Progress of Theoretical Physics, Vol. 48, No. 6B, December 1972

Thermodynamic Properties of the One-Dimensional Half-Filled-Band Hubbard Model. II[†]

——Application of the Grand Canonical Method——

Hiroyuki SHIBA*)

Department of Physics, University of California
Los Angeles, California 90024

(Received June 14, 1972)

In order to determine finite-temperature properties of the infinite one-dimensional Hubbard model for the half-filled band, finite systems such as chains with 2 to 5 atoms and rings with 4 and 6 atoms are studied with the application of the grand canonical ensemble. The obtained temperature dependence of the specific heat, the entropy, the magnetic susceptibility and some correlation functions clearly shows a rearrangement of the electronic state of the system with the increase of the strength of the Coulomb interaction relative to the transfer integral. In the light of our new results the functional integral approach recently proposed by Kimball and Schrieffer as well as Hubbard's approximate theory is examined.

§ 1. Introduction

In a previous paper,[1] of which this may be regarded as a continuation, we presented results of exact calculations on thermodynamic properties of finite systems described by the one-dimensional half-filled-band Hubbard model. There the canonical-ensemble method of statistical mechanics was applied, which may be appropriate to "real" molecules. In order to guess properties of the infinite systems from results for finite systems the grand-canonical-ensemble method should be better as will be explained later and shown in this paper clearly.

Let us start with a brief summary of previous studies for self-containedness. The Hubbard Hamiltonian, which consists of the tight-binding approximation plus short-range Coulomb interaction between two electrons with opposite spins, is a simplified model to investigate the origin of transition-metal magnetism, especially the role of the electron correlation.[2] An important conclusion of three representative theories[3)~5)] is that when electron-to-atom ratio is far from unity, as the result of the correlation effect electrons avoid each other at a sacrifice of their kinetic energy, and the effective interaction between electorons is reduced. Secondly Hubbard[3] pointed out that in the half-filled band, where the electron-to-atom ratio is equal to 1, the metal-insulator transition may occur as the relative

† Work supported in part by the National Science Foundation. Grant No. GP-21290.

*) Present address: Department of Physics, Faculty of Science, Osaka University, Toyonaka.

magnitude of Coulomb repulsion to transfer integral increases. Since the one-dimensional model of the Hubbard Hamiltonian is easy to handle mathematically and to give some exact conclusions without resorting to any approximations, one should be able to throw additional light on the correlation-effect problem. Besides that there are some reasons to believe it worthwhile to study thoroughly the one-dimensional Hubbard model. i) Low-dimensional systems such as one-dimensional ones must have their peculiar behaviors different from those of three-dimensional systems. Especially properties of one-dimensional itinerant-electron systems should be a fascinating problem, but it has not yet been well understood theoretically. ii) Experimental investigations have been reported on one-dimensional itinerant-electron systems such as "mixed-valence" square-planar complex salt $K_2Pt(CN)_4Br_{0.3}\cdot 2.3H_2O$[6),7)] and organic charge transfer salt *N*-methylphenazinium tetracyanoquinodimethan (NMP—TCNQ).[8),9)] In particular it is an controversial problem[10)] whether the effect of correlation is vitally important to understand NMP—TCNQ or not. Therefore it must be useful to study in detail the role of the electron correlation in the one-dimensional Hubbard model, a simple itinerant-electron system.

Let us review what is already known about the one-dimensional Hubbard model.

i) *Ground-state properties*

Lieb and Wu[11)] gave an excellent analysis, based on which the analytic expression has been obtained for ground-state energy[11)] and magnetic susceptibility[12)] of the half-filled band. It is also possible to study exactly those quantities for arbitrary values of electron-to-atom ratio.[13)]

ii) *Finite-temperature properties*

An integral-equation formulation was given[14)] on the basis of some plausible conjectures. It must be useful, but unfortunately the equations have not yet been solved. In the previous paper I we proposed a different approach to study the one-dimensional Hubbard model at finite temperatures. There all eigenvalues and eigenfunctions for finite half-filled-band systems with 2 to 6 atoms were calculated exactly and the temperature dependence of various thermodynamic quantities was determined by applying the canonical ensemble.

The purpose of this paper is to report the results of our new calculations on the same system as in I. The Hamiltonian is given by

$$\mathcal{H}=-\sum_{i,j,\sigma} t_{ij}C_{i\sigma}^{\dagger}C_{j\sigma}+U\sum_{i} n_{i\uparrow}n_{i\downarrow}, \tag{1·1}$$

$$n_{i\sigma}\equiv C_{i\sigma}^{\dagger}C_{i\sigma}$$

with $t_{ij}=t$ for $|i-j|=1$, and $t_{ij}=0$ otherwise. Here $C_{j\sigma}$ ($C_{j\sigma}^{\dagger}$) is the annihilation (creation) operator of an electron with spin σ at the j site. The grand-canonical-ensemble method is applied in this paper instead of the canonical en-

semble. It turns out that the present approach is better to guess thermal properties of the *infinite* one-dimensional Hubbard model from finite systems. Our basic standpoint is that most thermodynamic properties of the infinite chain of the Hubbard Hamiltonian (1·1) are well represented by those of small finite systems. Suppose an infinite chain is cut into segments, each of which consists of a finite number of atoms as shown in Fig. 1. One can expect that the properties of a segment asymptotically approaches those of the infinite chain irrespective of the

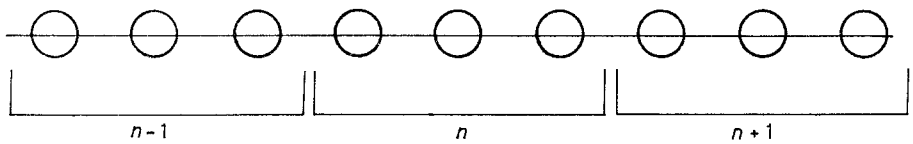


Fig. 1. An infinite Hubbard chain is cut into segments, each of which consists of a finite number of atoms (say, 3 atoms in this case). In the grand canonical ensemble for the half-filled band the average number of electrons in a segment is assumed to be equal to the number of atoms of the segment.

boundary conditions imposed on the ends of the segment, if the number of constituent atoms of a segment is increased. Since the nearest-neighbor transfer is assumed in our Hamiltonian, we hope even a segment with a small number of atoms should be able to describe essential features of the infinite one-dimensional Hubbard model. In order to make our argument convincing it is important to confirm that the convergence with respect to the size of the system is reasonably rapid. But the results in I are not satisfactory enough for these reasons: The high-temperature peak of the specific heat, which was found at $k_BT\sim\frac{1}{4}U$ when $U/t\gg 4$, depends on the size of the system too strongly to estimate the position and height of the peak for the infinite chain. For the same reason it was difficult to get a quantitative conclusion on the temperature dependence of the entropy and the internal energy of the infinite chain at high temperatures ($k_BT>\frac{1}{4}U$). The reason for the difficulty may be traced back to the following fact. In the canonical-ensemble treatment the total number of electrons in a segment is strictly kept constant, while if one regards the segment as a part of the infinite chain there always exist fluctuations of the electron number arising from charge transfers from one segment to another. In the grand canonical method this charge fluctuations are statistically taken into account. Since the dominant contribution to high-temperature properties comes from single-particle excitations (or charge-transfer excitations), one can expect that the grand canonical ensemble is a better approach to study thermodynamic properties of the *infinite* Hubbard chain from finite systems. The calculations presented in this paper show that it is the case. Another advantage of the grand canonical method is that in the atomic limit ($t/U\to 0$) it always gives exact thermodynamics of the *infinite* chain even when applied to a segment with a finite number of atoms.

Thus in this paper we will be able to determine in a considerable accuracy the temperature dependence of thermodynamic quantities of the infinite half-filled-band Hubbard chain. After the results of our calculations are presented, our next task will be to examine some approximate theories applied to the same system by comparing their conclusions with ours. Especially a recently proposed, sophisticated theory[15),16)] based on the functional integral formulation is worthwhile to discuss in this connection, because the adequacy of the approximations they used has not yet been examined in the light of such a comparison.

The program of this paper is as follows: In § 2 we describe the results of our calculations for finite systems and discuss the properties of the infinite chain. Section 3 is devoted to a comparison of approximate theories with our conclusions and a brief comment on their validity. Supplementary discussions are given in the last section.

§ 2. Thermodynamic properties of finite systems

2.1 *Scheme of calculation*

As emphasized in the previous section our approach is to perform exact calculations of thermodynamic quantities of *finite* half-filled-band systems described by the Hamiltonian (1·1). Two types of boundary conditions are imposed: (i) Chain—a system with free ends or (ii) ring—a system with cyclic boundary conditions. The total number of eigenvalues we need in the grand canonical ensemble is 4^N (N is the total number of atoms in the system), while in the canonical ensemble $(2N)!/(N!)^2$ eigenvalues are needed. The size of the eigenvalue matrix to be diagonalized can be reduced to a large extent by using the symmetry of the system:

(1) There is the electron-hole symmetry in rings with even number of atoms and in chains.
(2) The total spin and its z-component are conserved.
(3) The geometry of the system further simplifies the problem.

Actually we have calculated all eigenvalues (and eigenfunctions if necessary) for chains with 2 to 5 atoms and rings with 4 and 6 atoms. Thermodynamic properties such as specific heat, entropy and magnetic susceptibility have been evaluated by employing the elementary statistical mechanics of the grand canonical ensemble. In the half-filled band with the electron-hole symmetry the chemical potential μ is equal to $U/2$ independent of the temperature. Thus the grand partition function Z is given by

$$Z=\mathrm{Tr}\exp(-\beta\tilde{\mathcal{H}}), \tag{2·1}$$

where Tr denotes the trace and $\tilde{\mathcal{H}}$ is defined by

$$\tilde{\mathcal{H}}=\mathcal{H}-\mu\sum_{i\sigma}n_{i\sigma} \tag{2·2}$$

with $\mu=U/2$.

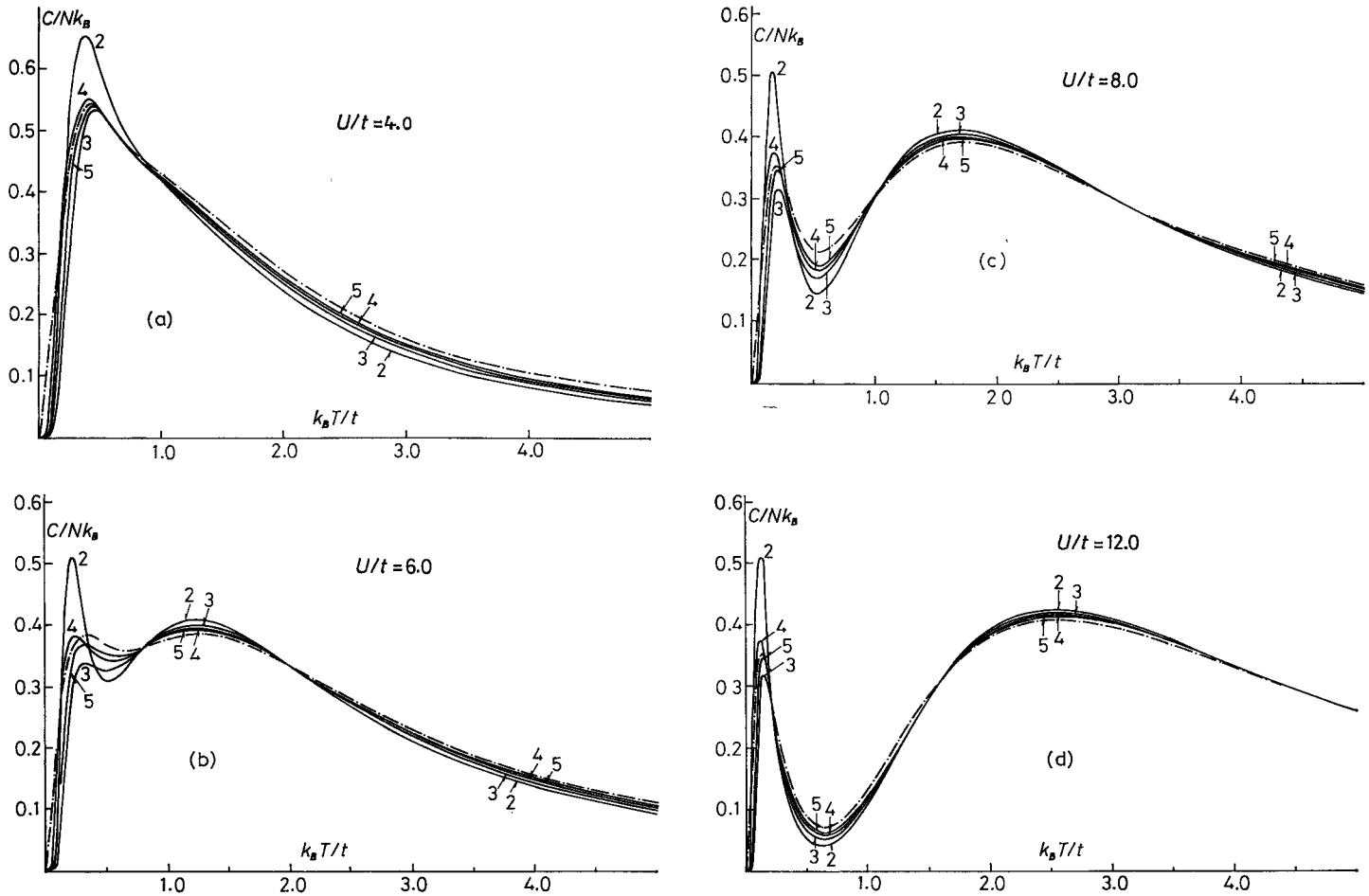


Fig. 2. Specific heat C/Nk_B of chains with 2 to 5 atoms vs temperature for four typical values of U/t: (a) U/t=4.0, (b) U/t=6.0, (c) U/t =8.0 and (d) U/t=12.0. The dot-dashed lines are extrapolations to the infinite chain (see the text).

2.2 *Specific heat, entropy and magnetic susceptibility*

The temperature dependence of the specific heat of chains with 2 to 5 atoms is shown in Figs. 2(a)$\sim$(d) for some typical values of U/t. When $U/t \ll 4$ the gross feature of the specific heat is essentially the same as that of the noninteracting electrons with $U/t=0$. As shown in Fig. 2 of I the specific heat of the infinite chain for $U/t=0$ has a peak at $k_BT/t \sim 0.65$. As U/t is increased, the peak splits into two. It clearly reflects a rearrangement of the electronic structure in the system. The low-temperature peak for $U/t \gg 4$ arises from low-lying collective spin-wave excitations, while the high-temperature broad peak comes from single-particle excitations (or charge-transfer excitations) across the Hubbard gap. That picture was first presented in I and we still believe it correct. Comparing the present calculation with I, one notices that in the present results the convergence with respect to the size of the system is excellent in contrast to I. In the low-temperature region, where charge-transfer excitations are not important, the present result is essentially the same as that of I, but at high temperatures, i.e., around the high-temperature peak, it is drastically different from the previous result (Figs. 1(a)$\sim$(c) of I) obtained by the application of the canonical ensemble. As far as the high-temperature peak is concerned, the size dependence of the present result is much weaker than that of the previous one. It is because in the temperature region near the high-temperature peak, charge fluctuations are dominant, which are in a statistical way taken into account in the grand canonical method. Thanks to the improvement we can now guess the specific heat of the *infinite* chain. A very accurate extrapolation from our results to the infinite system does not seem possible, for our calculations are limited to systems with less than 6 atoms. But we can make a semiquantitative guess of the specific heat of the infinite chain on the basis of our calculations, and it is shown in Figs. 2(a)$\sim$(d). The size dependence of our results for finite systems is not so large. Therefore we may expect that the specific heat of the infinite chain should be very close to our extrapolation shown in the figures. We also expect that the specific heat of the infinite chain is proportional to k_BT at very low temperatures and the coefficient becomes large with U/t.

The calculation of the entropy was also performed and the results are shown in Figs. 3(a)$\sim$(c). One finds at once that the size dependence of the entropy is quite small. The reason for that may be understood by writing the entropy $S(T)$ in the form

$$S(T)=\int^{T}\frac{C(T')}{T'}dT'$$

with the specific heat $C(T)$. Thus the overshooting and undershooting in the specific heat are considerably cancelled out in the entropy. Anyhow it is a great advantage of the present calculation based on the grand canonical method that the entropy does not strongly depend on the size of the system. Therefore one

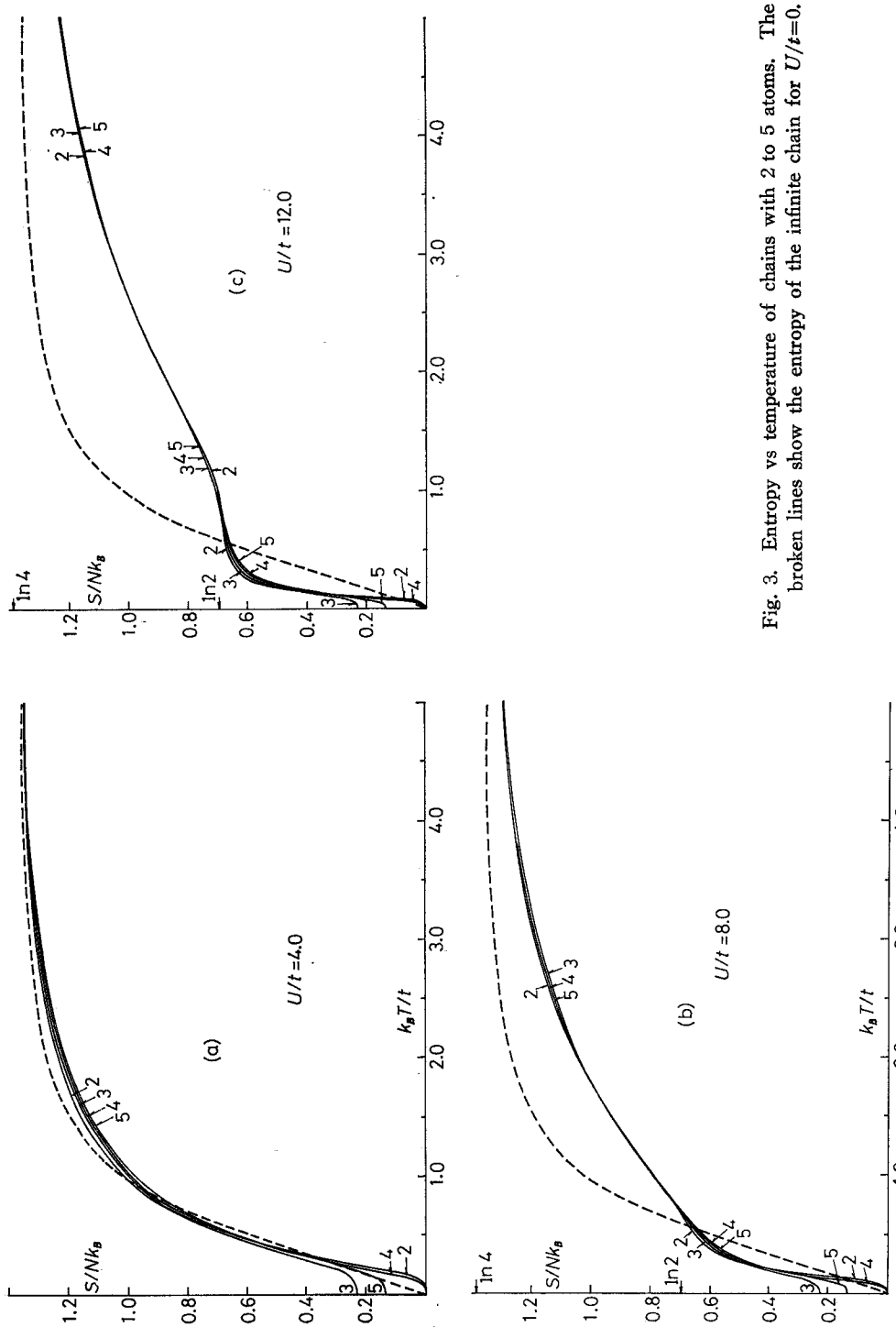


Fig. 3. Entropy vs temperature of chains with 2 to 5 atoms. The broken lines show the entropy of the infinite chain for $U/t=0$.

may easily guess the entropy of the *infinite* chain from our results. When U/t is increased two stages of excitations become distinct. Roughly speaking, the first stage up to $k_B \ln 2$ is connected with the spin-wave excitations and the second one from $k_B \ln 2$ to $k_B \ln 4$ arises from charge transfer-excitations, which create holes and doubly occupied states. As for the entropy of the infinite system we believe that at low temperatures it is linear in k_BT with the coefficient increasing with U/t, and that at high temperatures it is very close to the entropy of finite systems.

Let us turn to the magnetic susceptibility. The results for finite systems are given in Figs. 4 (a)$\sim$(c). The magnetic susceptibility of the infinite chain for $U=0$ is included in Fig. 4(a) for comparison. It turns out that in the region $k_BT>t$ the magnetic susceptibility of the infinite chain is close to that of finite systems. It is because the discreteness of energy levels of finite systems is not essential to thermal properties in that temperature region. On the other hand, at low temperatures $k_BT<t$, the even-odd effect is evident. The exact theory for the ground state[12] gives the zero-temperature susceptibility of the infinite chain as a function of U/t. Therefore using the exact result at $T=0$°K and our result at high temperatures, we can semiquantitatively estimate the magnetic susceptibility of the *infinite* chain at arbitrary values of U/t as shown in Figs. 4(b) and (c). We believe that the magnetic susceptibility of the *infinite* chain starts with a finite value given by Takahashi's theory, has a maximum around $k_BT\sim 2t^2/U$ when $U/t\gg 1$ and then goes down. The susceptibility $\chi(T)$ is enhanced over the value for $U/t=0$ due to the effect of correlation. The difference of the present calculation and the previous one (Fig. 4 in I) is small, but the convergence of the present results is a little better at high temperatures.

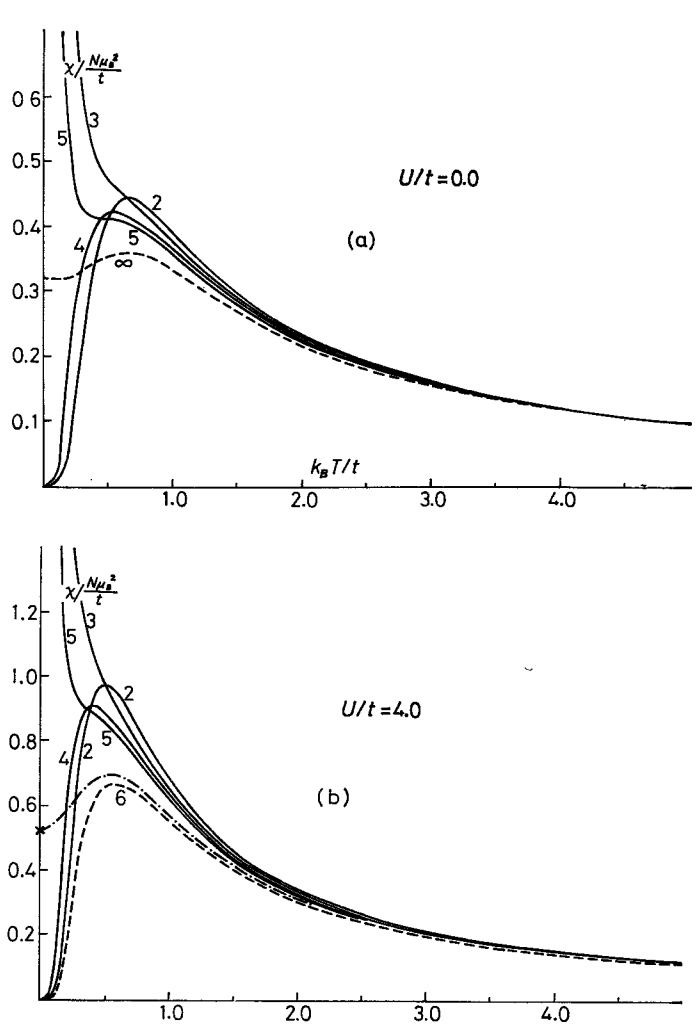
Summing up the results obtained so far, it is clear that the application of the grand canonical method has greatly improved the convergence in the high-temperature region. Therefore just by using the grand canonical ensemble the thermodynamic properties of the infinite chain seem to be quite well represented by those of small finite systems. The exact solution for the absolute-zero temperature is helpful to determine the thermodynamic behavior of the infinite chain throughout the whole temperature domain. The obtained results should be useful to examine the validity of approximate theories proposed so far. The discussion on the subject will be made in § 3.

2.3 *Correlation functions*

As we showed in I, the temperature dependence of the correlation function

$$L_\delta(T)=\frac{1}{N}\sum_j \langle \boldsymbol{S}_j\cdot\boldsymbol{S}_{j+\delta}\rangle \qquad (2\cdot 3)$$

is useful to obtain the detailed information on the electronic structure of the one-dimensional half-filled-band Hubbard model. Here $\langle\cdots\rangle$ denotes the average over



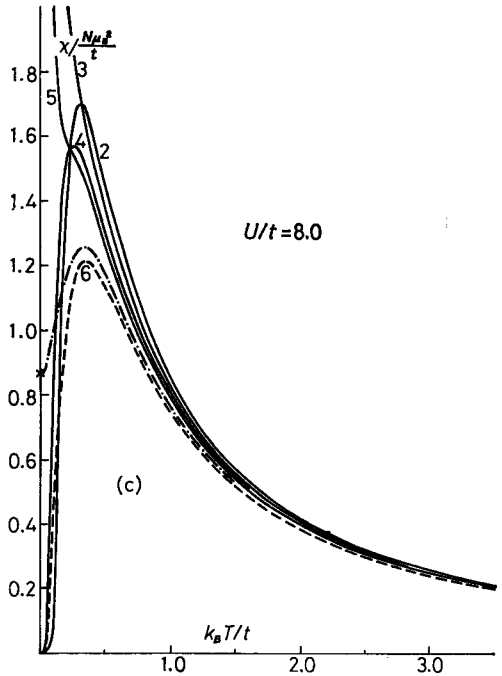


Fig. 4. Temperature dependence of the susceptibility $\chi/(N\mu_B^2/t)$ of chains with 2 to 5 atoms. The broken line in (a) is the magnetic susceptibility of the infinite chain for $U/t=0$. In (b) and (c) the results for the ring with 6 atoms are included. The cross at $T=0$°K shows the exact value for the infinite chain,[12] and the dot-dashed lines are extrapolations to the infinite chain.

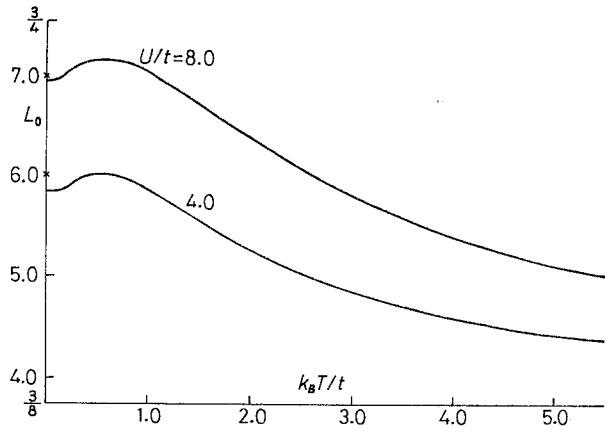


Fig. 5. Temperature dependence of L_0 for two typical values of U/t. L_0 was evaluated for the $N=6$ ring. The crosses at $T=0$°K show the exact values of L_0 obtained for the infinite chain.[1)]

the grand canonical ensemble and S_j is the spin operator at the j site $S_j = \sum_{\sigma\sigma'}\langle\sigma|S|\sigma'\rangle C^{\dagger}_{j\sigma}C_{j\sigma'}$. L_0, L_1 and L_2 were determined for the $N=6$ ring, the largest system in our calculation. The results for two typical values of U/t are shown in Figs. 5 and 6. Note that L_0 for completely localized electrons (one electron per atom) is equal to 3/4, while for half-filled-band free electrons $L_0 = 3/8$. Comparing the present results with the previous ones based on the canonical ensemble (Figs. 8 and 10 of I), one notices that the temperature dependence of L_0 of the present calculation is more rapid than that in the canonical ensemble, while the present results for L_1 and L_2 are essentially the same as the previous ones. We belive that the present L_0 should be closer to the corresponding quantity of the *infinite* chain, for as argued in § 2. 2, the charge fluctuations mainly responsible for the high-temperature properties of the infinite chain are statistically taken into account in the grand-canonical-ensemble treatment. In fact L_0 goes to 3/8 at $k_BT/U \gg 1$, which is independent of the size of segment N, while in the canonical ensemble the high-temperature limit of L_0 is $(3/8)2N/(2N-1)$ and is strongly size-dependent.

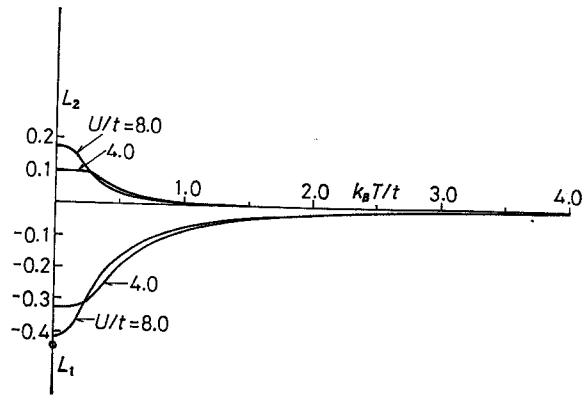


Fig. 6. Correlation functions L_1 and L_2 vs temperature. They were calculated for the 6-atom ring. The circle shows the value of L_1 for the infinite antiferromagnetic Heisenberg chain at $T=0$°K.[17)]

The physical picture emerging from the temperature dependence of L_0, L_1 and L_2 is as follows. Suppose U/t is large, say, $U/t>4$. Then as the temperature goes down, each site is occupied by one electron and local moments are formed. At low temperatures ($k_BT<2t^2/U$) the antiferromagnetic short-range spin ordering becomes evident. The short-range order manifests itself not only in the temperature dependence of L_1 and L_2 but also in the slight decrease of L_0 at low temperatures as explained in I.

2.4 *The case of the attractive interaction* ($U<0$)

Since the origin of the second term of the Hamiltonian (1·1) is Coulomb interaction between electrons, U should be regarded as positive, but a hypothetical system with $U<0$ is worthwhile to discuss.

Notice, first of all, that one can establish a simple relation between the cases with positive U and negative U, if the band is half-filled. Let us assume U is negative. The Hamiltonian $\widetilde{\mathcal{H}}$ relevant to the grand canonical ensemble for the half-filled system is given by Eq. (2·2) with the chemical potential $\mu=U/2$. With the use of newly defined creation and annihilation operators

$$\begin{cases} C_{j\downarrow}^{\dagger}=e^{i\pi j}b_{j\downarrow}, & C_{j\downarrow}=e^{-i\pi j}b_{j\downarrow}^{\dagger}, \\ C_{j\uparrow}^{\dagger}=b_{j\uparrow}^{\dagger}, & C_{j\uparrow}=b_{j\uparrow}, \end{cases} \tag{2·4}$$

we can transform $\widetilde{\mathcal{H}}$ into the form

$$\widetilde{\mathcal{H}}=-\sum_{i,j,\sigma}t_{ij}b_{i\sigma}^{\dagger}b_{j\sigma}-U\sum_{i}b_{i\uparrow}^{\dagger}b_{i\uparrow}b_{i\downarrow}^{\dagger}b_{i\downarrow}+\frac{U}{2}\sum_{i\sigma}b_{i\sigma}^{\dagger}b_{i\sigma}-\frac{U}{2}N. \tag{2·5}$$

Here the system is assumed to be a chain or a ring with even N. Therefore except for the constant term $-\frac{1}{2}UN$ $\widetilde{\mathcal{H}}$ is equivalent to the Hamiltonian having the interaction term $|U|$ instead of U. One of the consequences of this fact is that for the half-filled band the specific heat and entropy of a chain or a ring with even number of atoms is independent of the sign of U, because these quantities are determined just by the distribution of energy levels. The nature of wave functions for $U<0$ is of course quite different from that for $U>0$. The ground state for $U>0$ is antiferromagnetic, while for $U<0$ the ground state is, so to speak, the charge density wave, which may be visualized in Fig. 7 for $|U| \gg t$. Actually in the ground state for $U<0$ there exists a zero-point oscillation, which corresponds to the change of the places of a doubly occupied state and a neighboring vacant state with each other just as the spin flipping motion in the antiferromagnetic ground state. Since the charge density wave is the ground

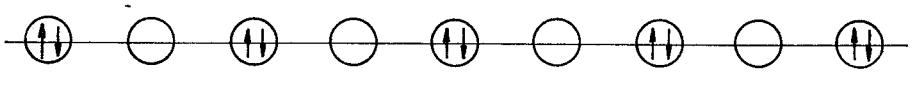


Fig. 7. A picture of the ground state for the large attractive interaction between electrons ($|U| \gg t$). A vacancy and a doubly occupied state are alternating. As a matter of fact a vacant state and a neighboring doubly occupied state are changing places with each other in the ground state.

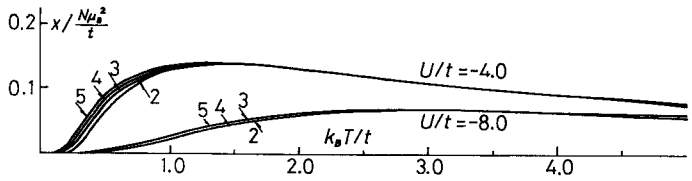


Fig. 8. Magnetic susceptibility vs temperature of chains with 2 to 5 atoms. Two typical values of the attractive interaction are taken. In contrast to Figs. 4(a)~(c) there appears no even-odd effect in this case, because for the attractive interaction the lowest state for an even number of electrons always has an eigenvalue of $\tilde{\mathcal{H}}$ lower than for any odd numbers of electrons.

state for $U<0$, the susceptibility at zero temperature is equal to zero.[12] The temperature dependence of the magnetic susceptibility for two typical values of U/t is shown in Fig. 8. Compared with the value for $U/t=0$, the susceptibility is clearly suppressed by the attractive interaction between electrons.

§ 3. Discussion of some approximate theories

In § 2 we have determined the thermodynamic properties of finite half-filled-band systems on the basis of the grand canonical treatment. Judging from the fact that the size dependence of the present results is weak compared with that of I using the canonical ensemble, we have concluded that the grand canonical approach is better to guess the thermal properties of the infinite system. Therefore our results should be useful to discuss the reliability of some of typical approximate theories proposed so far for the Hubbard model and to make some comments on them.

(i) *Functional integral method*

Recently Kimball and Schrieffer[15] have presented a theory of thermodynamic properties of the one-dimensional half-filled-band Hubbard model, employing the functional integral method and applying several steps of approximations described below. An analogous theory was proposed independently by Cyrot.[16] They use the identity

$$Un_{j\uparrow}n_{j\downarrow}=\frac{U}{4}(n_{j\uparrow}+n_{j\downarrow})^2-\frac{U}{4}(n_{j\uparrow}-n_{j\downarrow})^2 \qquad (3\cdot1)$$

and rewrite the partition function of the system exactly in terms of the functional integral over time-dependent fluctuations. To make this approach feasible they make the following approximations:

(1) It is assumed that magnetic fluctuations (coupled with $n_{j\uparrow}-n_{j\downarrow}$) are more important than charge fluctuations (coupled with $n_{j\uparrow}+n_{j\downarrow}$) and they replace the latter by the extremal value.

(2) The static part of the magnetic fluctuations are assumed to be the most important.

(3) The system is assumed paramagnetic.

(4) Under the static approximation one can establish the analogy between the present system and a binary alloy. On this basis they apply the coherent potential approximation (CPA).[18]

(5) Dynamical fluctuations are roughly taken into account as the Kondo spin quenching in essence.

For comparison with our results (Fig. 2) we show in Fig. 9 the specific heat calculated by Kimball and Schrieffer. At first glance both of them have a double-peak structure and resemble each other. But carefully examing Fig. 9, one notices that the high-temperature peak for a large U case (say, $U/t=8$) is located at a too low temperature compared with our curves. Secondly their theory is not applicable to the low-temperature region with large U because of the assumption (3). We have shown that the low-temperature peak has its origin in the short-range antiferromagnetic ordering contrary to the Kondo spin quenching. One of the apparent shortcomings of Kimball and Schrieffer's theory is, as pointed out by Bari,[19] that it predicts incorrect results for the atomic limit ($t\to 0$). This is due to the approximation (1), but may be overcome by using

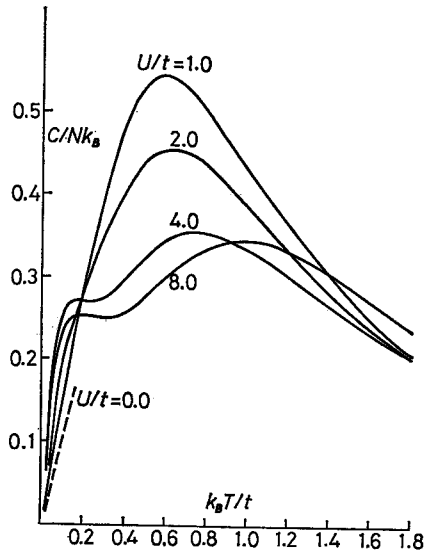


Fig. 9. Temperature dependence of the specific heat of the one-dimensional half-filled-band Hubbard model obtained by Kimball and Schrieffer.[15]

$$Un_{j\uparrow}n_{j\downarrow}=\frac{U}{2}(n_{j\uparrow}+n_{j\downarrow})-\frac{U}{2}(n_{j\uparrow}-n_{j\downarrow})^2 \qquad (3\cdot 2)$$

instead of (3·1), although the use of (3·2) brings difficulties in the RPA calculation.[21] In any case a big trouble about the functional integral method is that the approximations are not controlled.

(ii) *Hubbard's approximation*

In I we showed details of the results obtained by applying Hubbard's "improved" approximation[3] to the one-dimensional half-filled-band Hubbard model and assuming the system is paramagnetic throughout the whole temperature domain. His theory is based on a truncation scheme for coupled Green's functions, which is analogous to the CPA. We will not repeat the results in I. But since the thermal properties of the infinite chain have been determined with a good accuracy on the basis of the grand canonical ensemble, it is interesting to discuss briefly the Hubbard approximation in the light of the present calculations.

In the previous paper I the specific heat, the magnetic susceptibility and the

quantity $L_0(T)$ were determined for a typical large value U/t ($U/t=8$) by the Hubbard approximation. They should be compared with Figs. 2(c), 4(c) and 5 of this paper, respectively. One finds that at high temperatures (say, $k_BT/t>1.5$) the results by Hubbard's approximation remarkably coincide with our present ones. Therefore as far as thermal properties at high temperatures are concerned, Hubbard's theory may be regarded as a good approximation for large U/t in contrast to Kimball and Schrieffer's. We believe that the main reason for that is Hubbard's theory correctly reproduces the atomic limit ($t\to 0$).

At low temperatures the difference between Hubbard's and ours is striking. It is simply because in the latter the paramagnetism is assumed and the CPA-like approximation is used, in which the short-range spin ordering is completely ignored. Thus such behaviors characteristic of antiferromagnetic spin correlations as the low-temperature peak of the specific heat (Fig. 2(c)), the low-temperature maximum of the magnetic susceptibility (Fig. 4(c)) and the decrease of L_0 at low temperatures (Fig. 5) are completely missing in Hubbard's theory.

§ 4. Supplementary Discussion

In this section we will make comments on some problems related to the subject of this paper.

(i) The infinite one-dimensional half-filled-band Hubbard model is equivalent to a certain localized spin system. In fact introducing Pauli operators by[22]

$$\begin{cases} a_{j\downarrow}^{\dagger}=C_{j\downarrow}^{\dagger}\exp[i\pi\sum_{l=1}^{j-1}C_{l\downarrow}^{\dagger}C_{l\downarrow}], \\ a_{j\uparrow}^{\dagger}=C_{j\uparrow}^{\dagger}\exp[i\pi(\sum_{l=1}^{N}C_{l\downarrow}^{\dagger}C_{l\downarrow}+\sum_{l=1}^{j-1}C_{l\uparrow}^{\dagger}C_{l\uparrow})], \end{cases} \tag{4·1}$$

we can write the Hamiltonian $\widetilde{\mathcal{H}}$ ($=\mathcal{H}-(U/2)\sum_{i\sigma}n_{i\sigma}$) of a chain with N sites in terms of Pauli operators. It is more natural to use spin operators for spin 1/2

$$\begin{cases} S_{j\sigma}^{x}+iS_{j\sigma}^{y}=a_{j\sigma}^{\dagger}, \\ S_{j\sigma}^{z}=a_{j\sigma}^{\dagger}a_{j\sigma}-\frac{1}{2}. \end{cases} \tag{4·2}$$

Then the Hamiltonian $\widetilde{\mathcal{H}}$ is given by

$$\widetilde{\mathcal{H}}=-2t\sum_{j\sigma}(S_{j+1\sigma}^{x}S_{j\sigma}^{x}+S_{j+1\sigma}^{y}S_{j\sigma}^{y})+U\sum_{j}S_{j\uparrow}^{z}S_{j\downarrow}^{z}-\tfrac{1}{4}UN. \tag{4·3}$$

Therefore the grand partition function $Z(=\mathrm{Tr}\exp(-\beta\widetilde{\mathcal{H}}))$ of the one-dimensional half-filled-band Hubbard chain is equivalent to the partition function of a ladder consisting of localized spins (spin 1/2) shown in Fig. 10. In other words the present work may be regarded as a study of thermodynamic properties of such a ladder of localized spins. On the basis of this equivalence we can interpret our results in this way. When U is small compared with t, the ladder is essentially equivalent to two independent XY chains, and the correlation between

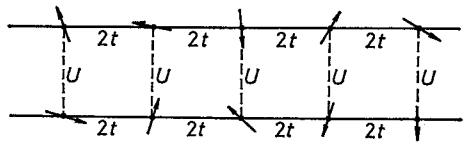


Fig. 10. A ladder of localized spins (spin 1/2) which is equivalent to the one-dimensional half-filled-band Hubbard model. Spins are coupled with each other by the nearest-neighbor XY interaction (with the coupling constant $2t$) as well as the Ising interaction (with the strength U).

two spins connected with each other by "steps" of the ladder is very weak. When U becomes larger than t, the Ising interaction corresponding to "steps" plays an important role. In fact, at low temperatures, the antiparallel alignment of $S_{j\uparrow}$ to $S_{j\downarrow}$ is favorable, and the correlation of this type brings the high-temperature peak of the specific heat. As the temperature goes down further, two neighboring spins connected by the XY interaction becomes antiparallel to each other. This short-range spin ordering gives the low-temperature peak of the specific heat.

(ii) In this paper we have restricted our discussions strictly to the one-dimensional case. One might ask what will happen in two- and three-dimensional systems. It is still an unsolved problem. The following is a conjecture based on our results. We have emphasized in § 2 that the high-temperature peak found in this paper for the one-dimensional system arises from excitations across the Hubbard gap[3] or the formation of local moments. There is no cooperative nature in its origin. Therefore the peak will remain broad even in two- or three-dimensional case. On the other hand the antiferromagnetic spin ordering accompanying the low-temperature peak of the specific heat will turn to a long-range order in the 3-dimensional case, which brings a singularity of the specific heat at Néel temperature T_N.

(iii) The last comment is concerning a controversial question on the role of the electron correlation in NMP-TCNQ.[10] Epstein et al.[8] concluded that the electron correlation is playing a crucial role in NMP-TCNQ and that it is a good example realizing the one-dimensional half-filled-band Hubbard model. According to their analysis U is estimated to be 0.17 eV, and $t \simeq 0.021$ eV. A completely different opinion was presented by Bloch et al.,[10] who argue that a certain disorderedness in the system is essential to understand the temperature dependence of the conductivity. Anyway a conclusive evidence has not been found. A comment we can make is the following. We believe that magnetic susceptibility of the one-dimensional half-filled-band Hubbard model starts with a finite value and has a maximum in the low-temperature region. If we use the value obtained for U and t by Epstein et al., χ should have a maximum around 60°K, while the experimental result of NMP-TCNQ does not seem to have such behavior.

Acknowledgements

The author would like to express his sincere thanks to Professor P. A. Pincus for many fruitful discussions. He is indebted to Professor J. R. Schrieffer and Professor T. A. Kaplan for sending him a preprint prior to publication and giving him valuable comments. He is also grateful to Professor Z. Soos, Professor A. Heeger and Professor M. Fisher for helpful discussions, and to Professor R. Orbach and Professor T. Holstein for hospitality during the author's stay in UCLA.

References

1) H. Shiba and P. A. Pincus, *Proceedings of the 17th Conference on Magnetism and Magnetic Materials* (Chicago, 1971) p. 434; Phys. Rev. B **5** (1972), 1966. This paper will be referred to as I.
2) See, for instance, C. Herring, *Magnetism* IV, edited by G. Rado and H. Suhl (Academic Press, 1966).
3) J. Hubbard, Proc. Roy. Soc. (London) A**276** (1963), 238; A**281** (1964), 401.
4) M. C. Gutzwiller, Phys. Rev. Letters **10** (1963), 159.
5) J. Kanamori, Prog. Theor. Phys. **30** (1963), 275.
6) M. J. Minot and J. H. Perlstein, Phys. Rev. Letters **26** (1971), 371.
7) D. Kuse and H. R. Zeller, Phys. Rev. Letters **27** (1971), 1060.
8) A. J. Epstein, S. Etemad, A. F. Garito and A. J. Heeger, Phys. Rev. B**5** (1972), 952.
9) E. Ehrenfreund, E. F. Rybaczewski, A. F. Garito and A. J. Heeger, Phys. Rev. Letters **28** (1972), 873.
10) A. N. Bloch, R. B. Weisman and C. M. Varma, Phys. Rev. Letters **28** (1972), 753.
H. R. Zeller, Phys. Rev. Letters **28** (1972), 1452.
11) E. H. Lieb and F. Y. Wu, Phys. Rev. Letters **20** (1968), 1445.
12) M. Takahashi, Prog. Theor. Phys. **43** (1968), 1619.
13) H. Shiba, Phys. Rev. **B6** (1972), 930.
14) M. Takahashi, Prog. Theor. Phys. **47** (1972), 69.
15) J. C. Kimball and J. R. Schrieffer, presented at the 17th Conference on Magnetism and Magnetic Materials (Chicago, 1971) and preprint.
16) M. Cyrot, J. de Phys. **33** (1972), 125.
17) H. Bethe, Z. Phys. **71** (1931), 205.
L. Hulthén, Ark. Mat., Astron. Fys. **26A** (1938), No. 11.
18) P. Soven, Phys. Rev. **156** (1967), 809.
19) R. A. Bari, Phys. Rev. B**5** (1972), 2736.
R. A. Bari and T. A. Kaplan, preprint.
20) S. Q. Wang, W. E. Evenson and J. R. Schrieffer, Phys. Rev. Letters **23** (1969), 92.
21) D. R. Hamann, Phys. Rev. Letters **23** (1969), 95.
22) E. Lieb and D. Mattis, Phys. Rev. **125** (1962), 164.