

Ground-state and thermodynamic properties of the Hubbard model applied to small clusters

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(Received 31 October 1986)

The Hubbard Model with nearest-neighbor hopping and one type of orbital is applied to small clusters, with emphasis on an octahedron (six sites). The complete eigenvalue spectrum is calculated. A rather complicated dependence of the spin of the ground state on occupation number, geometry, and model parameters is found. Thermodynamic properties are computed with use of a canonical ensemble. Results are reported for the specific heat, spin susceptibility, and spin-spin correlation functions.

I. INTRODUCTION

The Hubbard Hamiltonian has, for many years, been used to define a mathematical model of great interest in the study of the magnetic and electrical properties of solids, particularly transition metals and their compounds.¹ There are many versions of this Hamiltonian, the simplest one being

$$H = t \sum_{i,j,\sigma} C_{i\sigma}^\dagger C_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}. \quad (1)$$

The first term describes electron hopping between nearest-neighbor lattice sites i, j , on which there are a set of orthogonal nondegenerate orbitals to which the creation and destruction operators $C_{i\sigma}^\dagger, C_{j\sigma}$ (σ denotes spin) refer. The second term describes a short-range interaction between electrons of opposite spin on the same site ($n_{i\uparrow}$ is the number operator for electrons of spin up on site i). The model can be extended in a natural way to include more than one orbital per site, to allow hopping between more distant sites and between different orbitals, and to allow for electrostatic interactions between electrons on different sites. However, detailed consideration will be given here only to the simplest case, as specified in Eq. (1), and in addition, we consider only the case of a repulsive electron-electron interaction U ($U > 0$).

Even in the simplest case, definitive results have been difficult to obtain. Some exact results are available for one-dimensional systems. Lieb and Wu² obtained an exact expression for the ground-state energy of a one-dimensional system in the "half-filled"-band case. The ground state is antiferromagnetic although it lacks long-range order, and insulating for any nonzero U . The excited states of this system were studied by Ovchinnikov,³ who described spin-wave states and quasi-ionic states. The magnetic susceptibility at $T=0$ was calculated by Takahashi.⁴ Shiba⁵ extended the calculation of Lieb and Wu to arbitrary electron concentrations and determined the magnetic susceptibility at $T=0$. Coll⁶ worked out the excited states for arbitrary concentrations. Takahashi⁷ gave formal expressions for thermodynamic functions at finite temperatures in terms of some integral equations. We are not aware of specific computations based on the work of Ref. 7.

In the case of three-dimensional systems, there has been great interest in the question of the existence of a fer-

romagnetic ground state. Conventionally one describes systems in terms of two parameters. The first is the ratio of the electron interaction U to the hopping integral t . As we shall mainly be concerned with large values of this quantity, we will work with its reciprocal, denoted z ,

$$z = t/U.$$

The second is the ratio ρ of the number of electrons, n , to the number of sites N . It was shown many years ago, that ferromagnetism is not possible when ρ is sufficiently small regardless of how large U is.⁸ Likewise, it can be shown that the ground state will not be ferromagnetic for a system with exactly one electron for each site.⁹

Much controversy has arisen over the question as to whether the Hamiltonian of Eq. (1) ever has a ferromagnetic ground state. Nagaoka showed that in the case of a half-filled band with one extra electron or one hole, the ground state is ferromagnetic for certain lattice structures in the limit that U tends to infinity.¹⁰ The validity of Nagaoka's argument for systems with a finite density of holes or extra electrons in which a thermodynamic limit must be taken has, however, been questioned.¹¹ We will not be able to answer this question here precisely for infinite systems, but we will see that in finite systems the ground state has greater than the minimum spin in certain cases, and that the reasons for this are easy to understand.

This work attempts to explore ground-state and thermodynamic properties of the Hubbard model from a different point of view. We have obtained exact numerical results for several small clusters (four, five, and six sites). All the eigenvalues and eigenvectors of the Hamiltonian of Eq. (1) can easily be computed for these systems, so that thermodynamic functions can be obtained. The results obtained resemble, in a qualitative way, corresponding properties of bulk materials. Our study generates physical understanding of the relation between small and large systems, as well as leading to plausible inferences about properties of large systems for which exact calculations have so far not been possible.

The application of the Hubbard model to finite systems (clusters) also has a considerable history. The first study of this type of which we are aware was reported by Linderberg and Ohrn,¹² who considered states of the benzene molecule. Approximate solutions were obtained using Hubbard's Green's-function decoupling method. Heilmann and Lieb¹³ later obtained exact solutions for this

model (a regular hexagon). Shiba and Pincus¹⁴ broadened the scope of cluster investigations by calculating thermodynamic properties (magnetic susceptibility, internal energy, entropy, specific heat, and spin correlation functions) of small chains or rings with one electron per site (the half-filled band). This calculation uncovered interesting features, an important example being a two-peak structure in the specific heat, which survive when the number of sites in the chain or ring is allowed to become infinite. Cabib and Kaplan¹⁵ and Shiba¹⁶ extended this work further by making calculations for the same kinds of systems using the canonical ensemble.

More recently, attention has been devoted to systems with geometries other than rings or chains, and to excitations. Newman, Chan, and Ng¹⁷ classified the eigenstates for the square and tetrahedron according to symmetry and calculated correlation functions for these systems as functions of t/U . Falicov and Victora¹⁸ analyzed the eigenstates for a regular tetrahedron. Subsequently they have extended this model through a more realistic description of d bands and applied it to the description of the photoemission spectrum of nickel.¹⁹ Oleś, Oleś, and Chao described ground-state and thermodynamic properties for a tetrahedron.²⁰ Kawabata has studied the ground state for an eight-site cubic array²¹ containing from two to eight electrons. He found that in certain cases ($n=4$ and $n=7$) the ground state has the maximum possible spin for sufficiently large U ; while for $n=5$, an intermediate spin state ("weak ferromagnetism") was lowest for all values of U . For other occupancies ($n=2, 3$, and 6) the ground state is either a singlet (even n) or a doublet (odd n). Ishii and Sugano²² studied the ground state of four-site systems (tetrahedron, square, and rhombus) including second neighbor interactions. Oleś *et al.* have computed one- and two-hole excitation spectra for rings of four and eight sites.²³

We previously reported results for the ground-state spin of three four-site clusters (square, tetrahedron, and rhombus) and four five-site systems (pentagon, truss, square-based pyramid, and bipyramid) as a function of the number of electrons and the parameters of the Hamiltonian.²⁴ We also compared ground-state energies as a function of the site arrangement to determine the preferred geometry. Some thermodynamic functions including the spin susceptibility and the specific heat were determined.

In a gross, qualitative sense, the results we obtain for systems of different geometries are rather similar (for example, two peaks in the specific heat are found in almost all cases). We shall therefore emphasize here principally the octahedron (for which we are unaware of previous results) with lesser attention to a few other systems. We believe the resemblance between clusters and solids is greatest for highly symmetric clusters with a three-dimensional structure. Further, we will concentrate primarily on intermediate values of U/t (many examples have $U/t=10$). The octahedron is interesting in that for six electrons we find many properties similar to those of bulk antiferromagnets while for $n=5$ we find both a high-spin ground state (similar to saturated ferromagnetism) for sufficiently large U , and an intermediate-spin ground state (unsaturated ferromagnetism) in a small

range of intermediate values. These results are presented in Sec. III. Our methods are described in Sec. II. Section IV contains a brief summary.

II. METHOD

The Hamiltonian (1) is conveniently considered on a basis of states $|\hat{n}_{i\sigma}\rangle$ diagonal in all the occupation numbers

$$n_{i\sigma}|\hat{n}_{i\sigma}\rangle = \hat{n}_{i\sigma}|\hat{n}_{i\sigma}\rangle, \quad (2)$$

where " $\hat{}$ " denotes the eigenvalue. Then U occurs only on the diagonal and t on the off-diagonal terms. The eigenvalues can then be expressed as

$$E = U\varepsilon(t/U), \quad (3a)$$

or

$$E = t\varepsilon'(U/t), \quad (3b)$$

where (3a) is convenient if $|U| > |t|$, and (3b) is used for $|t| < |U|$. There is an electron-hole symmetry. Let E_n denote the energy of a system of N sites and n electrons. We have

$$E_n(-t) = E_n(t) + (N-n)U, \quad (4a)$$

where

$$n' = 2N - n. \quad (4b)$$

Hence it suffices to calculate $E_n(t)$ for all relevant n and positive t ; the values for negative t can then be obtained from Eq. (4a). Note that if $n=N$, the energies are even functions of t .

We constructed a computer program to diagonalize the Hamiltonian within subspaces of fixed values of S_z (or $n\uparrow - n\downarrow$). Since we desired to study different geometric structures with the same program, we did not form symmetrized combinations of basis states. For systems of no more than six sites, neglect of symmetry does not make the computer time excessively long. The program was checked by comparison of the results with those of Falicov and Victora¹⁸ for a tetrahedron.

All the eigenvalues and eigenvectors were obtained. We used these quantities to calculate the spin susceptibility χ in a canonical ensemble:

$$\chi = \frac{2}{n_x} \frac{1}{ZT} \sum_j e^{-\beta E_j} m_j^2. \quad (5a)$$

Here $n_x = n$, the number of electrons, if the number of electrons is equal to or less than the number of sites; otherwise $n_x = 2N - n$. Thus, the maximum possible spin of the cluster is $\frac{1}{2}n_x$. The index j denotes an eigenstate and m_j is given by

$$m_j = \frac{1}{2}(n\uparrow - n\downarrow)_j, \quad (5b)$$

so that m_j represents the azimuthal spin quantum number S_z in units of \hbar for the j th eigenstate. The quantity Z is the partition function

$$Z = \sum e^{-\beta E_j},$$

$$\beta = 1/k_B T, \quad (6)$$

k_B being Boltzmann's constant, and T is the temperature. The specific heat is

$$C = \frac{1}{k_B T^2 Z} \left[\sum_j E_j^2 e^{-\beta E_j} - \frac{1}{Z} \left[\sum_j E_j e^{-\beta E_j} \right]^2 \right]. \quad (7)$$

The correlation functions are defined as follows. Let

$$L_{\mu\nu}(j) = \frac{1}{4} \langle j | (n_{\mu\uparrow} - n_{\mu\downarrow})(n_{\nu\uparrow} - n_{\nu\downarrow}) | j \rangle \quad (8)$$

in which μ and ν denote sites. Then we form the thermal average, denoted

$$\langle L_{\mu\nu}(T) \rangle = \frac{1}{Z} \sum_j e^{-\beta E_j} L_{\mu\nu}(j). \quad (9)$$

In the systems considered in our calculations so far, the symmetry is high enough so that $L_{\mu\nu}$ depends only on the distance between sites. Then we refer to L_0 , the thermal average correlation function for a single site; L_1 is the first-neighbor correlation function; and L_2 is the second-neighbor correlation function.

III. RESULTS AND DISCUSSION

We shall first list the major features of the results which will be illustrated specifically below.

The ground state of the system shows various kinds of magnetic behavior that can be qualitatively characterized as saturated ferromagnetism, unsaturated ferromagnetism, antiferromagnetism, or paramagnetism depending on the geometry, occupancy, and Hamiltonian parameters of the system. Most of this behavior can be qualitatively predicted or explained by considering the spectrum of single-particle levels. The arguments are qualitatively similar to those of the band theory of ferromagnetism in solids. However, in the case of one electron per site, the ground state has the lowest possible spin (either a singlet or a doublet, depending on whether the number of sites is even or odd). As $z = t/U$ increases from zero, the ground-state correlation functions generally decrease in a manner interpretable as showing a transition from localized to itinerant behavior; however, occasionally there are changes including changes of sign which may occur when the spin of the ground state changes with z . When there is one electron per site, the excitation spectrum for large U clearly shows a Hubbard gap, with the low-lying excitations being just spin rearrangements, and the higher states involving electron transfer. The gap is not obvious for small U . When the occupancy is different from one per site, a gap is still present for large U , but the low-energy excitations include both hoppings and spin rearrangements. The Hubbard gap apparently disappears for a smaller value of z than in the half-filled case.

The temperature-dependent magnetic susceptibility resembles that of bulk systems, showing Curie or Curie-Weiss behavior at high temperatures. However, no singularities are possible for finite systems at finite temperatures, and at sufficiently low temperature the susceptibili-

ty either goes to zero rapidly (if the ground state is a singlet) or becomes infinite according to a Curie law (if the ground state has nonzero spin). For large enough U , the specific heat usually has a two peak structure, but occasionally there are three peaks. The magnitude of the spin correlation functions decreases with increasing temperature, rather gradually for the local moment, more sharply for functions involving different sites. In some systems, correlation functions change sign with increasing temperature.

We will now be more specific.

A. Ground-state spin

Results for systems of four and five sites were given in Ref. 24. As an example, the results for the tetrahedron are summarized below in the case of positive t (these are entirely in agreement with the work of Falicov and Victora, Ref. 18). For two electrons per site, states with $S=0$ and $S=1$ are degenerate for all U/t . In the case of three electrons per site, the ground state has maximum possible spin, $S = \frac{3}{2}$ (we call this ferromagnetic) for all U/t . For four electrons, the ground state always has $S=0$, and for five and six electrons, the ground state always has minimum spin ($S = \frac{1}{2}$ and $S=0$), respectively. In contrast, for a square we find that the ground state always is of the minimum possible spin except when there are three electrons, and $z = t/U < 0.055$.

The occurrence of the high-spin state for the tetrahedron when $n=3$ has a simple explanation: the lowest single-particle ground state is threefold-degenerate so that three particles of parallel spin can be put in this state. The electron repulsion term U in the Hamiltonian makes no contribution to the energy of this state. However, in the doublet state there is some repulsive interaction and this state remains at higher energies. However, for the square the lowest single-particle state is not degenerate, but the first excited state is doubly degenerate. Therefore the single-particle contribution to the energy of the three-particle system is higher (by $2t$) when $S = \frac{3}{2}$ than when $S = \frac{1}{2}$. Therefore, for small U/t , the low-spin state is preferred, but when U/t is sufficiently large (≈ 18) the interaction contribution raises the doublet above the quartet.

Let us now consider the two six-site systems, octahedron and hexagon. The single-particle energies and degeneracies are given in Table I. The spin of the ground state is given for all occupancies in Table II. Most of these results have at least a partial qualitative explanation in terms of occupancy of single-particle levels.

Consider first the octahedron. The lowest single-particle state is degenerate so two particles can be put in the triplet state without any contribution from the repulsive interaction U to their energy. In the singlet state there is a contribution and the triplet state is lower. This much is similar to the case of three particles in the tetrahedron. An additional particle must go into a single-particle state of higher energy so that for $n=3$ the doublet (which needs only the lowest single-particle state) has a lower energy than the quartet. (However, this argument does not demand that the doublet should be the

TABLE I. Single-particle energies and degeneracies for octahedron and hexagon. The number in parentheses is the degeneracy.

Octahedron	Hexagon
$-2t$ (2)	$-2t$ (1)
0 (3)	$-t$ (2)
$4t$ (1)	t (2)
	$2t$ (1)

lowest state for all U which actually is the case). In the case of $n=4$, all four particles can go into the lowest state in the case of the singlet, and this is lowest. For $n=5$, if U is small, the doublet will be lowest in energy since only one electron must be in the second single-particle state. However, in this case as the interaction increases, first the quartet, and later the sextet becomes stable. In other words, there is a small region of unsaturated ferromagnetism from, roughly, $U/t=9$ to $U/t=11$, and for larger U there is a saturated ferromagnet. For $n=6$, the lowest state for small U corresponds to doubly occupied single-particle states and the singlet state remains lowest for all U . For $n>6$, it is convenient to think of $12-n$ holes in a filled band but with a negative sign for t . In this case, the lowest single-particle state is nondegenerate. A favorable case for spin alignment corresponds to four holes, in which this state is doubly occupied and two spin aligned holes are in the next (triply degenerate) state. Here, a magnetic state is found but only for very large U (roughly $U/t>150$). The single-particle arguments also indicate that the low-spin state would be likely to be lowest for two and three holes, but in the case of five holes it is perhaps surprising that the quartet state is never lower than the doublet.

TABLE II. Spin of the ground state for the octahedron and hexagon as functions of occupation number and $z=t/U$. Results are given for $t>0$. For $t<0$, results apply for occupation numbers $n'=12-n$.

	Octahedron	Hexagon
$n=2$	$S=1$ all z	$S=0$ all z
$n=3$	$S=\frac{1}{2}$ all z	$S=\frac{3}{2}$, $z<0.097$ $S=\frac{1}{2}$, $z>0.097$
$n=4$	$S=0$ all z	$S=1$ all z
$n=5$	$S=\frac{5}{2}$, $z<0.089$ $S=\frac{3}{2}$, $0.089<z<0.113$ $S=\frac{1}{2}$, $z>0.113$	$S=\frac{1}{2}$ all z
$n=6$	$S=0$ all z	$S=0$ all z
$n=7$	$S=\frac{1}{2}$ all z	$S=\frac{1}{2}$ all z
$n=8$	$S=1$, $z<0.0065$ $S=0$, $z>0.0065$	$S=1$ all z
$n=9$	$S=\frac{1}{2}$ all z	$S=\frac{3}{2}$, $z<0.097$ $S=\frac{1}{2}$, $z>0.097$
$n=10$	$S=0$ all z	$S=0$ all z

In the case of the hexagon, similar arguments apply. In this case, the energies do not depend on the sign of t . The most favorable case for spin alignment is that of $n=4$ (or 8) with a doubly occupied lowest state and two aligned spins in the doubly degenerate next highest state. Here the triplet state is lowest for all U . An aligned state is also obtained for $U/t>10$ when $n=3$ or $n=9$.

These arguments, which emphasize the importance of degeneracy, can be regarded as an application of Hund's rule to the cluster treated as a single "structured atom,"¹⁸ in that when spin degeneracy is resolved by the formation of multiplets, the state of maximum spin tends to be the one of lowest energy. The reader should observe the close relation between this discussion and the ordinary energy-band theory of ferromagnetism. To appreciate this relation, make an analogy between a degeneracy of single-particle states in the cluster and a sharp peak in the density of states in an extended system. The occurrence of ferromagnetism in metals is favored by such a peak.

However, the present results do not support the simple idea of band ferromagnetism that a high-spin state will always have the lowest energy if the repulsive interaction is sufficiently strong. The situation is more complicated, and both the occupancy and the geometry are important. In the case of one electron per site ("half-filled band") the low-spin state is preferred in all the clusters we have studied as well as in an infinite system. Even in the case of partial occupancy (less or greater than half full), in many cases the low-spin state has the lowest energy. Some examples of this have been mentioned above, and a particularly simple case occurs in the square with $n=2$, in which the lowest singlet state has energy $E=-(2\sqrt{2})t$ as $U\rightarrow\infty$, while for the triplet, one has $E=-2t$. Hence, no matter how large U is the singlet state remains lower.

B. Ground-state correlation functions

The magnitude of the correlation functions, computed in the ground state, tends to increase with U from an itinerant to a localized limit. These functions may, however, change discontinuously if the ground state changes. The results for the octahedron in the half-filled-band case are shown in Fig. 1. For small z ($z<0.165$) we have a situation similar to antiferromagnetism in a bulk solid; a local moment close to the maximum value ($\frac{1}{4}$ in the scale used here), and relatively large first- and second-neighbor correlation functions of nearly equal magnitude but opposite sign (first neighbor negative, second neighbor positive). These functions slowly decrease as z increases. However, at about $z=0.165$ there is a discontinuous change to a situation with first- and second-neighbor correlation functions smaller in magnitude; here the second-neighbor function becomes negative and is close to zero. There is only a small drop in the local moment. The transition is due to a change in the spatial symmetry of the ground state; nondegenerate for $z<0.165$, triply degenerate for $z>0.165$. Because of the weaker first- and second-neighbor correlations, it is plausible to regard the transition as analogous to a metal-insulator transition in a solid.

Corresponding results for the octahedron with $n=5$

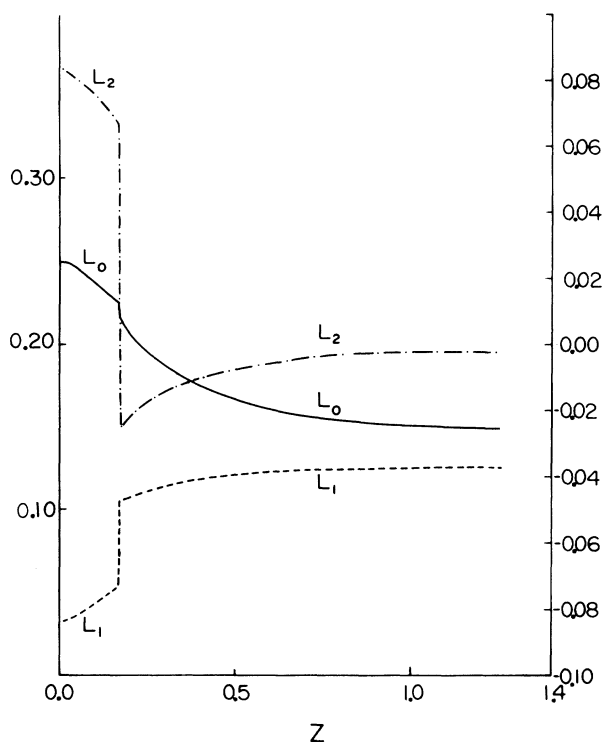


FIG. 1. Local moment (L_0 left-hand scale), and first- and second-neighbor correlation functions (L_1, L_2 , right-hand scale) are shown for the ground state of the octahedron in the half-filled-band case as a function of $z = t/U$.

(half-filled band minus one particle) are shown in Fig. 2. Here for small z we have a saturated "ferromagnetic" state as $z \rightarrow 0$ with the maximum local moment and positive, large, and equal first- and second-neighbor correlations. At $z=0.089$, there is a transition from the ground sextet to a quartet state (unsaturated ferromagnetism), with correlation functions smaller in magnitude and second neighbors negative. Then for $z=0.113$, there is a further transition to a doublet state (paramagnet) with a large change in correlation functions (both first and second neighbors negative, and second neighbors large in magnitude).

In contrast, the low-spin doublet is the ground state for all z for a hexagon with occupancy 5. Likewise, no transition occurs between different ground states in the hexagon in the $n=6$ case. Our results for the spin correlation functions in this case agree with those of Ramasesha and Soos,²⁵ and are not shown here.

C. Excitation spectrum

Energy-level diagrams are shown in Fig. 3 for five and six particles in an octahedron with $U=10t$ (only levels below $12t$ are shown). Consider the six-particle case first. A sparse group of low-lying levels corresponding to spin rearrangements is separated by a substantial gap (roughly $\frac{1}{2}U$) from a more dense manifold of higher energy states above it. These higher states contain a substantial component of doubly occupied sites.

The parameters of the $n=5$ case in this example are

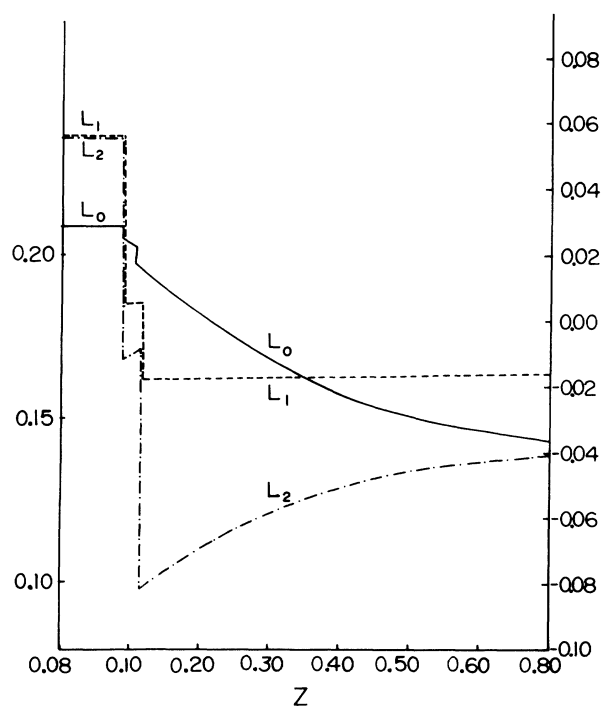


FIG. 2. Similar to Fig. 1 but with five particles (half-filled-band minus 1).

such that the $S = \frac{3}{2}$ state lies lowest. Note that the set of low-energy states is more numerous, presumably because of the possibility of electron motion without double occupancy. The "Hubbard gap" separating the lower and higher states is smaller than in the case of $n=6$.

The excitation spectrum determines the thermodynamics of the system. In particular, Fig. 3 leads us to expect a

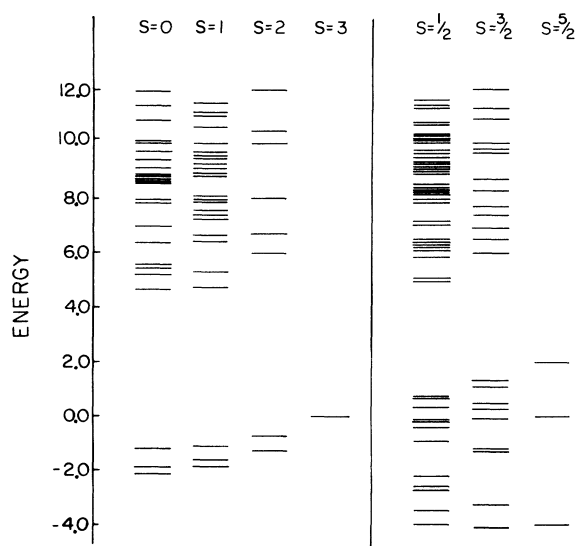


FIG. 3. Energy-level diagram (energies are in units of the transfer integral t) for the octahedron with $U=10t$, and occupancies $n=6$ (left) and $n=5$ (right). Levels are classified according to spin. Spatial degeneracies are not shown explicitly.

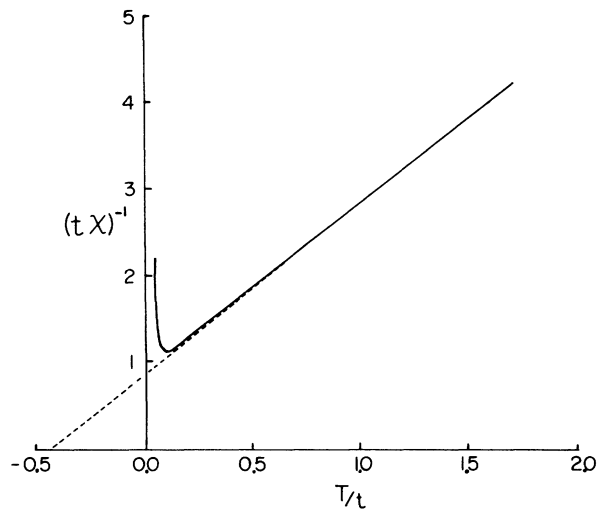


FIG. 4. The quantity $(t\chi)^{-1}$, where t is the transfer integral and χ is the spin susceptibility is plotted as a function of temperature in the form of T/t for an octahedron with $n=6$ and $U/t=10$. The dashed straight line shows a linear extrapolation to an intercept for a negative temperature.

two-peak structure in the specific heat in which the low-temperature peak is associated with the low-lying states, and a broader high-temperature peak results from excitation of the high-energy states. This structure is found in our calculations, as will be described below.

D. Magnetic susceptibility

The reciprocal of the magnetic susceptibility is shown as a function of temperature for several systems in Figs. 4–7. We begin by considering the octahedron with $n=6$ and $U/t=10$. It will be observed that the high-temperature portion of the curve is quite linear but that the intercept is at a negative temperature $-\Theta_N$. In this case $\Theta_N \approx 0.37t$. This type of Curie-Weiss behavior with

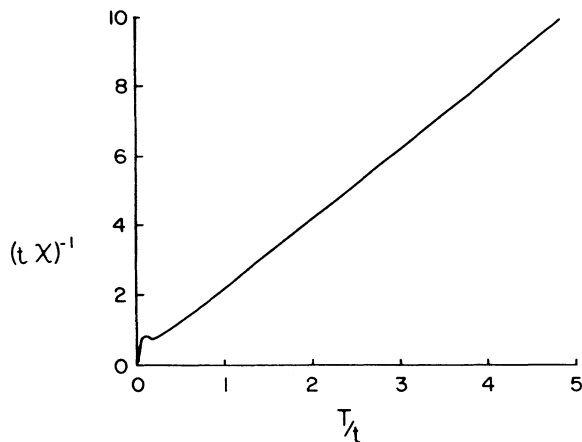


FIG. 5. Similar to Fig. 4 but for five electrons in a hexagonal system with $U/t=20$.

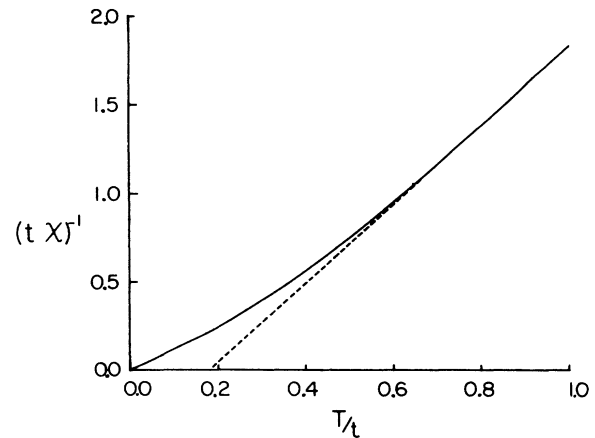


FIG. 6. Similar to Fig. 4 but for a system (the tetrahedron with $n=3$, $U/t=10$) with a high-spin ground state. The dashed line is a linear extrapolation of the high-temperature behavior.

negative Curie temperature is typical of bulk antiferromagnets, and in this respect the small cluster results resemble bulk materials. However, a least-squares fit at much higher temperatures gives a positive intercept. At low temperature (i.e., below the minimum in χ^{-1}) departures from behavior characteristic of bulk samples are found. At $T=0$, the magnetic susceptibility for a finite system with $S=0$ in the ground state must vanish, and hence χ^{-1} becomes infinite.

Figure 5 shows a similar plot for a hexagon with $n=5$ and $U/t=20$. The ground state has $S=\frac{1}{2}$. In this case, the high-temperature behavior follows a Curie-Weiss law with a positive (ferromagnetic) Curie temperature. At lower temperatures, χ^{-1} changes slope and shows a roughly linear portion with a negative intercept of approximately $-0.2t$. The curve has a minimum, as would be expected for an antiferromagnet, but the minimum is weak. In this case we have an odd number of electrons,

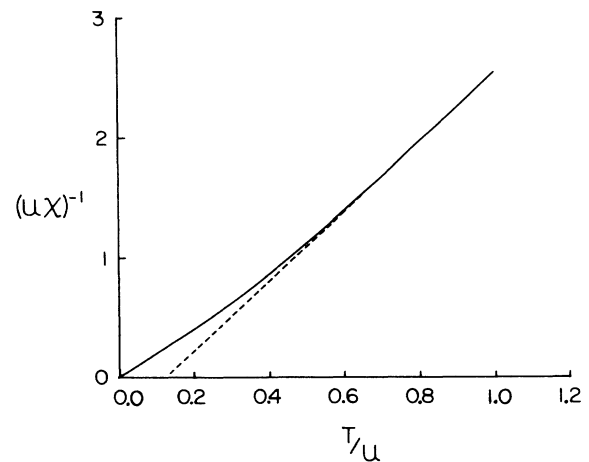


FIG. 7. Reciprocal susceptibility as a function of temperature for the octahedron with $n=5$ and $z=0.02$. In this case, the scale factor for temperature is U .

and in a finite system χ^{-1} must go to zero at $T=0$, as is shown.

Examples of χ^{-1} calculated for a hexagon with $n=6$ also show Curie-Weiss behavior at sufficiently high temperatures with a positive Curie temperature, although antiferromagnetic spin correlations are found at low temperatures. Two examples of Curie-Weiss behavior of the susceptibility in systems with a high-spin ground state are shown in Figs. 6 and 7. Figure 6 shows χ^{-1} for a tetrahedron with $n=3$. In this case the high-temperature behavior is quite linear and there is an intercept at a (paramagnetic Curie) temperature. For low temperatures, there is Curie-law behavior (rather than Curie Weiss) which is again a consequence of the finite size of the system.

Similar behavior is exhibited by the octahedron with $n=5$ as shown in the example of Fig. 7 with $z=0.02$. In this case the Curie-Weiss law is accurately obeyed only at quite high temperature ($T \approx \frac{1}{2}U$) and the intercept is also large.

E. Specific heat

As remarked previously, the nature of the level spectrum leads us to expect a two-peak structure in the specific heat. This was first noticed by Shiba and Pincus¹⁴ in their calculations for certain rings and chains (including the hexagon studied here). We find this behavior to be quite general. Figure 8 shows the specific heat for the octahedron with $n=6$ and $U/t=10$, the same case for which the energy levels and magnetic susceptibility have been shown above (Figs. 3 and 4). A second example is shown in Fig. 9 (the hexagon with $n=6$ and $U/t=10$). The relative positions and widths of the peaks depend on the geometry, occupancy, and U/t ratio of the system. Generally for small U/t , the first peak is less distinct, and may occasionally be reduced to a bump or shoulder on the high-temperature curve. In some circumstances, three peaks may be found, as was noted by Cabib and Kaplan.¹⁵ It is characteristic of a finite system that the specific heat is zero at $T=0$.

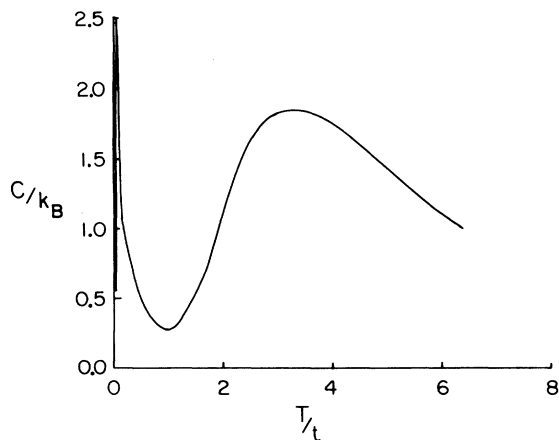


FIG. 8. Specific heat C (divided by Boltzmann's constant k_B) is shown as a function of temperature T , for the octahedron with $n=6$ and $U/t=10$.

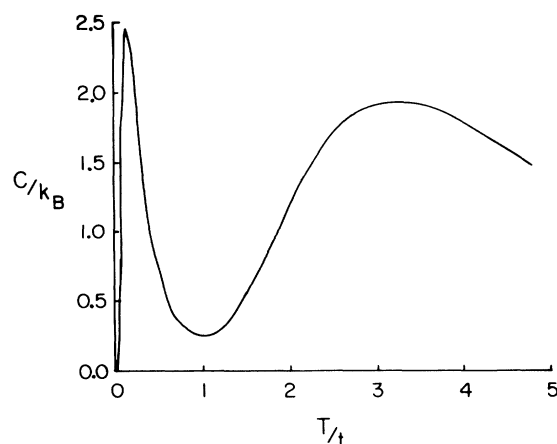


FIG. 9. Similar to Fig. 8 but for a hexagon with $n=6$ and $U/t=10$.

F. Temperature dependence of the correlation functions

First, we consider the temperature dependence of the local moment, L_0 . Our scale is such [see Eq. (8)] that the maximum value of this quantity is $\frac{1}{4}$. Results for the octahedron with $n=6$ and $U/t=10$ are shown in Fig. 10. The zero-temperature value for this quantity (0.237) is less than the completely localized limit, indicating there is still some itinerancy in this system, even though U/t is fairly large. Note also that L_0 does not have its maximum value at $T=0$, but rises for small T with a maximum near $T=1.1t$. (Similar behavior was noted for the hexagon by Shiba and Pincus¹⁴). The explanation is that several of the low-lying excited states of the system, particularly those with $S=1, 2$, and 3 have larger local moments, i.e., are more localized than the ground state. As the temperature increases, the contributions from these states are mixed in by the thermodynamic averaging process, and L_0 increases. As the temperature increases further, contributions from still higher, less-localized states become more important, and L_0 falls towards the itinerant limit [in this case 0.136 (Ref. 14)]. In the case of a high-spin

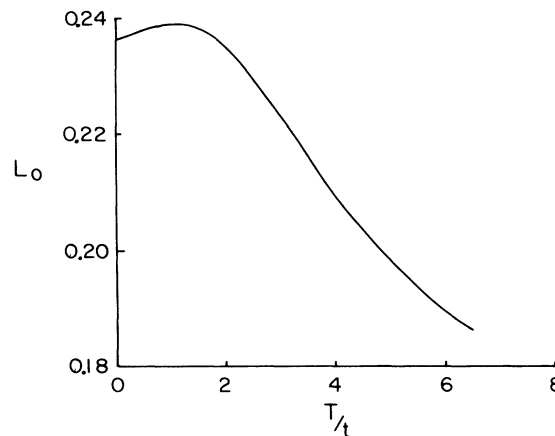


FIG. 10. Temperature dependence of the local moment L_0 for the octahedron with $n=6$ and $U/t=10$.

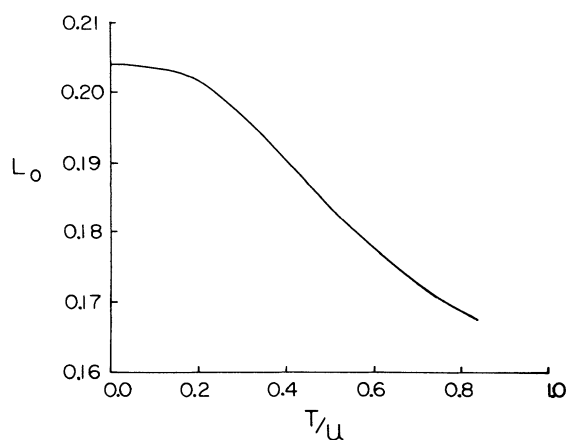


FIG. 11. Similar to Fig. 10 for an octahedron with $n=5$ and $U/t=10$. Note that the temperature scale factor is U .

ground state (Fig. 11), we see only a gradual decrease from a maximum at $T=0$ toward the itinerant limit.

The temperature dependence of other correlation functions is more rapid, with these quantities approaching zero at temperatures relatively much lower than that at which the local moment is reduced to the itinerant limit. This behavior was noticed by Shiba and Pincus, and we find here that it is quite general. We show in Figs. 12 and 13 two examples corresponding to "ferromagnetism" for the octahedron with $n=5$; the values of U/t being 50 and 10, respectively. The first case (Fig. 12) corresponds to saturated ferromagnetism; there is only a rapid decay of L_1 . In the second case where the ground state corresponds to unsaturated ferromagnetism, not only is the zero-temperature value much smaller (as is seen in Fig. 2) than in the saturated, but there is a low-temperature increase by a factor of about 2, followed by a rapid decrease leading to a change of sign, a minimum, and finally slow decay to zero. The explanation of this complicated behavior starts from the observation that at the lowest

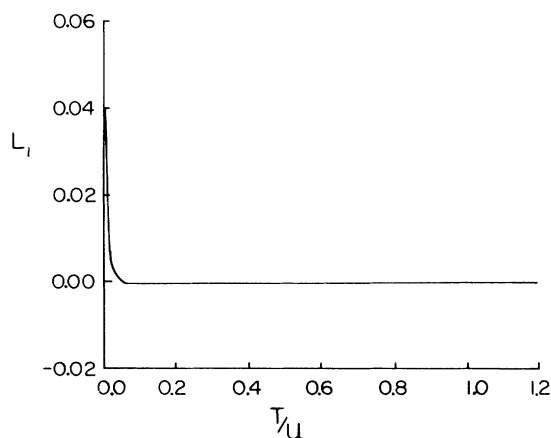


FIG. 12. First-neighbor correlation function L_1 for the octahedron with $n=5$ and $U/t=50$.

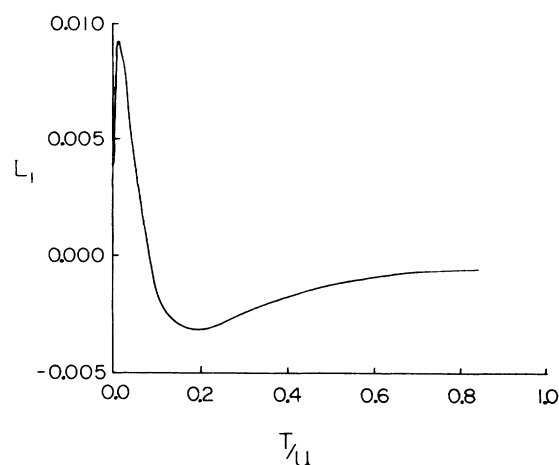


FIG. 13. First-neighbor correlation function for the octahedron with $n=5$ and $U/t=10$.

temperatures, the ground state with $S = \frac{3}{2}$ is energetically close to a higher spin state ($S = \frac{5}{2}$) with a much larger value of L_1 . These stronger correlations are included in the thermodynamic average. As the temperature increases still further, contributions from low-spin, antiferromagnetic states are mixed in, causing the sign reversal. Thereafter the mixture of a large number of states leads to cancellations and decay of the function.

First- and second-neighbor correlations functions for the antiferromagnetic system, the octahedron with $n=6$ and $U/t=10$, are shown in Figs. 14 and 15, respectively. These simply show rapid decay to zero from the $T=0$ value; the decay being somewhat more rapid in the case of the second-neighbor function.

It is apparent from the examples shown and from similar ones we have calculated but do not exhibit explicitly here, that the first- and second-neighbor correlations decay sharply over a range of temperatures in which there are only small changes in the value of the local moment.

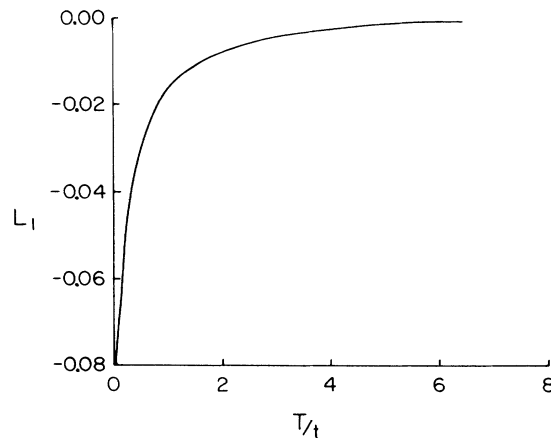


FIG. 14. First-neighbor correlation function for the octahedron with $n=6$ and $U/t=10$.

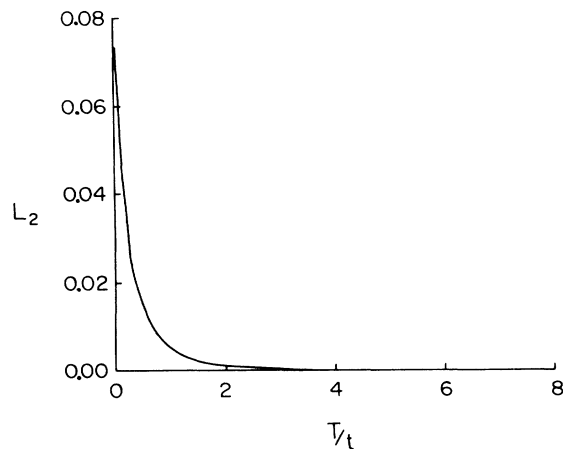


FIG. 15. Second-neighbor correlation function for the octahedron and $U/t=10$.

The explanation is evident from the energy spectra shown in Fig. 3. The local moment cannot decay substantially until the temperature is high enough so that states with appreciable double occupancies of sites can contribute. This requires temperatures which are an appreciable fraction of U . However, the low-energy excitations involve spin rearrangements, and as soon as the temperature is large enough for these states to be excited, the intersite correlations become small. The correlations between sites are quite sensitive to temperature; whereas local moment formation is gradual with a much lower sensitivity to temperature. This is, of course, characteristic of bulk systems as well, both from theoretical studies and experimental observations.

IV. SUMMARY

The principal conclusion of this work is that exact calculations for the ground state and thermodynamic properties of small clusters show complex magnetic properties in many respects typical of bulk materials. Specifically, we

find behavior characteristic of paramagnetism, antiferromagnetism, saturated ferromagnetism, and unsaturated ferromagnetism, illustrated in calculations of magnetic susceptibilities, specific heats, and spin correlation functions.

In a general way, as a sort of summary with respect to all geometries, occupations, and parameters, low spin ($S=0$ or $S=\frac{1}{2}$) is likely to characterize the ground state of the Hubbard Hamiltonian. If there is one electron per site the ground state will probably show spin correlations typical of antiferromagnetism. For specific occupancies, the ground state may have the maximum possible spin. This situation is favored by the existence of degeneracies in the spectrum of single-particle states. However, the existence of degeneracies is not required. Systems of low symmetry in which the single-particle spectrum has no degeneracies may have high-spin ground state for some occupancies and sufficiently strong electron-electron repulsion.²⁴

Many of the examples used in this paper to illustrate the thermodynamic properties pertain to the octahedron. We have shown examples illustrating Curie or Curie-Weiss behavior of the magnetic susceptibility at high temperatures: a two-peak structure in the specific heat and the temperature dependence of the local moment and of intersite spin correlation functions. Our results generally have simple explanation in terms of the level structure. In future work we will try to compare our cluster calculations for small systems with those obtained from quantum Monte Carlo studies of larger systems. We are encouraged to believe that exact studies for small systems offer a means of obtaining substantial physical insight into the properties of large systems where more exact analysis has either been impossible or has led to controversial results.

ACKNOWLEDGMENT

This work was supported in part by the National Science Foundation under Grant No. DMR-85-04259.

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