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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 discrepancies between similar calculations which have appeared. For weak interactions, a new kind of smooth magnetic transition (non-antiferromagnetic) 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 phenazinium tetracyanoquinodimethan (NMP)(TCNQ); the comparison suggests strongly that the Hubbard model is seriously deficient as a means of description of these experiments.

There has been considerable interest recently[1-3] 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 papers[4-6] 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 group[4] (SP) found one peak in the specific-heat-vs-temperature curve, the other group[5,6] (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 specific-heat 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 four-atom 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	$U-\langle H\rangle$	$\frac{1}{2}U^2\beta - U + \langle H\rangle$	$\lvert L_1\rvert/\beta^2$
25×10^{-3}	0.199 875 12	1.2×10^{-4}	0.127 003 20
25×10^{-4}	0.019 999 88	1.2×10^{-7}	0.125 207 55
25×10^{-5}	0.002 000 00	1.2×10^{-10}	0.125 020 78

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

$$H=\sum_{ij\sigma} b_{ij}c^{\dagger}_{i\sigma}c_{j\sigma}+U\sum_{i} N_{i\uparrow}N_{i\downarrow}\ . \tag{1}$$

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

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

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 ($\langle N_e\rangle=$ number 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 ($b/U\to 0$), any intensive parameter (e.g., the free energy per atom) is independent of the number of atoms N when calculated in the GCE. Therefore the GCE for small N can be expected to give results close to those for $N\to\infty$ for small b/U. The other point is that, since all results for CE and GCE become the same for $N\to\infty$, 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:

$$\langle H\rangle = U-\tfrac{1}{2}\beta U^2+O(\beta^2)\ , \tag{3}$$

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

where $L_n=\langle(N_{i\uparrow}+N_{i\downarrow})(N_{i+n\uparrow}-N_{i+n\downarrow})\rangle$. (Because of symmetry, L_n is independent of i.) The numerical results are given in Table I. We see that $U-\langle H\rangle$ is about 8β and that $\frac{1}{2}U^2\beta-U+\langle H\rangle$ is of order β^2 or higher; similarly $\lvert L_1\rvert/\beta^2$ is about $\frac{1}{8}$ and $-\lvert L_1\rvert/\beta^2+\frac{1}{8}$ is of order β, in agreement with (3) and (4).

(ii) In the two cases $U=0$ and $U=\infty$, the various $\langle O\rangle$ were again calculated analytically[8] 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

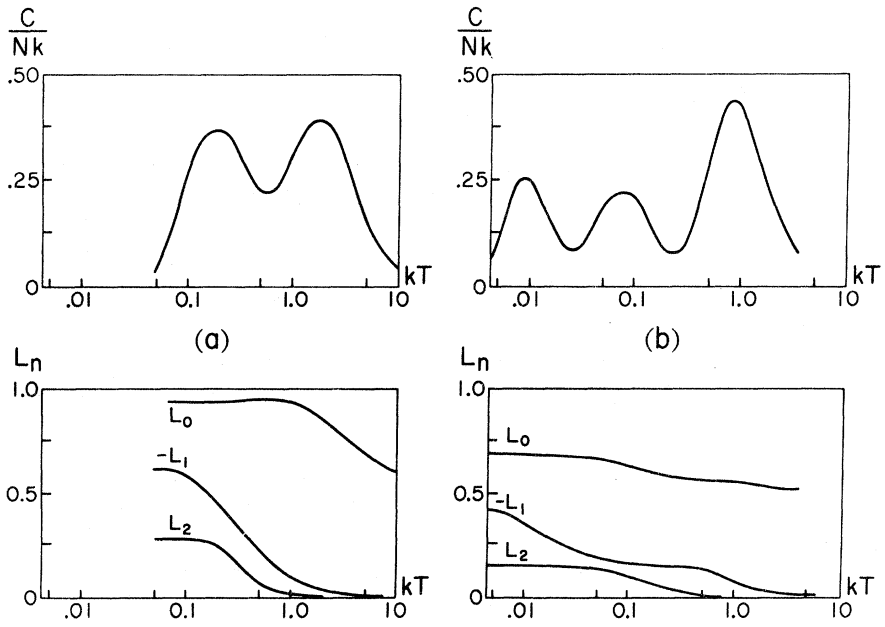

FIG. 1. Specific heat C and spin-spin correlation functions L_n vs temperature in the GCE. (a) $U=8$; (b) $U=0.7$.

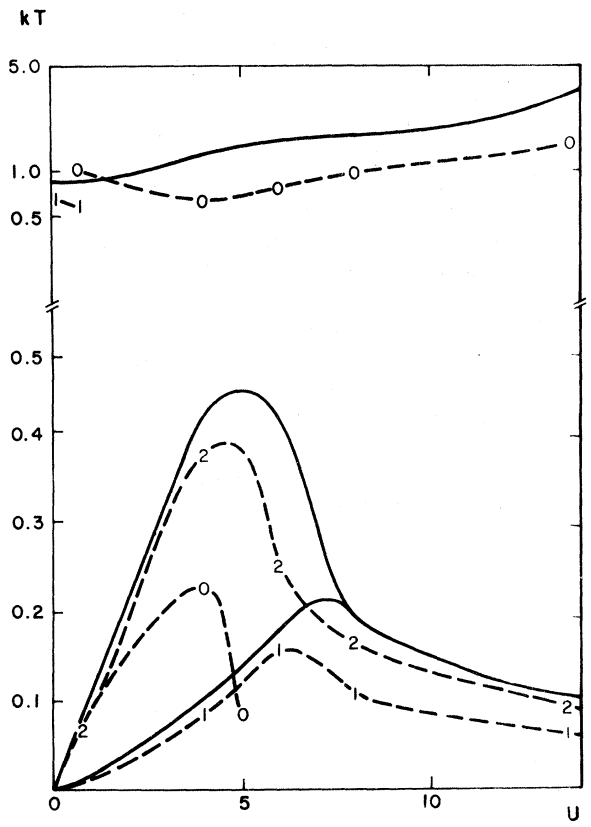

FIG. 2. Temperature at which the specific-heat maxima occur vs U are shown by the continuous lines. The dashed lines labeled by numbers n show the temperatures near which anomalies in L_n occur.

Bonner and Fisher[9] 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 $0<U\lesssim 6$ 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 2 of 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 $\frac{1}{4}L_n$, $n=0, 1, 2$. We note that the zero-field spin-susceptibility χ is related to this by

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

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 $T_{\rm I}=T_{\rm II}$, 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 $T_{\rm I}=T_{\rm II}$ the Néel 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 ($T_{\rm I}$) in C, L_2 is seen in Fig. 1(b) to have an essentially constant value different from zero up to the temperature ($T_{\rm II}$) 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 $T_{\rm I}$. The fact that $|L_1|$ and L_2 do not start to decrease sharply near the same temperature is in marked contrast to typical behavior at a magnetic transition. Hence the characterization[5,6] of $T_{\rm I}$ as a Néel temperature is misleading and unacceptable.

We also note that L_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 $T_{\rm III}$) to a characteristic change in L_0 has already been noted.[4-6,10] We see [Fig. 1(b)] an additional effect at small U, namely, L_1 also shows an anomaly near $T_{\rm III}$, which somewhat surprisingly disappears at a value of U roughly equal to one. This plus the other anomalies in L_n 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 the number of atoms $N\to\infty$ 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 degeneracy is seen by considering the occupancy of the one-electron levels $E_k=2b\cos k$, $k=0$, $\pm\frac{1}{2}\pi$, π. The minimum, which occurs either at $k=0$ or $k=\pi$, accomodates two electrons; but the other two electrons can occupy four one-electron states ($k=\pm\frac{1}{2}\pi$ 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 $N \to \infty$; e.g., the Curie-law 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 b 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 $\to 0$ 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 low-lying states is $O(b/N)$ for $U=0$. (It might be that as N increases for small U the peak splits, with the 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 $\langle N_{i\uparrow}N_{i\downarrow}\rangle \ll \langle N_{i\uparrow}\rangle\langle N_{i\downarrow}\rangle = \frac{1}{4}$, these correlations decreasing markedly as kT becomes $\simeq U$) is what we expected on the basis of earlier work.[3,11] There[3] 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 ($\sim 200\,^\circ$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 $kT_0 \simeq 2b^2/U \cong 60\,^\circ$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, T_0 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 $N \geq 4$ and that in the Hubbard model the exact value[12] 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 χ^{-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.

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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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Solvable Compressible Ising Model

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The results for the solvable Baker–Essam model of a compressible Ising lattice are rederived by utilizing the equivalence of the system to a set of linear chains each described by the Mattis–Schultz one-dimensional magnetostriction model.

The long-standing controversial question as to the effects of lattice compressibility on magnetic phase transitions has attracted especially wide interest in the last two years following the publication of a paper by Baker and Essam[1] (BE). These authors displayed an exactly solvable model of a compressible harmonic lattice of spins interacting via a spatially dependent ferromagnetic Ising coupling. They found that when the system is constrained to constant volume or constant positive pressure the magnetic phase transition is second order with renormalized[2] critical exponents. Subsequently, Gunther, Bergman, and Imry[3] (GBI) showed that when this system is constrained to constant negative pressure the system undergoes a first-order transition.

In view of the wide interest in this subject it is worthwhile to display an alternate derivation of the results for the BE model which is considerably more transparent both physically and algebraically. BE evaluate the partition function directly, treating the lattice vibrations classically and constraining the surface atoms to their appropriate crystal faces. By contrast, I first transform the model Hamiltonian to describe two independent systems. The first system is a set of independent harmonic linear chains and the second is a three-dimensional Ising system of *rigid* spins interacting via an effective exchange coupling. Evaluation of the partition function then follows trivially. The transformed Hamiltonian is obtained utilizing the equivalence of the BE model to a set of linear chains, each described by the one-dimensional magnetostriction model of Mattis and Schultz.[4] A canonical transformation removes the spin-phonon interaction terms for each linear chain. In contrast to BE, the lattice vibrations are treated quantum mechanically and terms are included in the Hamiltonian to describe the action of a constant and equal compressional or tensile force applied to each surface atom, rather than to constrain these atoms to their crystal faces.

The BE model is characterized by the following three features: (i) The crystal lattice is simple cubic (lattice spacing a); (ii) the interatomic potential links nearest neighbors only and is chosen as $V_{ij}=V(a)+\hat{e}_{ij}\cdot(\vec{u}_i-\vec{u}_j)\,V'(a)+\frac{1}{2}[\hat{e}_{ij}\cdot(\vec{u}_i-\vec{u}_j)]^2\,V''$, where $\vec{u}_i$, $\vec{u}_j$ denote the vector displacements of the nearest-neighbor atoms i, j from their thermal equilibrium positions, $\hat{e}_{ij}$ is a unit vector pointing from the equilibrium position of j to i, and V'' is a constant independent of a. The shear-term quadratic in atomic displacements $V'(a)[\hat{e}_{ij}\times(\vec{u}_i-\vec{u}_j)]^2/2a$ of a central interatomic potential is specifically excluded by BE. (iii) The Ising spin interaction links nearest neighbors only, and its spatial dependence is chosen as $J_{ij}=J(a)+\hat{e}_{ij}\cdot(\vec{u}_i-\vec{u}_j)J'$, where J' is a constant.

It is convenient to take the crystal as a cube of N^3 atoms whereby each surface atom is subjected to a constant and equal compressional or tensile force applied normal to the crystal faces. Thus we add to the Hamiltonian[5] a term, $-F\vec{u}_s\cdot\hat{n}$, for each atom s lying in a crystal face characterized by the unit vector $\hat{n}$, the outwardly directed normal to that face. Positive (negative) values of the force $F\hat{n}$ on the surface atom correspond to tension (compression). For the simple cubic lattice, one has the identity $-F\sum_{\hat{n}s}\vec{u}_s\cdot\hat{n}=-F\sum_{\langle i,j\rangle}(\vec{u}_i-\vec{u}_j)\cdot\hat{e}_{ij}$, where $\langle i, j\rangle$ means that the summation includes all distinct nearest-neighbor pairs of atoms comprising the crystal. Including the above term leads to the model Hamiltonian

$$H=3N^3\,V(a)+H_I+\sum_i\frac{p_i^2}{2M}+\sum_{\langle i,j\rangle}\{[V'(a)-F-J'\,\sigma_i\sigma_j]\hat{e}_{ij}\cdot(\vec{u}_i-\vec{u}_j)+\tfrac{1}{2}V''[\hat{e}_{ij}\cdot(\vec{u}_i-\vec{u}_j)]^2\}\,, \tag{1}$$