transfer integral b (and therefore the bandwidth) is small in comparison to U. and the lattice sites are quite distant from each other: it is intuitive therefore that two electrons on the same site repel each other with a force much greater than when they are located at different sites. This allows us to disregard the intersite repulsions. (It is worthwhile to note here that when b=0, the Hamiltonian describes a system of isolated atoms.) In the other extreme case when b>>U the Hamiltonian (1) may seem unrealistic not only because the repulsion between electrons on different sites becomes important, but also because other bands may start to come into play. On the other hand screening effects may reduce the inter- and intra-atomic interactions appreciably making it conceivable that (1) is still in some cases a good description of reality. In the present work our approach has been to study the Hamiltonian (1) from a phenomenological point of view: in other words we have been interested in the features of the theory as functions of the parameters b and U. This means also that we have not worried about the derivation of the Hamiltonian and its validity for the different physical situations, and the different values of the parameters b and U. Both cases b>>U and b<<U are very interesting: the first describes the situation of weakly interacting electrons in a band; the understanding of such



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a system is a fundamental theoretical problem not yet fully solved; the second, better understood in many respects, as we shall mention in the next Section, is equivalent to the Heisenberg model at low temperatures. In the rest of this Chapter we will discuss some aspects of the Hubbard model, such as the atomic limit and exact results; at the end we will review some of the most recent experiments related to the Hubbard model.

2. The Atomic Limit

It is worthwhile to focus our attention upon the "atomic limit" i.e. the case in which b=0, because it is an example of a problem with arbitrary number of strongly interacting particles that is very easily solved. Furthermore there have been theoretical works where this simplicity had not been recognized.

The Hamiltonian (1) reduces to

$$H = U \sum_{i} n_{i\uparrow\uparrow} n_{i\downarrow}$$
(6)

It was pointed out by Kaplan¹⁶ that a complete set of eigenstates of (6) are all the possible Slater determinants with Wannier functions occupied. The energy eigenvalues¹⁹ for a given eigenstate is given by U times the number of double occupancies in that state. The ground state (for half-filled band) has each site occupied by one electron, and it is degenerate 2^{N} times if N is the total number of



atoms. The total partition function Z in the Grand Canonical Ensemble is a product of identical partition functions ζ for each site: Z = ζ^N . ζ is obtained as a sum of exponential factors on the four states corresponding to $(n_{i\uparrow}, n_{i\downarrow}) =$ (0,0), (0,1), (1,0), (1,1), and is given by:

$$\zeta = 1 + 2e^{\beta\mu} \cosh(g\mu_{\rm R}/2H) + e^{-\beta(U-2\mu)}$$
 (7)

where: $\beta = 1/kT$, μ is the chemical potential, H is an external magnetic field acting on the spin magnetic moment only, g and μ_B are the g-factor of the electron and the Bohr magneton. In the case of the half-filled band μ is easily proved to be equal to U/2 and independent of temperature. Equation (7) was first given by Kaplan and Argyres, ¹⁷ with H=0.

The specific heat C and the susceptibility χ are easily obtained by the appropriate differentiations of Z. C/NT has a δ function singularity at T=0 to account for the degeneracy of the ground state, and has a broad peak with a maximum at a temperature of the order of U: the latter corresponds to the entropy gain in allowing for double occupancies when kT is of the order of the intraatomic repulsion energy. The spin susceptibility χ shows a 1//2 Bohr magneton Curie-Weiss behavior at high temperature (kT>>U) and a one Bohr magneton Curie law at very low kT<<U. The positive intercept of χ^{-1} does not denote forromagnetic



ordering (the sites are not correlated) but is due to the change in the local moment $<S_{iz}^2$ brought about by the formation of double occupancies when kT \simeq U. This discussion has been given by Kaplan.¹⁹ The local moment is never zero,²⁰ even when T $\leftrightarrow \infty$ because there is always a finite probability (\geq 1/2) to find singly occupied sites.

To complete this section, we mention that for $b\neq 0$ but satisfying b/U<<1, it is possible to show in perturbation theorv²¹ that the low lying energy levels of the Hubbard Hamiltonian are the same as those of the Heisenberg Hamiltonian (defined as $-J \sum_{\substack{i \ i > j}} \sum_{j < i} \cdot S_j$, i and j are nearest neighbor sites, \underline{S}_i is the spin at site i, J is the exchange integral) with antiferromagnetic $J = -2b^2/U$. Extensive work has been carried out at finite temperature in this range of the parameters, more or less successfully, and the physics is now quite well understood. For instance the work by Kaplan and Bari^{15,22} has been fundamental: both the exact results at b=0 for any T, and the mentioned Heisenberglike behavior at low T are necessary in the description of the model and its properties for b<<U. This field is very fertile in physical phenomena: it includes spin wave effects. second order phase transitions (Néel point) and therefore critical phenomena. The work on the Ising model that we describe in Part B of this thesis is also included in this field. In fact if we take into account spin orbit effects in the perturbation theory mentioned above to derive the


Heisenberg Hamiltonian from the Hubbard Hamiltonian, we would introduce an anisotropy. The Ising model is obtained in the extreme case of infinite anisotropy.

3. Exact Calculations

A brief summary of the existing exact results is useful and appropriate here, since most of the present work is concerned with exact calculations.

Unfortunately they are limited to few cases: this is so because they are very difficult to obtain; in fact the Hubbard Hamiltonian is more complex than the Heisenberg Hamiltonian (for example the first is a $2^{2N}x2^{2N}$ matrix whereas the second is a $2^{N}x2^{N}$ matrix), and the latter has been solved exactly only at zero temperature in the case of infinite one-dimensional lattice.

The ground state energy, wave function and chemical potential of an infinite chain have been obtained by Lieb and Wu⁷ (LW) in the half-filled band. They have used a method similar to the one used for the solution of the Heisenberg chain, and of the one-dimensional fermion gas with δ -function interactions,²³ they give a set of integral equations to be solved simultaneously for the lowest energy eigenvalue corresponding to a fixed value of the total spin projection S_z. The solution was given explicitly for the absolute ground state, which has S_z=0. It is interesting to note that this ground state need not be antiferromagnetic in general: as a matter of fact when



U=O it is not antiferromagnetically ordered and it is plausible that the same holds when b>>U; on the other hand when b<<U, we expect the system to behave similar to the Heisenberg chain (antiferromagnetic): to the extent that the Heisenberg ground state is believed to be antiferromagnetically ordered so it is Hubbard's (for b<<U). There are arguments in support of this belief (such as the symmetry of the spin waves), but there is no rigorous calculation of $<\underline{S_i}\cdot\underline{S_j}>$, as far as we know, which would clearly show the kind of order.

Finally, with the help of the chemical potential LW have argued that at any finite U at T=O the system is insulating and is conducting only at U=O or away from the halffilled band.

LW's work⁷ was the starting point of subsequent exact calculations at T=0, and for this it was of great fundamental importance. In fact, using LW's method and results Ovchinnikov⁹ calculated the spectrum of the lowest excitations with total spin 0 and 1 and Takahashi⁸ obtained the magnetization and the zero-field susceptibility (both works refer to the half-filled-band case). Shiba¹² extended LW's and Takahashi's calculations to arbitrary number of electrons (not necessarily half-filled band). Griffiths' work²⁴ on the magnetization and susceptibility of the infinite antiferromagnetic Heisenberg chain was also used by Takahashi⁸ and Shiba¹²; therefore it appears that the



same problems of rigor pointed out by Griffiths²⁴ apply to Takahashi's and Shiba's work as well (the lack of rigor is in the characterization of the lowest energy levels for a given total S_z , although there may be very plausible arguments in support of the assumptions made).

The papers by Shiba and Pincus¹⁰ uses a different approach: they diagonalize by computer the Hamiltonian (1) for chains and rings of up to N=6 atoms, and then they compute the thermodynamics in the Canonical¹⁰ Ensemble. As reported in Chapter II this is essentially our approach; our calculations were carried out (both in the Canonical and Grand Canonical Ensemble) simultaneously with and independently of Shiba and Pincus' and concerned rings of four atoms. After our work was presented (Magnetism Conference, Nov. 1972), further work within the same approach appeared.¹¹ For more extensive discussion of the motivations, the checks of the computer program, presentation and interpretation of the results and further references we refer here to Section AII.1.

<u>N-methyl Phenazinium Tetracyanoquinodimethan</u> (NMP-TCNQ)

An extensive and detailed description of the systems that will be the subject of the present Section can be found in the works by Fritchie,²⁵ Epstein <u>et al.</u>,³ Shchegolev²⁶ and Heeger and Garito.²⁷ We report here some of the properties of the TCNQ organic solids (especially of the NMP-TCNQ)

because the experiments on NMP-TCNQ have been closely related 3,27 to the recent theoretical studies of the Hubbard model.

There is a class of so-called "organic charge transfer salts" that are characterized by interesting features. First of all they are organic solids composed of two types of molecules, a donor and an acceptor giving rise to the presence of unpaired electrons in the crystal. These unpaired electrons are generally thought³ to be responsible for the magnetic and electric properties of the system (due to the nature of the molecular orbital involved), along with the crystal structure of each solid. Second these salts are highly anisotropic, displaying a very pronounced one-dimensional behavior, the unpaired electrons moving along the chains made up of the acceptor molecules. (The effect of other bands is usually considered negligible.³) The one-dimensionality is clearly displayed by the conductivity measurements by Shchegolev.²⁶ The anion in these salts is the TCNQ molecule, a planar molecule of the form:



Figure AI.1.--TCNQ molecule.



it is capable of combining with other melecules that play the role of cation. The negative charge resides in the lowest π level and is localized near the cyanide groups, because of their strong electron affinity.³ In particular TCNQ can combine with the NMP molecule of the form:



Figure AI.2. -- NMP Molecule.

in this cation the positive charge resides on the nitrogen and carbon atoms involved in the bond between the methyl group and the phenazinium, and all the electrons of the cation are paired. Furthermore the methyl group can be bound to either N at random so that there is also a randomness in the position of the positive charge. Both NMP and TCNQ form alternating chains of stacking blanar molecules as shown in the following schematic figure:

TCNQ chain→ NMP chain→ TCNQ chain→ (a

TCNQ chain→ () () NMP chain→ () () TCNQ chain

U ' (

Figure AI.3.--Chains of stacking planar NMP-TCNQ molecules: (a) side view of the chains; (b) front view of the chains.



As seen in Figure AI.3(a) they stack face to face to each other and the interplanar distance is roughly 3.3 Å; in (b) the distance between TCNQ's is roughly 7.8 Å. This picture shows that the TCNQ chains are far apart and it is reasonable to think of the electrons as bound to move in one dimension. Each TCNQ can accommodate two extra electrons with opposite spin assuming that it has associated with it one spatial wave function, but the total number of these electrons is equal to the number of TCNQ molecules so that the band in which the electrons move is half filled. Certainly the electrons in the band interact via Coulomb forces, and this complicates the physics of this one-dimensional electron gas, even if we neglect the interactions with the phonons and with the highly polarizable NMP molecules.

The experimental measurements^{3,26} refer to lowtemperature specific heat, up to about 20 degrees Kelvin, d.c. conductivity and spin susceptibility up to about 400 degrees K (above which the substance melts) and electric permeability.

Epstein <u>et al.</u>³ tried to interpret their experimental results with the Hubbard model. The few exact theoretical results existing at zero temperature⁸ and a calculation of Hubbard's gap based on Ovchinnikov's excitation spectrum⁹ were the theoretical basis for establishing the values of U and b appropriate to the NMP-TCNQ. In



Sections AII.1 and AII.2 we show the serious difficulties this approach runs into.

Later Heeger and Garito²⁷ tried to change the theoretical picture allowing for the parameters b and U to vary with temperature; this was done to better account for their experimental data. In Sections AII.3 and AII.4 we will discuss this aspect of the problem in greater detail.



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PART A

CHAPTER II

STATISTICAL MECHANICS OF THE HALF-FILLED-BAND

HUBBARD MODEL

Statistical Mechanics of the Half-Filled Band Hubbard Model (Phys. Rev. B7, 2199 (1973), with T. A. Kaplan).



PHYSICAL REVIEW B

VOLUME 7, NUMBER 5

1 MARCH 1973

Statistical Mechanics of the Half-Filled-Band Hubbard Model

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We have calculated thermodynamic properties of the half-filled-band Hubbard model for a ring of N-4 atoms. Our results resolve serious discregnancies between similar calculations which have appeared. For weak interactions, a new kind of smooth magnetic transition (nonantiferromagnetic) is found at low temperature. For strong interactions, properties are approximately independent of N when the grand canonical ensemble is used, enabling contact to be made with recent experimental work on N-methyl phenazimium tetracyanoputcodimethan (NMP/ITCNQ); the comparison suggests strongly that the Hubbard model is seriously deficient as a means of description of these experiments.

There has been considerable interest recently1-3 in the Hubbard model for electrons in a half-filled band. Since exact results are extremely limited. particularly in the intermediate temperature range and for bandwidth b of the order of the Coulomb interaction U, we began a study of exact numerical solutions for small numbers of atoms. Since that time three papers4-6 have appeared giving results of similar calculations. Their results disagree with each other in several important qualitative respects: in the region of large b/U one group⁴ (SP) found one peak in the specific -heat-vs-temperature curve, the other group5,6 (HM) finding three peaks: for $b/U \simeq 1$, the groups again disagree as to the number of peaks found. (These statements concern the four-atom ring, the only case common to both groups.)

Here we resolve these important theoretical discrepancies. We agree with the number of specificheat peaks found by HM; however, numerical comparison is not possible because of inconsistencies in their results. We also disagree with their interpretation of these peaks and find instead a new kind of smooth magnetic transition. Further, the extrapolation to large systems as to the existence of the low-temperature peaks for large b/U is shown to be not possible on the basis of the fouratom results in disagreement with HM: whenever one-half the number of atoms is even, we show that there is a low-T peak for large b/U which does not scale with the size of the system. The behavior for small b/U does not appear to be spurious in relation to macroscopic systems, and we therefore carefully examined the susceptibility to compare with recent experimental results.7 Whereas the previous calculations were made using the canonical ensemble, we have also made calculations in the grand canonical ensemble, as motivated below.

We consider a system of four atoms at the cor-

TABLE I. Comparison of results with high-temperature expansion.

β	$U - \langle H \rangle$	$\frac{1}{2}U^2 \ \beta = U + \left< H \right>$	$ L_1 /\beta^2$
25×10 ⁻³	0.19987512	1.2×10^{-4}	0.12700320
25×10^{-4}	0.01999988	1.2×10^{-7}	0.125 207 55
25×10^{-5}	0.00200000	1.2×10^{-10}	0.12502078

ners of a square. As usual the Hubbard Hamiltonian is written

$$H = \sum_{ij\sigma} b_{ij} c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_{i} N_{i}, N_{i}. \qquad (1)$$

We include only nearest-neighbor hoppings (b_{ij} = b when i and j are nearest neighbors). Unless specified otherwise, b = 1. All energy eigenvalues and eigenfunctions are calculated numerically for several values of D_j from these the statistical average of any operator O (expressed as a function of the creation and destruction operators c_{is}^{\dagger} and c_{pl} , can be calculated either in the grand canonical or canonical ensemble (GCE or CE) according to the equation

$$\langle O \rangle = \frac{\operatorname{Tr} O e^{-\beta(H-\mu N_e)}}{\operatorname{Tr} e^{-\beta(H-\mu N_e)}},$$
 (2)

where $\beta = 1/kT$, $\mu = chemical potential$. The trace runs over all states in the GCE, and only over states with fixed number of particles N_e in the CE. It turns out that for the half-filled band $\langle\langle N_{\mu} \rangle = num$ ber of atoms) $\mu = \frac{1}{2}U$ independent of T.

The motivation for calculating in both the GCE and the CE is twofold. One point is that in the atomic limit (b/U-0), any intensive parameter (e,g., the free energy per atom) is independent of the number of atoms N when calculated in the GCEs. Therefore the GCE for small N can be expected to give results close to those for $N- \propto$ for small b/U. The other point is that, since all results for CE and GCE become the same for $N- \sim$, any qualitative feature that we may discover for small N will be considered suggestive as to the large-N behavior only if such a feature occurs both in CE and in GCE.

The checks of our computer program are: (i) At high temperatures for all U we expanded the exponentials in (2) in powers of β retaining only terms of the first few orders in β . We compare the numerical results with the expansion coefficients. For instance we have computed the following quantities for U = 4 in the GCE:

$$(H) = U - \frac{1}{2}\beta U^2 + O(\beta^2)$$
, (3)

$$L_1 = -\frac{1}{8}\beta^2 + O(\beta^3), \qquad (4)$$

where $L_{\mu} = (\langle N_i + *K_i \rangle \langle N_i + _{\mu \pi} - *V_i + _{\mu} \rangle)$. (Because of symmetry, L_{μ} is independent of *i*.) The numerical results are given in Table I. We see that $U - \langle H \rangle$ is about $\beta\beta$ and that $\frac{1}{2} U^2\beta - U + \langle H \rangle$ is of order β^2 or higher; similarly $|L_1|/\beta^2$ is about $\frac{1}{8}$ and $-|L_1|/\beta^2$ is about $\frac{1}{8}$ and $-|L_1|/\beta^2$.

(ii) In the two cases $\tilde{U}=0$ and $U=\infty$, the various $\langle O \rangle$ were again calculated analytically⁴ in GCE and compared with the numerical results. There is agreement in at least the first eight figures,

(iii) In the case of large U and low T we checked the magnetic susceptibility against the results of



FIG. 1. Specific heat C and spin-spin correlation functions L_n vs temperature in the GCE. (a) U=8; (b) U=0.7.





FIG. 2. Temperature at which the specific-heat maxima occur vs U are shown by the continuous lines. The dashed lines labeled by numbers n show the temperatures near which anomalies in L_n occur.

Bonner and Fisher⁶ for the Heisenberg model which is expected to reproduce the behavior of the Hubbard model under these conditions when the exchange constant $J = -2b^2/U$. We find convergence with increasing U of our peak location and height to within about 12 and 6%, respectively, by the time U=15.

The specific-heat vs T is shown in Fig. 1 for U=8 and 0.7 for the GCE. In qualitative agreement with HM we find three peaks in the specific heat at least for 0.02 \pm 6 both in CE and GCE. For U=8 there is rough agreement with SP's results, but disagreement for lower U. Quantitative comparison with the work of HM is not possible because of inconsistencies in their results. (Figures 1 and 20 Ref. 5 give appreciably different peak locations.) In Fig. 2 we summarize the temperatures at which the peaks in the specific heat occur.

To understand the physics of these peaks, we studied the spin-spin correlation function $\frac{1}{4}L_m$, n = 0, 1, 2. We note that the zero-field spin-susceptibility χ is related to this by

$$\chi = (kT)^{-1}(L_0 + 2L_1 + L_2) . \qquad (5)$$

As shown in Fig. 1, L_0 , $-L_1$, and L_2 undergo a more or less sudden change in correspondence to one or another of the peaks in the specific heat. For clarity, we discuss separately the two regions, U > 6 and U < 6 (where there are two and three specific-heat peaks, respectively).

For U>6 we see from Fig. (1a) that $|L_1|$ and L_2 simultaneously decrease sharply at temperatures near $T_1 = T_{II}$, the low-T peak in the specific heat, while L_0 remains essentially constant through this temperature region. Aside from the lack of any mathematical singularity in these functions, this behavior is very similar to the well-known antiferromagnetic transition in large three-dimensional systems. We will therefore adopt the terminology, used in the literature, ⁴⁻⁶ which calls $T_1=T_{II}$ the Neel temperature. We note that this temperature $\simeq 2b^2(U)$ as expected from the relation between the Hubbard and the Heisenberg model mentioned above.

In the small-U region, we note a remarkable fact. Although χ has a peak near the lowest temperature peak (T_1) in C, L_2 is seen in Fig. 1(b) to have an essentially constant value different from zero up to the temperature (T_{11}) at which the middle peak in C occurs, and above this temperature it goes rapidly to zero. $|L_1|$, on the other hand, is seen to start to decrease sharply near T_1 . The fact that $|L_1|$ and L_2 do not start to decrease sharply near to the constrast to typical behavior at a magnetic transition. Hence the characterizations⁴⁶ of T_1 sa a Néel temperature is misleading and unacceptable.

We also note that $L_{\rm 0}$ is essentially constant near $T_{\rm I},$ and decreases rapidly near $T_{\rm II},$ for U small.

The relation of the high-T C peak (at $T_{\rm HI}$) to a characteristic change in L_0 has already been noted.^{4-6,10} We see [Fig. 10b] an additional effect at small U, namely, L, also shows an anomaly near $T_{\rm HI}$, which somewhat surprisingly disappears at a value of U roughly equal to one. This plus the other anomalies in L_a are indicated by the numbers accompanying the curves in Fig. 2.

We consider the significance of the unusual results obtained, namely, the low-T peaks in C for small U and their physics. In fact, one cannot expect these effects to continue to exist as athe number of atoms $N - \infty$ because of the following reason. Consider first the four-atom four-electron system. For U = 0, the ground state is sixfold degenerate, including a triplet and three singlets. This degenerate is seen by considering the occupacy of the one-electron levels $E_{k} = 2b \cosh k = 0$, $k = \frac{1}{2}\pi$, π , accomodates two electronss but the other two electrons can occup four one-electron states $k = \frac{1}{2}\pi$ spin up and down) all with the same energy. The existence of the triplet among these ground states

implies, of course, that χ will exhibit Curie-law behavior at low T. Furthermore, C will show a low T peak when U increases from zero because of the splitting induced in this ground level. Clearly, this effect occurs whenever $\frac{1}{2}N$ is even, but it will become negligible as $N \rightarrow \varphi$; e.g., the Curielaw term in χ will approach zero since the total magnetic moment is always from a triplet, and will not increase with N.

On the other hand, when $\frac{1}{2}N$ is odd, the ground state for U = 0 is a singlet, so that the above effect will not occur. Clearly, for N = 2 or 6, the first excited state lies above the ground state by an energy of the order of h for U small, so that no low-T peak (at $kT \ll b$) in the specific heat will occur. Hence, in these very small systems, there is no "band antiferromagnetism" (for which, by definition, the Néel temperature -0 with decreasing U). One cannot conclude from this that such antiferromagnetism does not occur for macroscopic systems, since for large N the separation of the lowlying states is $O(\delta/N)$ for U = 0. (It might be that as N increases for small U the peak splits, with lower-T peak moving to low temperature.)

Although as we have just seen, one clearly cannot use the four-atom results to guess about large systems for small U, this is not so for large U. In fact, when $U = \infty$, we have noted above that the GCE results for small N give the large-N behavior exactly. Furthermore, the qualitative behavior that we find (a Néel-like smooth transition at kT_N $\simeq 2b^2/U$, a highly correlated nonmagnetic system for $kT_N \ll kT \ll U$ with $\langle N_{i*}N_{i*} \rangle \ll \langle N_{i*} \rangle \langle N_{i*} \rangle = \frac{1}{4}$, these correlations decreasing markedly as kTbecomes $\simeq U$) is what we expected on the basis of earlier work.3,11 There3 essentially the same physical picture was found for large U on the basis of a variational single-determinant approximation, in which the best one-electron states were found to be the Wannier functions for all T.

Therefore we felt that one should look carefully at χ vs T for a sign of the leveling off of χ^{-1} found by Epstein *et al.*⁷ at high T (~200 °K). Using their values b = 0.021, U/b = 8, we looked closely in the region of temperature corresponding to the experimental anomaly. We found no such effect. Furthermore, the location of the minimum in χ^{-1} (at $kT_0 \simeq 2b^2/U \cong 60$ °K for the above values of b and U) occurs at much higher temperature (by a factor of about 3) than the temperature at which a rounding off occurs in the experiment.7 We can get a suggestion as to whether T_0 might reduce by the needed factor when N increases from 4 to ∞ from the results on the Heisenberg chain,9 and from comparison with the easily solved N = 2 Hubbard model. For the Heisenberg chain, To decreases by about 20% when N goes from 4 to ∞, and for the Hubbard model by about 10% when N goes from 2 to 4. Thus it seems unlikely that T_0 for $N = \infty$ will be low enough.

Furthermore, we expect the qualitative behavior to be similar to that for the Heisenberg model, for which χ^{-1} shows a minimum and then levels to a finite nonzero value at T=0.9 In support of this extrapolation, we note that the minimum value of χ^{-1} in the Heisenberg model is insensitive to N for N ≥4 and that in the Hubbard model the exact value12 of χ^{-1} at T=0 lies well above this minimum calculated for N=4 (for U=8, b=1); this is consistent with an extrapolated $\chi(T)^{-1}$, which is qualitatively similar to that found for the Heisenberg chain.9 Such qualitative behavior is very different from the experimental results. In view of this discrepancy at low T and the above failure to find the experimentally observed leveling off in y-1 at high T, one is led to suggest that major modifications of the Hubbard model are needed to explain essential features of the high-T transition (called a "metal-insulator transition" by Epstein et al.) and the low-T antiferromagnetic behavior.

We thank Professor S. D. Mahanti for valuable discussions.

Note added in proof. For additional aspects of the comparison with experiment on (NMP) (TCNQ) and the extrapolations see D. Cabib and T. A. Kaplan, AIP Conference Proceedings No. 5, Magnetism and Magnetic Materials, edited by C. D. Graham, Jr. and J. J. Rhyne (AIP, New York, 1972).

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 Static Properties of the Half-Filled Band Hubbard Model [AlP Conference Proceedings, Magnetism and Magnetic Materials, Vol. 10, 1504 (1972)], with T. A. Kaplan

Exact calculations on the 4 atom ring Hubbard model¹ had resolved serious confusion existing in the literature on the subject.^{2,3} More specifically the qualitative behavior of the specific heat agrees with that found by Heinig and Monecke,³ (even though the quantitative results are appreciably different) and disagrees with Shiba and Pincus² (for weak to intermediate interactions). The results obtained with the grand canonical ensemble¹ do not differ qualitatively from those obtained with the canonical ensemble; but the use of the GCE is important for the extrapolation to a large number of atoms, N, because in this case when the ratio of hopping integral to Coulomb repulsion, b/U+0, any intensive parameter is independent of N (we take U and b > 0).

The specific heat has three peaks for $0 < U/b \le 6$ and two peaks for $U/b \ge 6$ both in the CE and GCE. The results obtained for the spin-spin correlation function, defined as $L_n = <s_{1Z}s_{1+n,Z} >$ where s_{1Z} is the z-component of spin at site i, are very illuminating on the physical significance of these specific heat peaks: the various anomalies in L_n were shown to occur always at temperatures very close to the ones at which one or another specific heat peak occurs. Since the large U/b region had been essentially understood



previously^{4,5} and since we agree qualitatively with the existing results 2,3,4,5 in this region, we will focus for the moment on the small U/b region. Here the specific heat has three peaks at temperatures $T_T < T_{TT} < T_{TTT}$. (T_T and $T_{II} \rightarrow 0$ as U/b $\rightarrow 0$.) We found that $-L_1$ decreases rapidly near T_{τ} , approaching a constant different from 0, and again near T_{III} , approaching 0. L₂ decreases from a constant value to O near T_{TT} . From this picture we cannot characterize T_{τ} as being similar to a Néel temperature (as HM do) because the first and second-neighbor correlations L_1 and L_2 do not have anomalies at the same temperature. This type of transition had not been found previously. HM argued, by extrapolation, that the low-T specific heat peaks will occur for large N, but we showed that this was wrong. Let us summarize here the reason. First of all this phenomenon occurs only when N/2 is even; in fact in this case the oneparticle energy levels for U=O are given by

$$E_k = -2b \cos k \quad k = 0, \ \pm \frac{2\pi}{N}, \ \frac{4\pi}{N}, \ \ldots, \ \pi$$

and the N-electron ground state (half-filled band) fills completely the states with k=0, $\pm 2\pi/N$, . . , $(2\pi/N) \cdot (N/4 - 1)$ leaving 2 more electrons the possibility of occupying the four states k= $\pm \pi/2$ (s_z= $\pm 1/2$) which all correspond to the same one-electron energy. This gives rise to a six-fold degeneracy of the ground state which is removed when a small U is



turned on, explaining the existence of the low-T peaks in the specific heat per atom.⁶ This degeneracy will remain six-fold for all even N/2 and its effect will therefore become negligible when N+ ∞ , the height in the above peaks decreasing as 1/N. One is naturally led to ask what the situation is for a chain. In this case the hopping integral b is taken to be the same for every nearest neighbor pair of sites, the end-sites having only one-sided hopping. The oneelectron energies are

$$E_k = -2b \cos k$$
, $k = \frac{\pi \lambda}{N+1}$, $\lambda = 1, 2, ..., N$

Therefore, when the number of electrons is even, the ground state is non-degenerate. Hence, when U increases from zero, no appreciable low-T peak in C will occur in contrast to the behavior discussed above for the ring. By appreciable we mean f(C/T) dT integrated over the peak is $\simeq k_B/N$ and by low-T we mean the peak location, $T_0 << b/N$ and $T_0 + 0$ as U+0 (we have small N in mind). In other words, we cannot expect to find in this case the new type of smooth magnetic transition which was found for the ring.

 $\rm HM^7$ also stated that the low-lying specific heat peaks should not occur for the chain, but gave an incorrect argument. Namely they said that the vanishing of the conductivity σ for the chain implied the vanishing of the peaks in C, presumably because they had established a causal relation



between anomalies in σ with those same low-T peaks in C. A reason for the incorrectness of this argument is that their calculation of σ is seriously in error, as we now show.

HM's results imply that $\sigma(\omega=0)\neq 0$ at zero temperature for any U/b. A calculation from Kubo's formula for the conductivity yields:

$$\sigma(\omega) = \frac{\pi}{Z} \sum_{nm}^{r} |\mathbf{j}_{nm}|^2 \frac{e^{-\beta \widetilde{E}_m - e^{-\beta \widetilde{E}_n}}}{E_{nm}} \delta(\omega + \widetilde{E}_{nm})$$

$$+ \frac{\pi}{Z} \beta \sum_{n}^{r} e^{-\beta \widetilde{E}_n} [|\mathbf{j}_{nm}|^2 + \sum_{\substack{m \neq n \\ m \neq n \\ m \text{ degenerate} \\ with n}} |\mathbf{j}_{nm}|^2] \delta(\omega)$$

Z is the partition function. Σ' is extended to states such that $E_n \neq E_m$ (E_n is the energy eigenvalue corresponding to the n-th energy eigenstate in zero electric field), $\tilde{E}_k = E_k - \mu n_k$ (n_k =number of electrons in the state corresponding to E_k), j_{nm} is the matrix element of the current operator,

 $\underline{j} = -ie \Sigma b_{ij} (\underline{R}_i - \underline{R}_j) c_{i\sigma}^{\dagger} c_{j\sigma}.$

Clearly for a small system (with discrete energies) only the sum involving the square brackets contributes to $\sigma(0)$. States with an even number of electrons can always be chosen to give a zero contribution to the sum involving the first term in square brackets. (For an even number of particles


the time reversal operator θ and H can be simultaneously diagonalized and since \underline{I} changes sign under time reversal, $\underline{I}_{nn}=0$ in this basis.) Since in our case the ground state has an even number of particles, this sum must vanish at zero T. Hence the only contribution to $\sigma(0)$ at zero T is the second sum in square brackets. For it to be different from zero at zero temperature it is necessary that the ground state be degenerate. Explicit calculations for four atoms showed that the ground state is non-degenerate for finite U and hence the HM result is incorrect. The error can be traced to the paper by Monecke, $\frac{9}{4}$ upon which the conductivity calculations for 4 atoms are based.

Since the 4-atom calculations for U/b>>1 do not give special results whose significance is restricted to small systems, and the GCE for b=0 does not depend on N, we¹ tried to compare zero magnetic field susceptibility calculations with the experimental measurements by Epstein et al.¹⁰ (see Figure AII.1). To this end we discuss the extrapolation to large N.

First of all, it is known that for large enough U/b and kT<<U, the Hubbard model approaches the Heisenberg model $-\Sigma_{nm}J_{nm}S_n \cdot S_m$, with $J_{nm}=2b_{nm}^2/U$; for the proposed value¹⁰ U/b=8 and small N we find behavior very similar to that of the Heisenberg model¹¹; therefore we expect similar behavior for U/b=8 and increasing N. The similarity can be described in terms of the following important features: the existence





Figure AII.1.--Inverse susceptibility vs temperature. The exact value at T=0 for the infinite chain is shown by x.

of a minimum in χ^{-1} , its location, and the behavior in the Curie-Weiss region. As seen in Figure AII.1 the exact value¹² of χ^{-1} at T=0 (shown as x) lies above the minimum for N=4 by about 50%; this suggests strongly that the minimum will persist when N→∞, as it does in the Heisenberg model,¹³ because the height at the minimum appears to be relatively insensitive to N (it changes by \sim 15% in the Hubbard model from N=2 to 4,¹⁴ and by about 7% in the Heinsenberg model¹¹ from N=4 to ∞). The location T₀=2b²/U (N=60°K for the experimental values of U and b) only varies about 10% from 2 to 4 atoms in the Hubbard model¹⁴ and about 20% from 4 to ∞ in the Heisenberg model.¹¹ Finally,



the theoretical 4-atom result for χ above \sim 60°K approaches closely to the Heisenberg-model Curie-Weiss behavior (with a moment of one Bohr magneton and a $0\sim$ -60°K as seen in Figure AII.1). The use of the 4-atom χ as an approximation to the many-atom χ in this higher-T region seems very reliable because in this region the results of Bonner and Fisher¹¹ are very insensitive to N, in the Hubbard model χ^{-1} changes by only about 12% from 2 to 4 atoms, ¹⁴ and the correlation L_n is short-ranged for N=4 (see Figure 1, ref. 1). Thus we are led to suggest that the curve χ^{-1} vs. T for N+ ∞ will be closely approximated by the dotted line in Figure AII.1 for kT/b<.17 and by the 4-atom curve for larger kT/b.

The experimental curve is seen to differ radically from this theoretical curve. The reduction in the moment from $l\mu_B$ was noted by Epstein <u>et al.</u>,¹⁰ who gave the not implausible argument that it might be expected because b/U is large enough to give appreciable mixing of ionic states into the singly-occupied states; however, the fact that our calculations show no such reduction forces us to conclude that such an argument is highly questionable. In fact the mixing effect discussed certainly occurs for systems with small N, but as seen in Figure AII.1, it is negligible for these purposes.

We conclude that drastic changes in the Hubbard model are needed to explain the so-called¹⁰ "metalinsulator transition" at high T and the low-T antiferromagnetic behavior.



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6. In the case of 4 atoms it is possible to see, directly or by perturbation theory, that the splitting between the ground state (singlet) and the first excited state (triplet) is of order U², whereas the next two excited states (singlets) differ from the ground state (and remain degenerate) in first order in U. This agrees with the small-U behavior of the specific heat peaks at low T displayed in figure 2 of the previous work (refer to reference 1 above).

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14. Because the number of nearest neighbors changes from 1 to 2 when N changes from 2 to >2, we expect larger changes in behavior in going from say N=2 to 4 than from N=4 to 6 or 6 to 8, etc.



Attempts to Explain the Susceptibility of NMP-TCNQ by Modifying the Hubbard Model

In the previous two Sections we were concerned. among other problems, with the comparison of the theory with the experiments. It had been claimed by some authors³ (the Penn group), that the organic solid NMP-TCNO can be fairly well represented by the one-dimensional half-filled-band Hubbard model if we appropriately choose the values of the parameters b and U. Later the same group 27 suggested that the experimental data would be better explained by letting the parameter b increase with temperature. The needed change would be of roughly a factor of two on going from low T ($b_{0.02}$ ev.) to T_200 °K ($b_{0.05}$ ev.) so that the ratio U/b goes from ~ 8 to ~ 4 . However, these conclusions were based on admittedly crude theoretical considerations, so that we did not expect them to be taken seriously. In Sections AII.1 and AII.2 we showed the serious difficulties encountered by the claim³ that a T-independent b and U theory represents the behavior of NMP-TCNQ and we stressed the necessity of drastically changing the model.

In what follows we shall describe the attempts we made to explain the experiments by changing the model discussed in Sections AII.1 and AII.2. They were of two types: in the first attempt we modified the Hamiltonian, but we considered only temperature-independent parameters; in the



second, following later emphasis put by the Penn group²⁸ on the temperature dependence of b, we tried to qualitatively fit the experimental susceptibility (χ) using the half-filled-band Hubbard model but allowing the hopping integral to change with temperature.

Let us now describe the first attempt. We tried a canonical calculation of χ for a system of four atoms on the corners of a rectangle, instead of a square as described in Section AII.1: that is, there are two hopping integrals b and b'. Furthermore the number of electrons is fixed and equal to 2 to account for the total number of unpaired electrons in a TCNQ chain. The justification for trying such a model is essentially the idea that each TCNQ molecule in the organic solid NMP-TCNO may contribute two spatial orbitals (instead of the one proposed by Epstein et al. 3), that can be filled by a maximum of four electrons (because of the spin), and in our calculation the four atoms on the rectangle correspond to the four cyanide groups on two adjacent TCNQ's (see Figure AI.3). The picture given by Epstein et al.³ describes the electrons as occupying a π orbital which is concentrated mainly at the two terminal cvanide groups in a TCNO molecule; furthermore, according to the same authors, if two electrons happen to be simultaneously on the same molecule they will be located at the two far ends of the molecule so as to minimize the Coulomb repulsion. But this picture is actually impossible with a



single molecular orbital (because in the two-electron state constructed in this way, there is high probability of finding the two electrons at the same end). Hence our model seems more reasonable because we let each cyanide group in a TCNO molecule contribute a spatial orbital that can be occupied by a maximum of two paired electrons (so that the whole molecule contributes a total of four one-electron states). If these two spatial orbitals overlap appreciably, they would make up two bands very different in energy from each other: in this case one could neglect the higher energy band and end up with Epstein et al.'s single π -orbital picture. On the other hand if the two orbitals do not overlap very much the two bands will be nearly degenerate and there is no justification for neglecting one of them. A calculation of a 4-atom Hubbard model on a rectangle with two electrons as described above, would hopefully account for the physics of this latter case, apart from the usual problems of extrapolating the results to an infinite system. We tried a few sets of parameters: i) b=1, b'=.5, U=8, ii) b=1, b'=2, U=8, iii) b=b'=1, U=1, 4, 8. b represents the hopping between the two orbitals within the same molecule, b' the hopping between two orbitals on near cyanide groups on neighboring molecules. U is the Coulomb repulsion of two electrons on the same orbital. Unfortunately the results were discouraging; none of the main features of the experimental x^{-1} curve vs. temperature were recovered: the

high-temperature leveling off is absent in the theoretical curve, and there still remains a minimum (the location of the minimum is shifted toward higher temperatures compared to the previous results showed in Figure 1 of Section AII.2); finally the slope in the Curie-Weiss region of temperature is unchanged with respect to the same previous results. Especially this slope should not depend on the size of the system as explained in Section AII.2. Thus, these seemingly reasonable generalizations of the Hubbard model apparently do not overcome its deficiencies vis a vis the experiments.

As for the second attempt, let us now describe its conceptual significance and our results.

To let the parameters of the Hamiltonian change with temperature has very subtle conceptual implications. What is usually done to test the validity of a theory is to calculate the thermodynamic properties of the Hamiltonian with fixed parameters and then compare with experiments. Furthermore in general one expects a Hamiltonian to be able to fit any experimental results, if it is a function of a sufficiently large number of temperature-dependent parameters.

On the other hand the concept of a temperaturedependent Hamiltonian is not completely extraneous to a theory of the Hubbard type. In fact we have to bear in mind that the Hubbard Hamiltonian is an approximate one: it has to be justified in terms of a derivation from the exact N-electron and N-nucleus Hamiltonian. Important



physical effects may occur in a real system that are completely neglected in a temperature-independent theory of the Hubbard type such as the ones induced by electron-phonon, other bands or long-range electron-electron interactions. As a matter of fact a derivation of the Hubbard Hamiltonian based on Bogoliubov's variational principle¹⁸ would give a temperature dependent theory; and it would also give the best Hubbard Hamiltonian which approximates the exact Hamiltonian of the crystal. In any case if one is forced to let the parameters of his approximate theory vary appreciably with temperature, to be able to make contact with experiments, that suggests at least that the neglected interactions are not negligible, i.e. the starting Hamiltonian has to be appreciably changed.

We tried to check Heeger and Garito's^{27,28} (HG) suggestion of a band broadening with temperature; we found that their data on NMP-TCNQ could be fit quantitatively with a temperature dependent bandwidth as follows. We plot the experimental inverse susceptibility $S^{-1} = (\chi U/N\mu_B^2)^{-1}$ as a function of kT/U; then we plot on the same graph the theoretical S^{-1} for different ratios of b/U: when b/U is in the range $1/8 \sim 1/4$ we use our 4-atom results (Section AII.1) and Shiba's¹¹ 6-atom results and extrapolation. In Figure AII.2 theoretical curves (for N= ∞) vs. kT/U for U/b=4 and 35have been added to Figure AII.1, and the plot



is changed $(\chi b \rightarrow \chi U, kT/b \rightarrow kT/U)$ because U is presumed²⁸ a constant independent of temperature.



Figure AII.2.--Determination of b/U as function of temperature.

As seen from Figure AII.2, the U/b=8 and the U/b=4 curves intersect the experimental curve respectively at T=0 and $kT/U\sim2(b/U)^2$; the U/b=3 curve agrees roughly with experiment above $kT/U\sim.1$ Furthermore the minimum value of S⁻¹ increases with b/U and shifts to higher temperatures: when U/b=0 the theoretical curve is at infinity. The fact that the minimum shifts to higher temperatures is very plausible (because $kT_{min}\sim b^2/U$ for b<< U and $kT_{min}\sim b/U$ for b>> U). Therefore, at least in principle, one can determine b/U as a function of T by determining the intersection points between the experimental S⁻¹ and the various theoretical S⁻¹ curves: to each temperature there corresponds a theoretical curve



with a particular b/U that crosses the experimental curve at that temperature. This correspondence gives b/U as a function of T.

From Figure AII.2 we see that within this scheme b/U does indeed increase by roughly a factor of two on going from 0° K to $\sim 200^{\circ}$ K in agreement with HG's suggestion²⁸; but we also see that at every b/U the minimum in the theoretical ${\rm S}^{-1}$ as a function of T lies to the right of the intersection point with the experimental S^{-1} . Since this minimum is the ordering temperature which marks a smooth but rapid transition from weakly correlated spins ($|\langle S_{iz}S_{iz}\rangle|\langle \langle \langle S_{iz}^2\rangle$, $i \neq j$) to strongly correlated spins $(|\langle S_{iz}S_{iz}\rangle| \approx |\langle S_{iz}^2\rangle|$, $i \neq j$)²⁹, the interpretation of the experimental results is totally different from that given by Epstein et al.³ and HG^{28} : the spin variables S_{iz} are strongly correlated in the region of temperature < 200°K, instead of being uncorrelated. In other words the straight-line portion of S⁻¹ below 200°K in the NMP-TCNQ would not correspond at all to a Curie-Weiss behavior above the ordering temperature as suggested^{3,28}, where the spins are weakly correlated, but would correspond to a long and appreciable short-range order of the electron spins. Clearly, a crucial experiment for testing the model is a measurement of the spin-spin correlation function, which at least in principle should be possible via neutron scattering.

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29. Note that even in the limit of zero interactions, U=0, these spin observables S_{1Z} are strongly correlated for $T<T_0$ and for short distances (due to the Pauli exclusion principle).



4. Expansion in Powers of U/kT

In the last Section we were concerned with the determination of a function b(T) that at least would allow a phenomenological interpretation of the experimental measurements of the susceptibility in NMP-TCNQ. Mathematically the conclusions were not rigorous (even though we feel they were semiquantitatively accurate) because they were based on extrapolations from small-system caculations to infinite systems.

One central point of the discussion was the fact that the minimum in theoretical $S^{-1} = (\chi U/N \mu_p^2)^{-1}$ as a function of temperature lies always at the right of the intersection point with the experimental S^{-1} curve for any given b/U, at least as long as b/U is in the region $\sim 1/8$ - $\sim 1/4$. This point is fundamental for the physical interpretation of the experiment because this minimum indicates a smooth but marked transition from weak to strong spin-spin correlations. Thus assuming with the Penn group 27,28 that the Hubbard model with b=b(T) is a correct description of NMP-TCNO, we were led to conclude that the physics in the region T<200°K would be drastically different from that described by the Penn group. No uncertainty in this conclusion would exist if we knew rigorously the position T_{o} of the minimum in S^{-1} for the infinite chain as function of b and U. The following discussion is aimed at investigating further this function.



The rigorous information available up to now about T_0 is very limited: at U=0, S has a broad maximum at $kT_0^{\simeq}.7b^{10}$; at b=0, S + ∞ as T+0 and monotonically decreases with T, therefore $kT_0^{=0}$; for b≠0 but satisfying b/U<<1 S has a maximum at $T_0^{\sim}2b^2/U$ (assuming the validity of perturbation theory). Taking this information into account we can expand kT_0 in the following form for x small:

$$t_0 = kT_0/U = f(x) + \sum_{n=-1}^{\infty} a_n x^n$$
 (1)

where x=U/b. We assume f(0)=0, and either $f(x)\equiv 0$ or f(x) has an essential singularity at x=0, and contains no part with an expansion in powers of x with a finite number of negative powers.

The known behavior of $t_0(x)$ can be summarized in the following qualitative plot



Figure AII.3.--kTo/U vs. b/U.



The curve starts off quadratically in b/U; it will then asymptote to a straight line at large b/U with a slope a_{-1}° .7 and an unknown intercept with the t_0 -axis equal to a_0 ; the way the curve approaches the straight line for $x \rightarrow 0$ is not known: in principle it may be from below, above or may be oscillatory; the deviation from the quadratic behavior at small b/U could be investigated using the next higher term in the appropriate perturbation theory, but this seems to be more difficult than the analagous small U/b behavior, and at present we are investigating only the region x=U/b small. This is being done by an expansion of S in powers of βU (β =1/kT). In this expansion we assume kT>>U but not necessarily greater than b (in the case U<<b). From this one can calculate the coefficients in the expansion (1) for t_0 .

We add here that the interest in such an expansion transcends the above discussion. The susceptibility of an interacting electron gas has been of interest in the literature²⁹⁻³¹ where the RPA approach is used. Although it seems that usually RPA is thought to be appropriate in the weak-interaction limit³¹, we could not find in the literature a clear-cut statement that RPA is exact in first order in the interaction (U in the Hubbard model). Certainly RPA is not exact to all orders because it does not account for the shift in t_o on going from U=0 to U≠0.



Our expansion in β U in the Hubbard model is exact and would give an opportunity to check the RPA result for the susceptibility (for b>>U). So far we have carried out the first term of the expansion and up to the first order in β U and first order in U/b the result agrees with RPA³¹; the second order term is under study.

If we define H_0 , Z_0 and $\chi_0/N\mu_B^2$ to be the Hamiltonian, partition function, and susceptibility per particle respectively, when U=0 (see Equation (1) of Chapter I), we have, in first order in β U:

$$\chi/N\mu_{B}^{2} = 1/N\mu_{B}^{2} (\chi_{0} + \chi_{1}) = (g^{2}\beta/4NZ_{0}) \text{ tr} \{\exp[-\beta(H_{0} - \mu N_{e})] \cdot [\sum_{k} (n_{k+} - n_{k+})]^{2} (1 - \beta H_{1} - Z_{1}/Z_{0})\} + O[(\beta U)^{2}]$$
(2)

Since

$$\chi_{0}/N\mu_{B}^{2} = (g^{2}\beta/4NZ_{0}) \text{ tr } \exp[-\beta(H_{0} - \mu N_{e})] \left[\sum_{k} (n_{k\uparrow} - n_{k\downarrow})\right]^{2}$$
$$= g^{2}\beta/4 \times [1 - (2/N)\sum_{k} f_{k}]$$
(3)

Equation (2) defines $\chi_1,\,N_e=\sum\limits_{k\sigma}n_{k\sigma},\,\mu$ is the chemical potential, H_1 is the Coulomb repulsion

$$H_{1} = (U/N) \sum_{k,k',q}^{\Sigma} a_{k+q,\uparrow}^{+} a_{k,\uparrow}^{+} a_{k'-q,\downarrow}^{+} a_{k',\downarrow}$$
(4)


written in the Bloch-function basis. Z_1/Z_0 is defined as:

$$Z_{1}/Z_{0} = -\beta \text{ tr } \exp[-\beta(H_{0} - \mu N_{e})] H_{1}$$
 (5)

Finally in (3) f_k is the Fermi function $f(\varepsilon_k)$ at wavevector k. (2) and (5) are obtained taking into account the non-commutativity of H₀ with H₁. If we restrict ourselves to the half-filled-band case where the average number of electrons $\langle N_e \rangle$ is equal to N, $\mu=U/2$ and is independent of temperature. Expanding the exponential factor in (2) and (5), Equation (2) becomes, up to first order in βU ,

$$\chi/N\mu_{B}^{2} = -Z_{1}\chi_{0}/Z_{0}N\mu_{B}^{2} + (g^{2}\beta/4NZ_{0}) \text{ tr } \exp(-\beta H_{0}) \cdot \\ \cdot [1 + (\beta U/2)N_{e} - \beta H_{1}] [\sum_{k} (n_{k\uparrow} - n_{k\downarrow})]^{2}$$
(6)

Using repeatedly the rule that the thermal average ${}^{<n}k_1\sigma_1^{\ n}k_2\sigma_2^{\ \dots n}k_k\sigma_k^{\ >}$ with the Hamiltonian H_0 is equal to ${}^{<n}k_1\sigma_1^{\ ><n}k_2\sigma_2^{\ 2}\cdots {}^{<n}k_k\sigma_k^{\ >}$ if $(k_1,\sigma_1) \neq (k_j,\sigma_j)$ for each pair $k\neq j$, we find:

$$\chi_1 / N \mu_B^2 = (g^2 \beta^2 U/8) [1 - (2/N) \sum_k f_k]^2 = (2U/g^2) (\chi_0 / N \mu_B^2)^2$$
(7)

It is easy to see that this first order correction does not affect t_0 if we assume that $d^2\chi_0/dT^2|_{T_0}$, $U=0^{\neq 0}$, which we checked numerically. Therefore in the expansion (1), $a_0=0$,



and the intercept of the straight line asymptote with the coordinate axes coincides with the origin. We can also write

$$\chi/N\mu_B^2 = \chi_0/N\mu_B^2 (1 + 2U\chi_0/N\mu_B^2 g^2) + O((\beta U)^2)$$
 (8)

and it is easily seen that if U is treated as a perturbation parameter, in first order in U (8) agrees with the RPA expression obtained by Hubbard and Jain.³¹ Therefore the RPA is exact for the Hubbard model in this order. (For a more general type of interaction the exact and the RPA results need not agree in first order in the interaction.)

In conclusion, in this Section we have calculated the susceptibility of the half-filled-band Hubbard model to first order in β U, and, concentrating on the U<
b region, we compared our exact results with the RPA: we found that the two agree in first order in U/b, which means that RPA is exact to this order. We found also that $t_0=kT_0/U$ (the position of the maximum in χ_0) does not shift to first order in β U with respect to the case U = 0.



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PART A

CHAPTER III

ON THE DEFINITION OF THE CURRENT OPERATOR-APPLICATION TO THE HUBBARD MODEL*

 $^{^{*}}$ Physica Status Solidi (b) <u>58</u>, (July 1973), with T. A. Kaplan.



1. Introduction

The calculation of the response to a small electric field in the one-band Hubbard model has been of interest in the recent literature. Such calculations need the current-current correlation function which involves the current operator j_n , defined in general as¹

$$\underline{\mathbf{j}}_{g} = \sum_{i} \mathbf{e} \, \underline{\mathbf{v}}_{i} = \frac{\mathbf{e}}{\mathbf{i}} \, [\underline{\mathbf{X}}, \mathbf{H}], \tag{1}$$

where

 $\underline{X} = \sum_{i} \underline{x}_{i}$

H is the Hamiltonian of the system and the index i refers to the i-th particle. For the purposes of working with a singleband model there is some question as to how one defines a current operator. K. Kubo² and Bari <u>et al.</u>³ obtained an expression for the current <u>j</u> analogous to (1) in the following way: the Hamiltonian is replaced by

 $H = \sum_{i,j} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$

where $c_{i\sigma}^{+}$ and $c_{i\sigma}$ are the creation and destruction operators of an electron with spin projection σ at site i, in the Wannier function basis, and U is the intraatomic coulomb repulsion ($n_{i\sigma} = c_{i\sigma}^{+} c_{i\sigma}$); the polarization operator e <u>X</u> is replaced by



$$e \underline{R} \equiv e \Sigma \underline{R}_{i} n_{i\sigma}$$
(2)

where \underline{R}_{i} are the position vectors of the atoms; then

$$\underline{j} \equiv \frac{1}{i} [e \underline{R}, H]$$
(3)

= - ie
$$\Sigma$$
 $t_{ij}(\underline{R}_i - \underline{R}_j) c_{i\sigma}^{\dagger} c_{j\sigma}$. (4)

Several authors²⁻⁷ have used an expression for \underline{j} which is formally like eq. (4), but different in the case of the linear chain with periodic boundary conditions as we shall see below.

Bari and Kaplan⁶ found, in agreement with K. Kubo,² that the conductivity shows an absorption and emission spectrum with a line at $\omega = U$ (in the atomic limit); this corresponds to the increase in energy by about U when an electron hops from an otherwise empty site to a site already occupied by another electron. A line at $\omega = 0$ was also obtained.^{2,6}

However, Monecke,⁷ in a similar calculation, using (3) explicitly does not find such behavior, namely he finds free electron behavior with absorption only at $\omega = 0$. Furthermore, he shows that the matrix elements $\langle n|\underline{j}|m\rangle$ are zero for $n \neq m$ if the basis set {|n>} is chosen in such a way that each |n> is a simultaneous eigenfunction of the Hamiltonian and the lattice translation operator. Cabib and Kaplan⁸



showed that the conductivity calculations by Heinig and Monecke⁹ for the ring of 4 atoms, based on Monecke's work,⁷ are wrong, by showing that the zero temperature d.c. conductivity vanishes, in contrast to the result given by those authors.⁹

A very simple and direct argument that shows the incorrectness of Monecke's analysis is that from his equation for $\langle n | \underline{j} | m \rangle$ on pg. 372, it immediately follows that the diagonal elements are also zero. Hence his argument must lead him to the conclusion that the operator \underline{j} of eq. (3) above is zero, a conclusion which is evidently wrong.

However, finding the explicit error was subtle and the result somewhat surprising, so we will now present the arguments. The essential point is that Monecke's proof⁷ of $\langle n|\underline{j}|m \rangle = 0$ for $n \neq m$ was based on the assumption that \underline{j} is invariant under the lattice translations. In the next Section we show that this assumption is incorrect.

Lack of Translational Invariance of j; <u>Resolution of the Disagreement in</u> <u>the Literature</u>

Let us first consider the case of a ring. Here the lattice translation operation is an N-fold rotation about the axis perpendicular to the plane and passing through the center of the ring, with N equal to the number of atoms. If T is the operator which performs this rotation



$$T_{\underline{j}}T^{-1} = -ie \sum_{\substack{i,j=1\\\sigma}}^{N} t_{ij}(\underline{R}_{i} - \underline{R}_{j}) T_{i\sigma}^{+} T^{-1} T_{c_{j\sigma}} T^{-1}$$
$$= -ie \sum_{\substack{ij\\\sigma}} t_{i-1,j-1}(\underline{R}_{i-1} - \underline{R}_{j-1}) c_{i\sigma}^{+} c_{j\sigma}$$
$$= -ie \sum_{\substack{ij\\\sigma}} t_{ij}(\underline{R}_{i-1} - \underline{R}_{j-1}) c_{i\sigma}^{+} c_{j\sigma}$$

Thus

$$[\mathsf{T},\underline{j}] \neq 0 \tag{5}$$

because clearly $\underline{R}_{i-1} - \underline{R}_{j-1} \neq \underline{R}_i - \underline{R}_j$. (These two vectors have the same length but different direction).

In the case of a chain of N atoms with periodic boundary conditions $c_{N+i,\sigma}^{+} = c_{i\sigma}^{+}$ and $t_{N,N+1} = t_{N,1} = t_{12}$ because the Wannier functions $w(\underline{r}-\underline{R}_{i})$ and $w(\underline{r}-\underline{R}_{N+i})$ are equal, making H translationally invariant. However, we now point out that despite this, \underline{j} as in (4) is not translationally invariant. This is so because there appears a term (we take nearest neighbor hopping for simplicity)

- ie
$$t_{12}(\underline{R}_N - \underline{R}_1)$$
 $(c_{N\sigma}^+ c_{1\sigma} - c_{1\sigma}^+ c_{N\sigma});$ (6)

clearly $\underline{R}_{N} - \underline{R}_{1} \neq \underline{R}_{N} - \underline{R}_{N+1}$, and this is sufficient to spoil the translational invariance. (As stated in the Introduction the failure of Monecke's argument in either case is in the



fact that he incorrectly assumed that \underline{j} as calculated from eq. (3) is translationally invariant.)

If one simply replaces, ad hoc, the term (6) in eq. (4) by -ie $t_{12}(\underline{R}_N - \underline{R}_{N+1})$ ($c_{N\sigma}^+ c_{1\sigma} - c_{1\sigma}^+ c_{N\sigma}$), then we obtain a new operator <u>J</u>, which is translationally invariant. In fact one can see that it is <u>this J</u> that has been used in the literature²⁻⁷ in connection with the calculation of the current-current correlation function (with the reservation noted above in connection with ref. 7). This concludes the resolution of the disagreement between the results of different workers who began with apparently the same definitions.

3. How to Define the Current Operator?

There remains the question, how <u>should</u> one define the current operator? That there is ambiguity stems from the fact that the operations of commuting the polarization operator and the Hamiltonian (to find the current) and projecting these operators on to the space of functions spanned by the single-band states, do not commute. That is, suppose P is this projection operator, $e\underline{X} \equiv \sum_{i} e\underline{x}_{i}$ and $H \equiv \sum_{i} p_{i}^{-2}/2m + V(. r_{j}..)$ are the polarization and Hamiltonian respectively. Then commutation followed by projection gives

$$P_{\underline{i}g}P = P_{\underline{i}}^{1} [e\underline{X}, H] P = \frac{eP}{i} (\underline{X}H - H\underline{X}) P$$
(7)



whereas projection first gives 10

$$\underline{j} = \frac{1}{i} [Pe\underline{X}P, PHP] = \frac{e}{i} (P\underline{X}P HP - PH P\underline{X}P); \quad (8)$$

the two expressions on the right of (7) and (8) are seen to be unequal in general (they are unequal if H and \underline{X} connect single-band states with at least one common state which is orthogonal to all the single-band states).

In the case of a linear chain with periodic boundary conditions, the lack of translational invariance of \underline{j} is an unsatisfactory property. Apart from the fact that this lack of symmetry is contrary to the usual concept of current (\underline{j}_g) , it is easy to see in the simple special case of U=0, that the expectation value of \underline{j} in the Bloch-function energy eigenstates is zero for finite N (also contrary to the usual expectation).

In our opinion, \underline{J} is a satisfactory choice at least from the viewpoint of satisfying the right symmetry (again for the chain with periodic boundary conditions). For our nearest neighbor example, with N > 2, we have (for t_{12} real)

$$\underline{J} = -\frac{e}{i} \underbrace{R}_{12} t_{12} \underbrace{\Sigma}_{i=1} \Sigma_{\sigma} (c_{i\sigma}^{+} c_{i+1,\sigma} - c_{i+1,\sigma}^{+} c_{i\sigma})$$
(9)

Furthermore, under rather loose restrictions as specified below, <u>J</u> can be chosen to be the same as P \underline{j}_n P, in which



case the definition is a natural one. To see this we note that we can write (in the absence of an external vector potential):

$$P_{\underline{j}g} P = -\sum_{m \ ij\sigma} \langle i | \underline{p} | \mathbf{j} \rangle c_{i\sigma}^{\dagger} c_{j\sigma}$$
$$= -\sum_{m \ \underline{k}\sigma} \langle k | \underline{p} | k \rangle n_{\underline{k}\sigma}$$
(10)

where $n_{\underline{K}\sigma}$ are the Bloch-function occupation-number operators, and p is the electron momentum. Also from (9) we have

$$\underline{J} = e \sum_{\underline{k}} (\nabla_{\underline{k}} \in \underline{k}) n_{\underline{k}\sigma}.$$
(11)

where

$$\varepsilon_{\underline{k}} = \frac{1}{N} \sum_{i,j} e^{i\underline{k} \cdot \underline{R}} ij t_{ij}$$
(12)

Clearly (10) and (11) are equal if

$$\frac{1}{m} < \underline{k} | \underline{p} | \underline{k} > = \nabla_{\underline{k}} \varepsilon_{\underline{k}}, \qquad (13)$$

a relation found in many solid-state texts.

Since this $\varepsilon_{\underline{k}}$ must be differentiated in order to obtain (11), it must be defined for continuous <u>k</u>; to every choice of the <u>R</u>_i (to within crystal lengths) there corresponds a different function ε_k ; all of these functions



have identical values at the discrete wave-vectors in the Brillouin zone, but they differ in their derivatives at these wave-vectors. The particular choice of the \underline{R}_1 leading to (9) yields that continuous function $\underline{e}_{\underline{k}}$ which would be approached by the set of discrete values when N+ ∞ , whereas other choices will lead to different $\underline{e}_{\underline{k}}$ and different currents (e.g., if \underline{R}_{N+1} is replaced by \underline{R}_1 then \underline{J} will be replaced by \underline{j}).¹¹

Equation (13) will not be true for arbitrary Bloch-functions $|\underline{k}\rangle$ and energies $\varepsilon_{\underline{k}}$, since the derivation¹² depends on the assumption that $|\underline{k}\rangle$ and $\varepsilon_{\underline{k}}$ are eigenstates and eigenvalues of a Hamiltonian of the form

$$h = \frac{p^2}{2m} + v(\underline{r})$$
(14)

where $v(\underline{r})$ is a periodic k-independent local potential.¹² Nevertheless it is clear that there exists a variety of $v(\underline{r})$ and their resulting $|\underline{k}\rangle$ and $\varepsilon_{\underline{k}}$ which will provide a sufficiently rich variety of sets of parameters t_{ij} =

 $(w_i, hw_j) = \frac{1}{N} \sum_{\underline{k}} e^{i\underline{k} \cdot \underline{R}} ij\epsilon_{\underline{k}}$ to probably be able to achieve any Hubbard Hamiltonian one desires; for any of these the above discussion shows that the remaining ambiguity in the definition of the current operator (the choice between \underline{J} and $P\underline{i}_{n}P$) does not exist.



4. Summary

In the above discussion we first reviewed the general definition of the current operator as it is used by different authors in the calculation of the electric conductivity in the one-band Hubbard model. We pointed out the disagreement existing in the results of different authors, one^7 finding free electron behavior (absorption only at $\omega=0$), the others^{2,6} finding also high frequency absorption (ω =U in the atomic limit); we settled the controversy by showing that Monecke's discussion⁷ leads him to the obviously incorrect conclusion that $j \equiv 0$. In Section 2 we showed that his assumption, that j as defined in (3) is translationally invariant, is wrong in both a ring and a chain of N atoms with periodic boundary conditions. The other authors 2^{-6} used a definition much closer to J than to i: if we presume they had in mind periodic boundary conditions, then their definition was identical to J; if they had in mind a finite crystal, then their definition would differ from J by only surface terms (whose effect becomes negligible for macroscopic crystals), in contrast to the difference between J and the definition i for periodic boundary conditions, ¹¹ as used by Monecke, ⁷ Also, they $^{2-6}$ did not use the commutator (3) subsequent to obtaining an explicit form for the current. Since the lack of translational invariance in j makes this j an unsatisfactory current operator, in Section 3 we approached the problem



of the definition of a "good" current operator; after having explained that there is still an ambiguity in this definition due to the fact that the projection of the product of two operators is not in general equal to the product of the respective projections, we showed that the ambiguity disappears under broad conditions: the "good" current is proportional to $\sum_{k\sigma} (\nabla_k \ \varepsilon_k) n_{k\sigma}$ provided that we properly define the one-particle energies ε_k at those vectors k away from the discrete values $\frac{2\pi \lambda}{N}$.



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CHAPTER III

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10. For simplicity we use in Eq. (8) the same symbol \underline{j} as in Eq. (3), although P \underline{X} P differs from R by off-diagonal elements of \underline{x} between Wannier functions (which were argued to be small in ref. 3).

11. It is interesting to note that, even though for large N there are very few terms involved in the difference $\underline{J} - \underline{j}$, (presuming short-range t_{ij} of course), there contribution is as large as that of all the other terms. In our nearest-neighbor example, the function (12) appropriate to \underline{j} is $\overline{\epsilon}_k = (2t/N)[(N-1) \cos ka + \cos (N - 1) ka]$, as compared to $\epsilon_k = 2t \cos ka$, appropriate to \underline{J} . It is easy to verify that the term cos(N-1) ka gives as large a contribution to



 $d\bar{\epsilon}_k/dk$ as that of (N - 1) cos ka. Furthermore, $(d\bar{\epsilon}_k/dk)_k=\frac{2\pi\lambda}{N}$ with λ integral, becomes physically meaningless in the limit of large N, in contrast to the well-behaved $d\epsilon_k/dk$.

 See, e.g. J. C. Slater, <u>Insulators, Semicon-</u> ductors and Metals, Quantum Theory of Molecules and Solids, Vol. 3, McGraw-Hil, 1967, App. 1.

13. Not only does the standard derivation assume this locality, but one can show that locality is necessary for the result Eq. (13), a fact which we believe has not been noted previously. The proof is based on the fact that the velocity operator \underline{v} for electrons in a periodic potential is equal to $\frac{D}{(p)}$ (p = momentum operator, m = electron mass) only when the position operator \underline{r} commutes with the potential: in the case of a non local potential this commutativity does not hold.






PART B

CHAPTER I

ONE-DIMENSIONAL ISING MODEL WITH RANDOM EXCHANGE INTERACTIONS



1. Introduction

Thermodynamic properties of a spin system with random exchange interaction have been of considerable interest recently.¹⁻⁴ There are two important aspects in the study of the properties of a random spin system: the effect of randomness of the exchange interaction on the sharpness of the phase transition and on the low temperature behaviour of the thermo-dynamic quantities such as specific heat (C) and susceptibility (χ).

McCov and $Wu^{1,2}$ have studied the effect of randomness on the sharpness of the phase transition of a two dimensional rectangular Ising lattice with a special type of randomness. In their model, the horizontal interactions (J_1) between all the spins are the same, but the vertical interactions (J_2) , which connect spins of the ith row with those of the j+lth row are the same for all the spins in the jth row, but vary randomly from one row to the other. Using a narrow distribution $P(J_{2})$ of width $O(N^{-1})$, (N being the total number of spins), they find that the critical temperature is shifted by an amount $O(N^{-1})$ and the specific heat deviates by an amount O(1) for large N from Onsager's value only for T - $\rm T_{c}$ \sim O(N $^{-2})$. However, for a finite but narrow width w of $P(J_2)$, in the thermodynamic limit $(N \rightarrow \infty)$, McCoy and Wu² find that



the logarithmic divergence in the specific heat is absent. In fact, C is an infinitely differentiable function of temperature at T_c even though it is not an analytic function. For $(T - T_c) >> w^2$, it approaches Onsager's value.

The second interesting aspect in the study of a random spin system is the behaviour of the thermodynamic properties such as specific heat, susceptibility, away from the region of the phase transition. In one dimension, since there is no phase transition, this second aspect, in particular the low and high temperature behaviour of C and χ becomes more relevant. Fan and McCoy^4 have used the method of McCoy and Wu¹ to analyze the thermodynamic properties of a one dimensional Ising model with random nearest neighbor exchange and with an external magnetic field. They have studied a system where the distribution of exchange P(J) has a width of order N^{-1} .

In this paper, we have studied in detail the properties of the one-dimensional random Ising model for various types of distribution P(J) in the case of zero magnetic field. In particular we have analyzed the case of constant distribution, P(J) = constant for J in the interval $[0, J_m]$ and P(J) = 0 otherwise for both the ferro $(J_m > 0)$ and the antiferromagnetic $(J_m < 0)$ cases. (In the present paper, J_m is always a finite number and this distribution will be referred to as "constant distribution".) In



addition, the effect of distributions of the form $P(J) = A |J|^{\nu} \quad \text{for } J \quad \text{in the interval } \begin{bmatrix} 0, J_m \end{bmatrix} \quad \text{and} \\ P(J) = 0 \quad \text{otherwise, on the low temperature} \quad (kT << |J_m|) \\ \text{behaviour of } C \quad \text{and} \quad \chi \ , \ \text{has been studied.}$

We find that the low temperature behaviour of $\chi_{||}$, χ_{\perp} and C is very sensitive to the nature of the distribution P(J). In the case of constant distribution, C(T) $\propto \gamma T$ for low T. This behaviour is quite similar to that of a more general random spin system interacting via a long range RKKY interaction.⁵ The physical origin of this linear behaviour can be ascribed to the finite density of low lying excited states present because of non-zero P(0). Furthermore a direct comparison (see Fig. 1) of the random chain C-curve with the periodic C-curve with J = $J_m/2$ shows that the height of the peak (occurring at about .25 J_m in the former and .2 J_m in the latter case) is lower (~ 40%) and broader in the former. The same behaviour is expected in the more general cases of v > 0, but as vincreases the effect will be less pronounced.

The effect of randomness on the temperature dependence of the parallel susceptibility $\chi_{||}(T)$ is quite dramatic. For a periodic Ising chain, it is known⁶ that $\chi_{||}(T)$ goes to zero with T exponentially in the antiferromagnetic (AF) case and diverges exponentially in the ferromagnetic case (F). However, in the random case with constant P(J), we find that $\frac{\chi_{||}(0)}{N\mu_{R}^{2}} = \frac{\log 2}{|J_{m}|}$ in the AF case and







diverges as $|J_m|/(kT)^2$ in the F case. This indicates that the essential singularity of $\chi_{||}(T)$ at T = 0 present in the periodic system is removed by the randomness: $\chi_{||}(T)$ is either regular or has a pole singularity at T = 0, in the random system. The major effect of the randomness is the removal of the gap that is present for a periodic system. This then alters the low lying excitations significantly. The results for more general distributions are discussed in the next Section.

In contrast to $\chi_{||}(T)$, $\chi_{\perp}(T)$ does not depend upon the sign of J_m and therefore its value is the same in the F and AF cases. We have found that the value of $\chi_{\perp}(0)$ is enhanced from its value in the periodic case⁷ by the amount 2 log 2 in the case of constant P(J). In addition, a remarkable effect of the randomness is to remove the peak in $\chi_{\perp}(T)$ as a function of T which is present in the periodic case. Again, these effects can be understood by noting that the gap in the excitation spectrum that occurs in the periodic case is absent in the random system.

At high T i.e. $kT >> |J_m|$, χ_{\perp} exhibits a Curie like behaviour. The Weiss part in χ_{\perp}^{-1} is absent due to the absence of the interaction along the x and y directions. We have made some attempts to study the effect of an interaction of the type $-2\sum_{i=1}^{\infty} J_{i}^{\perp} (S_{ix}S_{i+1x} + S_{iy}S_{i+1y})$ (we will refer to this operator as xy interaction) on the thermodynamic properties of the system.



We have carried out a high temperature expansion to the leading order in $J_{\frac{1}{4}}^{\perp}/kT$ and J_m/kT and found that the inclusion of the xy interaction leads to a Weiss term in χ_{\perp}^{-1} . The low temperature behaviour of the random Ising system with small xy interaction is quite interesting but difficult. For an arbitrary distribution of $J_{\frac{1}{4}}^{\perp}$, $P(J_{\perp}^{\perp})$, the ground state is not known. It is known⁸ that for a special class of $P(J_{\perp}^{\perp})$, namely $J_{\frac{1}{4}}^{\perp} = \gamma J_{\frac{1}{4}}^{\perp}$ and $0 < \gamma < 1$, the ground state is ferromagnetic for $J_{\frac{1}{4}}^{\perp} > 0$. However, in the general case $J_{\frac{1}{4}}^{\perp} = \gamma_i J_{\frac{1}{4}}^{\perp}$, the ground state is more complex. The nature of the ground and low-lying excited states is presently under study.

In Section 2, we present all our results for the Ising chain. Section 3 deals with the effect of the xy interaction on various physical and thermodynamic properties.

2. The Model and its Solution

The Hamiltonian describing a system of N Ising spins interacting via nearest neighbour exchange J_{ij} in the presence of an external magnetic field \vec{H} is given by:

$${}^{H}{}_{I} = -\sum_{\langle ij \rangle} \frac{1}{4} J_{ij} \sigma_{iz} \sigma_{jz} - \frac{g\mu_{B}}{2} \sum_{i} \vec{\sigma}_{i} \cdot \vec{H}$$
(1)

 J_{ij} 's are a set of random numbers with a distribution P(J) . We will be concerned with a distribution P(J) different from zero for $J_{min} \leq J \leq J_{max}$. By choosing J_{min}



and J_{max} appropriately, one can have a system with (a) ferromagnetic coupling $(J_{min}, J_{max} \ge 0)$ (b) antiferromagnetic coupling $(J_{min}, J_{max} \le 0)$ and (c) mixed coupling $(J_{max} > 0, J_{min} < 0)$. In this paper we shall be concerned with cases (a) and (b) only and report the results for different distributions P(J) of the exchange parameters J_{ij} for a one dimensional system.

Fan and McCoy⁴ have studied the thermodynamics of the system given by eqn. (1) in the one-dimensional case with H = 0. P(J) is taken in their work as a peaked function with width proportional to N⁻¹. and the corrections to the thermodynamic quantities of the periodic chain are calculated in different orders of N⁻¹.

Our approach in this paper is to generate ensembles of random spin systems by computer, calculate the thermodynamic properties of each member of the ensemble and then take an average. We have limited ourselves to finite chains consisting of 500 - 2000 spins. We have found that the spin correlation functions and other thermodynamic quantities as calculated for these finite chains already exhibit the $N + \infty$ behaviour in the sense that increasing the number of spins does not alter the numerical results in significant figures.

The partition function in the absence of the external field can be obtained by using the transfer matrix method 9



and is given by:

$$Z = 2^{N} \begin{pmatrix} \pi^{N} \cosh K_{i} + \pi^{N} \sinh K_{i} \end{pmatrix}$$
(2)
i=1

where $K_i = \beta J_i/2$ and N is the number of spins, and we have assumed periodic boundary conditions. The second term inside the bracket of eqn. (2) would not appear if we had used the open end boundary conditions. All our numerical calculations have been performed in the thermodynamic limit $(N+\infty)$, where the second term in eqn. (2) does not contribute.

In the presence of a magnetic field H, one cannot obtain a closed form expression for Z by using the same method as for the H = 0 case. This is so because the transfer matrices T_i¹⁰ whose matrix elements are given by

$$(\sigma|T_{i}|\sigma') = e^{\frac{\beta}{2}(J_{i}\sigma\sigma' + h(\sigma+\sigma'))}$$
(3)

where $h = \frac{1}{2} g\mu_B H_z$ and $\sigma, \sigma' = \pm 1$,

do not commute in general if $h \neq 0$. Therefore one cannot diagonalize all T_i 's simultaneously. In order to obtain the partition function in this case, one has to first multiply N (2 x 2) nondiagonal matrices and then diagonalize the resulting (2 x 2) matrix. An alternate procedure is to use the method given by McCoy and Wu.¹

We now present the results for various thermodynamic quantities in the absence of magnetic field.



A. Specific heat

Using eqn. (2) for the partition function, we can obtain the specific heat per spin

$$C/_{NK} = \frac{\beta^2}{4N} \sum_{i=1}^{N} J_i^2 \operatorname{sech}^2 \kappa_i$$
(4)

where we have omitted terms which approach zero in the thermodynamic limit. In terms of the distribution function P(J) for the random variable J_i , we can replace the summation in eqn. (4) by an integration for large N and eqn. (4) becomes

$$C/_{Nk} = \frac{\beta^2}{4} \int_{J_{min}}^{J_{max}} P(J) J^2 \operatorname{sech}^2 K dJ$$
 (5)

where $K = \beta J/2$ and

$$\int_{J_{min}}^{J_{max}} dJ P(J) = 1$$
 (6)

defines the proper normalization condition for P(J) .

The specific heat C/Nk has been computed by using eqns. (5) and (6) for P(J) given by:

$$\begin{array}{c|c} & \frac{\nu+1}{|J_{m}|^{\nu}+1} & |J|^{\nu} , \quad 0 < J < J_{m} \quad \text{for } J_{m} > 0 \quad (F) \\ \hline P(J) = & \text{or } J_{m} \leq J \leq 0 \quad \text{for } J_{m} < 0 \quad (AF) \quad (7) \end{array}$$

0 otherwise



For the sake of comparison we have plotted C/Nk for v = 0 in fig. 1 together with C/Nk for the periodic chain with J = $J_m/2$. The important effects of randomness can be summarized as follows: at low temperatures $(kT<<|J_m|)$, for v = 0, the specific heat is linear in T in contrast to the exponential behaviour in the periodic system; in addition, from the figure we see that the effect of randomness is to reduce and broaden the peak in the specific heat. From eqns. (5) and (7), it is easily seen that at low temperatures, for a general v>0

$$C/Nk \sim (kT)^{\nu+1}$$
(8)

This behaviour is understood if we note that the energy spectrum does not have a gap.

B. Spin-spin Correlation Function and χ_{11}

The spin-spin correlation function $\,<\!\sigma_{iz}\,\sigma_{jz}^{>}\,$ is easily obtained by differentiating 10 the partition function Z .

$$L_{ij} = \langle \sigma_{iz} \sigma_{jz} \rangle = \frac{1}{Z} \frac{\partial j \cdot i z}{\partial K_{j-1} \partial K_{j-2} \dots \partial K_{i+1} \partial K_{i}} \quad \text{for } i < j$$
(9)

Using eqn. (1) for Z in eqn. (9) and taking the limit



 $N \rightarrow \infty$ we find ,

$$L_{ij} = \frac{\pi}{p=i} tanh K_p$$
(10)

The zero field $\chi_{||}$ is related to L_{ii} by

$$\frac{|X|}{|N\mu_R^2|} = \frac{g^2}{4kTN} \sum_{ij} L_{ij}$$
(11)

In the periodic case, where $K_p = K$, $L_{ij} = (tanh K)^{j-i}$ and is a function of j-i only. In this case eqn. (11) for $x_{||}/N\mu_B^2$ reduces to the one given by Bonner and Fisher.⁶ We note here that if we fix the index i, L_{ij} is not a smooth function of j because of the randomness. This is shown in Fig. 2, where we have plotted L_{1j} for a particular set J_1 , J_2 , ..., J_N randomly generated by computer; nevertheless it is a monotonically decreasing function which falls off rapidly for j large. To see how L_{1j} approaches zero as a function of j, we take an ensemble average: this is done by generating a number of similar random chains and taking an arithmetic average of L_{1j} . This smoothes out L_{1j} as a function of j and makes it a function only of r = j-1. Furthermore it can be shown that $L_{1i}=L(r)$ becomes equal to $L(1)^r$

For a general distribution of the exchange interaction J defined in eqn. (7) , we obtain for the ensemble averaged





Figure 2.--Spin-spin correlation function L1j = L(r) (r=j-1) as a function of distance r at kT = $.05\,|J_{\rm m}|$. The continuous and the dashed lines refer to an average on 10- and 500-member ensemble respectively.



 $\langle \sigma_{iz} \sigma_{i+1z} \rangle$ the following expression:

$$\overline{L(1)} = \frac{\nu+1}{J_m^{\nu+1}} \int_0^m J^{\nu} \tanh \frac{\beta J}{2} dJ \qquad (12)$$

For $T \rightarrow 0$, $\overline{L(1)}$ behaves asymptotically as

$$\overline{L(1)} \propto (1 - b_{v}(kT)^{v+1}) \frac{J_{m}}{|J_{m}|}$$
(13)

with

$$b_{v} = \frac{2(v+1)\Gamma(v+1)}{|J_{m}|^{v+1}}$$
(14)

In the special case v = 0, $\overline{L(r)}$ can be written as

$$\overline{L(r)} = \left(2 \frac{kT}{J_m} \text{ ln cosh } \frac{J_m}{2kT}\right)^r$$
(15)

We have calculated $\overline{L(r)}$ using eqn. (15) and we display it in Fig. 3 at different temperatures. One can see from the figure that the range of correlation increases with decreasing temperature, and decreases exponentially with r for a fixed temperature. For the sake of comparison, we have also plotted L(r) for the periodic case at $kT/J_{max} = 0.1$. The effect of randomness is to drastically reduce the range of spin correlation at low temperatures. However as the temperature is increased, the effect of exchange fluctuation is not as important because thermal fluctuations are large.

From eqn. (11) , realizing that $rac{1}{N} \, \Sigma_{\, \mathbf{i}}$ is equivalent





Figure 3.--Spin-spin correlation function $\overline{L(r)}$ as a function of r: (a) $kT/J_m = .5$, (b) $kT/J_m = .3$, (c) $kT/J_m = .1$. The continuous and dashed lines refer to the random (v=0) and periodic ($J=J_m/2$) ferromagnetic Ising chains respectively.



to taking an ensemble average, we obtain:

$$\frac{\chi_{||}}{N\mu_{B}^{2}} = \frac{q^{2}}{4kT} \frac{1+\overline{L(1)}}{1-\overline{L(1)}}$$
(16)

The parallel susceptibility is shown in Fig. (4) in the F and AF cases for v = 0. The very interesting results at low temperatures can be summarized as follows: $\chi_{||}/N\mu_{B}^{2}$ is finite in the AF case and equal to $\frac{\log 2}{|J_{m}|}$ at T = 0; it behaves as $\frac{1}{T^{2}}$ in the F case, contrary to the usual periodic Ising model where the existence of a gap makes $\chi_{||}/N\mu_{B}^{2}$ vanish (AF), or blow up (F) exponentially at T = 0. Furthermore, these results generalize in the following way for P(J) of eqn. (7).

For
$$J_{m} < 0$$
 (AF), $\frac{\chi_{\parallel}}{Nu_{2}^{2}} \sim \frac{g^{2}b_{\nu}}{8} (kT)^{\nu}$ (17)

For
$$J_{m} > 0$$
 (F) , $\frac{X_{||}}{N\mu_{B}^{2}} \sim \frac{g^{2}}{2b_{v}} - \frac{1}{(kT)^{v+2}}$ (18)

From eqns. (17) and (18) we can see that the low temperature behaviour depends crucially on the distribution of the exchange interactions. The absence of a gap for any $v \ge 0$ makes $\chi_{||}$ (AF) vanish and $\chi_{||}$ (F) blow up only as a power in T instead of exponentially. In fact it is instructive to note that we can recover the exponential behavior of $\chi_{||}$ at low temperature if we allow P(J) to be a constant







between J_1 and J_2 and 0 otherwise (when J_1 , J_2 are both <0 (AF) or >0 (F)).

C. Zero Field Perpendicular Susceptibility

A detailed study of the perpendicular susceptibility was made by Fisher⁷ for various one-and two-dimensional periodic Ising lattices. Two interesting features of one dimensional periodic Ising systems are the finiteness of χ_{\perp} at T = 0, and the smooth peak in the susceptibility as a function of temperature. We have analyzed the effect of randomness on these features. To obtain χ_{\perp} , we introduce a field H_{χ} in the x-direction. The Hamiltonian is given by

$$H = -\frac{1}{2} \sum_{i} J_{i} \sigma_{iz} \sigma_{i+1z} - \frac{1}{2} g_{\mu} B H_{x} \sum_{i} \sigma_{ix}$$
(19)

Taking into account the noncommutativity of the second term in the Hamiltonian with the first term (H_{o}) , we obtain,

$$\frac{\chi_{\perp}(T)}{N\mu_{B}^{2}} = \frac{g^{2}}{4N} \sum_{ij}^{\beta} \int_{0}^{\beta} \langle \sigma_{ix}(y) \sigma_{jx}(0) \rangle dy \quad (20)$$

 $^{-\beta H}_{0}$ $^{\beta H}_{0}$ and <A> refers to the usual zero field thermal trace. It is easily seen that only the terms with i = j contribute to χ_{\perp} . After taking the trace and carrying out the y integration, we

have

$$\frac{\chi_{\perp}}{N\mu_{B}^{2}} = \frac{g^{2}}{4NkT} \sum_{i=1}^{N} \frac{\kappa_{i} \tanh \kappa_{i} - \kappa_{i-1} \tanh \kappa_{i-1}}{\kappa_{i}^{2} - \kappa_{i-1}^{2}}$$
(21)

Equation (21) in the periodic limit $(K_{i-1} = K_i = K)$ reduces to⁷

From eqns. (21) and (22) it is seen that χ_{\perp} is independent of the sign of J_i and therefore its behaviour is the same in the ferro and antiferromagnetic cases. In Fig. (5), we have plotted $\chi_{\perp}|J_m|/N\mu_B^2$ for random and periodic chains in the case of constant distribution. The two pronounced effects of randomness are: (1) $\chi_{\perp}(0)$ for the random system is enhanced by an amount log 2 over $\chi_{\perp}(0)$ for the periodic system with $J = J_m/2$. (2) The peak in $\chi_{\perp}(T)$ as a function of T that occurs for a periodic chain is completely washed out. However we believe that $\chi_{\perp}(T)$ has still an essential singularity at T = 0 in the random case.

In addition to the low and intermediate temperature $(kT\ \ _{\sim}\ J_m)$ behaviour of χ_{\perp} that we have discussed above, we find that for $kT{>>}J_m$

$$\frac{\chi_{\perp}}{\mu_{\mu}^2} \sim \frac{1}{k_T}$$
(23)







The absence of a Weiss term can be ascribed to the absence of exchange interaction along x and y directions. The effect of incorporating such interactions on χ_1 will be discussed in the next Section.

3. Effect of Random xy Interaction

In the presence of an xy interaction with random exchange J_i^{\perp} , the total Hamiltonian is given by

$$H = H_{I} + H_{XY}$$
(24)

where $\rm H_I$ is the Ising Hamiltonian given in eqn. (1) which includes the interaction with an external magnetic field and $\rm H_{y,v}$ is given by

$$H_{xy} = -\frac{1}{2} \sum_{i} J_{i}^{\perp} (\sigma_{ix} \sigma_{i+1x} + \sigma_{iy} \sigma_{i+1y})$$
(25)

 J_i^{\perp} is the random exchange interaction along the x and y directions. An exact solution of the Hamiltonian H for an arbitrary distribution J_i^{\perp} is difficult. However, the effect of including H_{Xy} on the high temperature behaviour of χ_{\perp} and $\chi_{\mid\mid}$ can be obtained by using a perturbation theory.



order $(\beta H)^2$.

Let \vec{M} be the magnetic moment operator $(\vec{M} = \frac{1}{2} g\mu_B \sum_i \vec{\sigma}_i)$. In the presence of the total Hamiltonian $H = H_I + H_{xy}$, one has

$$\langle \vec{M} \rangle = Tr e^{-\beta H} \vec{M} / Tr e^{-\beta H}$$
 (26)

Expanding the right hand side of eqn. (26) up to terms of order $\left(\beta H\right)^2$, we have

$$\langle \vec{M} \rangle = \frac{1}{\langle 1 \rangle_{\infty}} \left[-\beta \langle H\vec{M} \rangle_{\infty} + \frac{\beta^2}{2} \langle H^2\vec{M} \rangle_{\infty} \right]$$
(27)

Where $\langle X \rangle_{\infty}$ denotes the infinite temperature trace of any operator X. In obtaining eqn. (27), we have made use of the fact that $\langle \vec{M} \rangle_{\infty} = \langle H \rangle_{\infty} = 0$. From eqn. (27), we can obtain χ_{\perp} by taking the magnetic field Halong the x-direction and calculating dM_{χ}/dH_{χ} at $H_{\chi} = 0$. We obtain

$$\frac{\chi_{\perp}}{N\mu_{\rm p}}_2 = \beta + \frac{\beta^2}{N} \sum_{i} J_{i}^{\perp}$$
(28)

From eqn. (28), one finds that the Curie Weiss constant $\boldsymbol{\theta}_{\parallel}$ is given by

$$k\theta_{\perp} = \frac{1}{N}\sum_{i} J_{i}^{\perp} = \int P(J^{\perp}) J^{\perp} dJ^{\perp}$$
(29)



A similar expansion can be performed for $\chi_{||}$ by taking the field along the z-direction and one finds that

$$\frac{X|}{N\mu_{B}^{2}} = \beta + \frac{\beta^{2}}{N} \sum_{i}^{N} J_{i}$$
(30)

from the above equation, we see that up to order β^2 there is no contribution to $\chi_{||}/N\mu_B^{-2}$ from $H_{\chi y}$, and therefore the Curie Weiss constant $\theta_{||}$ given by

$$k \theta_{||} = \frac{1}{N} \sum_{i} J_{i} = \int JP(J) dJ$$

is unaffected by the inclusion of $H_{_{\rm X\,V}}$.

The ground and low lying excited states of the system described by the Hamiltonian $H_I + H_{xy}$ depend crucially on the probability distributions P(J) and $P(J^{\perp})$. However, for the ferromagnetic coupling between spins with $0 < J_i^{\perp} < J_i^{}$, the ground state is the one where all the spins are either pointing up or down. In case of a more general distribution of J_i^{\perp} , the ground state need not be the same anymore.

4. Conclusions

Our calculations show that the low temperature (T+ 0) behaviour of different thermodynamic quantities such as C, $\chi_{||}$ and $\chi_{|}$ are affected differently by



the randomness. For example, in case of ferromagnetic coupling, the essential singularity in $\chi_{||}$ at T = 0 changes to a pole singularity by introducing a randomness which removes the gap in the energy spectrum that exists in the periodic Ising case. In contrast, the specific heat which also has an essential singularity at T = 0 for the periodic chain becomes analytic in the random case. These results are consistent with the findings of McCoy and Wu² (specific heat) and Griffiths¹¹ (susceptibility) for a two dimensional Ising system.



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