Antiferromagnetic Ground State in the s-Band Hubbard Model*

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(Received 19 May 1975)

We have extended the Gutzwiller variational scheme to investigate the antiferromagnetic ground state in the Hubbard model with one electron per atom. Virtual electron hopping is found to be essential for the antiferromagnetic ordering. A paramagnetic-metallic to antiferromagnetic-insulator state transition is obtained with increasing U/W ratio. The V_2O_3-type phase diagram follows from the present theory.

In accordance with experiments, the ground state of the Hubbard Hamiltonian[1] at the atomic limit should be the antiferromagnetic (AFM) insulator state. With decreasing U/W ratio, where U is the intra-atomic correlation energy and W is the bare bandwidth, AFM ordering disappears, while the system becomes metallic. However, Mott[2] and Herring[3] have pointed out that these two transitions are due to different mechanisms.

Consider a half-filled s-band Hubbard Hamiltonian

$$H=\sum_{gg'\sigma} t_{gg'} a_{g'\sigma} + U\sum_{g} n_{g\uparrow} n_{g\downarrow}. \tag{1}$$

At the atomic limit electron hopping can be treated as a perturbation. The ground state of the unperturbed Hamiltonian is highly degenerate due to the random distribution of the electronic spins. In second-order perturbation, electron virtual hopping lifts this degeneracy. If we retain only the nearest-neighbor hopping t, the energy correction per electron is simply $-Zt^2/U$, where Z is the mean number of antiparallel-spin nearest neighbors. Since the nearest-neighbor exchange energy is much smaller and does not show up in H, electron virtual hopping invariably provides an AFM coupling in the Hubbard model.

On the other hand, the metallic conductivity requires the formation of polar states. It needs an activation energy about the order U. For sufficiently large U the metal-insulator-transition (MIT) temperature should therefore be higher than or equal to the Néel temperature. In an insulator state far away from the MIT, the role of electron virtual hopping has been discussed by Caron and Pratt[4] and Esterling and Lange.[5] Near the MIT, the importance of virtual hopping relative to the possible transitions between the AFM insulator, paramagnetic insulator, and paramagnetic metallic states will be investigated in this Letter. The Gutzwiller variational scheme[6] is particularly useful for the present problem because of its emphasis on the localized properties in constructing the trial function.

We extend the Gutzwiller variational method by introducing a parameter ζ in terms of which we can calculate the probability of having an antiparallel-spin nearest neighbor. To avoid ambiguity in our presentation, we separate the lattice into two interpenetrating sublattices $L(\uparrow)$ and $L(\downarrow)$. This does not necessarily mean the presence of sublattice magnetization which leads to Slater's split-band model.

When $U=0$, the Fermi sea K of a half-filled s band consists of the inner half of the first Brillouin zone. For $k\in K$, define the single-particle creation operators

$$d_{k\sigma}{}^{\dagger}=S\Big\{\sum_{g\in L(\sigma)} e^{ikg} a_{g\sigma}{}^{\dagger}+\zeta_k \sum_{g\in L(-\sigma)} e^{ikg} a_{g\sigma}{}^{\dagger}\Big\}, \tag{2}$$

where S is a normalization factor. ζ_k is a variational parameter to be determined later.

Using Gutzwiller's projection operator,[6] the ground-state trial function for a correlated system can be expressed as

$$\Psi=\prod\{1-(1-\xi)n_{g\uparrow}n_{g\downarrow}\}\sum_{k\in K} d_{k\uparrow}{}^{\dagger} d_{k\downarrow}{}^{\dagger}|0\rangle, \tag{3}$$

where ξ is the second variational parameter, and $|0\rangle$ is the vacuum. If G (or F) is a set of $N/2$ lattice sites to be occupied by up (or down) spin electrons, a localized many-electron wave function can be defined as

$$\Phi(GF)=\sum_{g\in G} a_{g\uparrow}{}^{\dagger}\prod_{g\in F} a_{g\downarrow}{}^{\dagger}|0\rangle. \tag{4}$$

Substituting (2) into (3), we have

$$\Psi=\sum_{G,F} A(\xi^{\nu},\{\zeta_k\},G,F)\Phi(GF), \tag{5}$$

where ν is the number of lattice sites common to both G and F. The coefficient A is too complicated to be given explicitly in this Letter.

We will use the quasichemical approximation (QCA)[7] to calculate the energy of the trial ground state. In doing so one should be aware of the possibility that if the fluctuation of ζ_k is large, it may affect the validity of QCA. Hence we assume that ζ_k depends on the ratio U/W but not on k. This approximation becomes exact for the nonmagnetic state where $\zeta_k = 1$. On the other hand, it increases the energy of the AFM state. Consequently the criterion for AFM ordering should be less stringent than what will be predicted from the present theory.

To calculate the energy, we directly incorporate electron virtual hopping into the Hubbard Hamiltonian instead of using the second-order perturbation formalism. If an up-spin electron is adjacent to a down-spin electron, virtual hopping will lower the energy of each electron by $V(U)$. For a given value of U, we see from the following [Eq. (9)] that the ground state has an optimum number ν of doubly occupied atoms. Therefore, if a doubly occupied atom is next to an empty one the energy should increase by $V(U)$. For the region of large U which we are interested in, ν is very small and $V(U)$ asymptotically approaches t^2/U. Consequently the contribution from the second case is negligible.

The effective Hamiltonian can then be written as

$$H = \sum_{gg'\sigma} t_{gg'} a_{g\sigma}{}^{\dagger} a_{g'\sigma} + U \sum_{g} n_{g\uparrow} n_{g\downarrow}$$
$$- V(U) \sum_{g,\sigma} \{ n_{g\sigma}(1 - n_{g-\sigma}) n_{g'\sigma}(1 - n_{g'\sigma}) - n_{g\sigma} n_{g-\sigma}(1 - n_{g'\sigma})(1 - n_{g'-\sigma}) \}. \qquad (6)$$

The detailed calculation in QCA for the energy per electron $E = \langle \Psi | H | \Psi \rangle / N \langle \Psi | \Psi \rangle$ is straightforward and will not be given in this Letter. We define $\bar{\epsilon}$ as the average band energy per electron and normalize it to $\bar{\epsilon} = 0$ for a full band. Let $\epsilon = E/4|\bar{\epsilon}|$, $\alpha = U/4|\bar{\epsilon}|$, and $\beta = ZV(U)/4|\bar{\epsilon}|$; then we have

$$\epsilon = -\eta(1+\zeta)^2(1+2\eta+\zeta^2)^{-2} + (\eta\alpha - \beta)(1+2\eta+\zeta)^{-1}, \qquad (7)$$

where $\eta = \xi\zeta$ is the parameter originally defined by Gutzwiller[6] to measure the correlation strength. The probability for an atom being doubly occupied is also obtained:

$$\nu = \eta(1+2\eta+\zeta^2)^{-1}. \qquad (8)$$

The parameter ζ has a value between 0 for the AFM state and 1 for the nonmagnetic state. For given values of α and β, η and ζ are determined by minimizing ϵ. From the condition $\partial\epsilon/\partial\eta = 0$, we have

$$\nu = \{(1+\zeta)^2 - \alpha(1+\zeta^2) - 2\beta\}/4(1+\zeta)^2, \qquad (9)$$

$$\epsilon = -\{2(1+\zeta)^2\nu^2 + \beta\}/(1+\zeta^2). \qquad (10)$$

For a given value of ζ, ν decreases monotonically with increasing U. When U reaches the critical value

$$U_0(\zeta) = \{4(1+\zeta)^2|\bar{\epsilon}| - 2ZV(U_0)\}/(1+\zeta^2), \qquad (11)$$

ν vanishes, indicating a metal-to-insulator transition. Under this condition, the energy contains only the virtual hopping energy,

$$\epsilon(U \geq U_0) = -4ZV(U)|\bar{\epsilon}|/(1+\zeta^2). \qquad (12)$$

The minimum energy obviously corresponds to $\zeta = 0$. Hence the ground state for large U is the AFM insulator.

At the other limit of small U, $V(U)$ can be neglected. It is easy to see from (9) and (10) that ϵ is less for large values of ζ. Consequently in this region the ground state is paramagnetic metallic. The exact transition from this region to the AFM-insulator state depends on the form of $V(U)$. $V(U) = t^2/U$ derived from the second-order perturbation is valid only for large U. Since for small U the ground state is paramagnetic, the

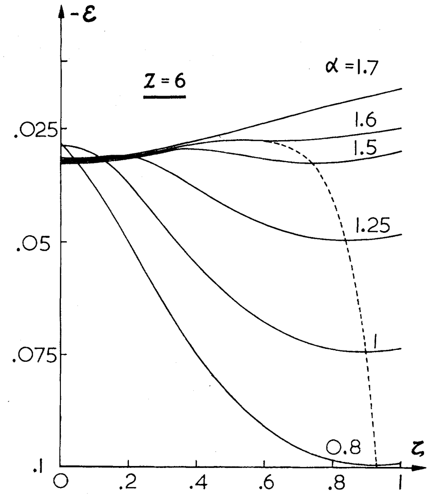

FIG. 1. Average energy per electron ϵ versus ζ for different correlation energies. The dashed curve marks the positions of minima.

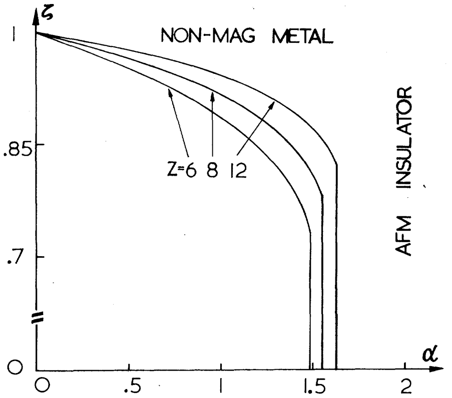

FIG. 2. Spin-ordering parameter ζ as a function of $\alpha = U/4|\bar{\epsilon}|$. Z is the coordination number.

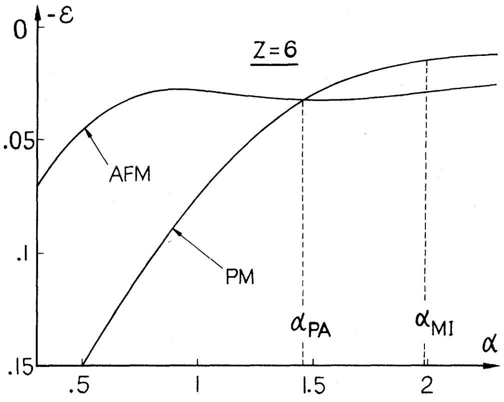

FIG. 3. Energies per electron for the AFM state and for the paramagnetic state as functions of $\alpha = U/4|\bar{\epsilon}|$.

exact form of $V(U)$ is no longer important as long as it is small. In this region we can join t^2/U smoothly to a monotonically increasing function of U. Without further information except that $V(U) \to 0$ as $U \to 0$, we assume the following form for the numerical calculation:

$$V(U)=\begin{cases} W^2/4Z^2U, & U \geq U_0(\zeta=1)=8|\bar{\epsilon}|, \\ \dfrac{W^2U(12|\bar{\epsilon}|-U)}{1024Z^2|\bar{\epsilon}|^3}, & U \leq 8|\bar{\epsilon}|, \end{cases} \tag{13}$$

where $W=2Zt$ is the bare bandwidth. Note that around the region of interest, namely $U \simeq 8|\bar{\epsilon}|$, $V(U)$ is continuous with continuous first derivative.

Using a parabolic density of states and (13), the minimum value of ϵ is obtained numerically. In Fig. 1 we plot ϵ as a function of ζ for various values of $\alpha = U/4|\bar{\epsilon}|$. The minimum of each curve is marked by the dashed curve. For $\alpha \geq 1.5$ the absolute minimum is located at $\zeta = 0$. Therefore, a first-order transition is shown in Fig. 2 where the value of ζ for the ground state is given as a function of α. We have tried different forms of $V(U)$ and found that the ζ versus α exhibits the same characteristic first-order transition as indicated in Fig. 2.

In Fig. 3 we illustrate a paramagnetic metallic ground state for $\alpha < \alpha_{PA}$ and an AFM insulator ground state for $\alpha > \alpha_{PA}$. We also found from (11) that the paramagnetic state is metallic for $\alpha < \alpha_{MI}$. Since the paramagnetic state has more entropy than the AFM state, an AFM-insulator to paramagnetic-metallic transition occurs at the Néel temperature if $\alpha < \alpha_{MI}$. On the other hand, if $\alpha > \alpha_{MI}$, the transition should be from the AFM insulator to the paramagnetic insulator state, and then to the paramagnetic metallic state as the temperature is raised. This behavior has been observed in V_2O_3.[8]

We would like to point out that recently Ogawa, Kanda, and Matsubara[9] have tried to extend the Gutzwiller variational method to treat the AFM state. They have fixed the ζ_k of (2) by use of the Hartree-Fock approximation, and therefore the ζ_k's are no longer variational parameters. The ζ_k so determined vary strongly with k. For this case, the energy calculation scheme of the Gutzwiller variational method may not be valid. Consequently, the ground state of Ogawa, Kanda, and Matsubara is just the Hartree-Fock solution which predicts a too small critical value $\alpha_{PA} \simeq 0.8$ for the existence of an AFM ground state.

One of the authors (K.A.C.) would like to thank Professor N. F. Mott, Professor K.-F. Berggren, and Dr. M. C. Gutzwiller for very stimulating discussions.

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*Work partially supported by Banco Nacional do Desenvolvimento Econômico, Conselho Nacional de Pesquisas, and CAPES (Brasilian government).

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Observation of a Spin-Peierls Transition in a Heisenberg Antiferromagnetic Linear-Chain System*

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(Received 16 June 1975)

Magnetic-susceptibility and EPR measurements are reported which provide the first unambiguous evidence for a spin-Peierls transition in a system of linear one-dimensional antiferromagnetic Heisenberg chains. The material studied is $\mathrm{TTFCuS_4C_4(CF_3)_4}$ (TFF stands for tetrathiafulvalinium). At 12 K, the spin-lattice system undergoes a second-order phase transition to a singlet ground state.

There has been much interest recently in the unusual electrical conducting properties of quasi-one-dimensional systems such as tetrathiafulvalene tetracyanoquinodimethane. Several of these materials seem to undergo a Peierls transition[1] to an insulating ground state.[2] The magnetic analog, the spin-Peierls transition, has been discussed theoretically[3,4] for antiferromagnetic (AF) chains. At this transition the spin-lattice system dimerizes and the material undergoes a second-order transition to a singlet ground state with a magnetic gap. We report the first unambiguous evidence, from magnetic measurements, for such a transition.

The material studied is tetrathiafulvalinium bis-*cis*-(1, 2-perfluoromethylethylene-1, 2-dithiolato)-copper [or, $\mathrm{TTFCuS_4C_4(CF_3)_4}$]. It is a member of a series of $\mathrm{TTF}M\mathrm{S_4C_4(CF_3)_4}$ (M=Cu, Au, Pt, or Ni) donor-acceptor compounds, whose preparation and characterization are reported elsewhere.[5] These materials are obtained as needlelike crystals, 2–3 mm long and ~0.05 ×0.3 mm^2 in cross section, by slow cooling of acetonitrile solutions. Their formulation as ionic materials rests on the results of solution-conductivity measurements, spectral studies, EPR, and magnetic-susceptibility measurements.[5] The TTF cation should have one unpaired electron located in a singly degenerate π orbital of b_{1u} symmetry[6] (D_{2h}). On the other hand, the $M\mathrm{S_4C_4(CF_3)_4}$ anion (M =Cu or Au) is diamagnetic with two electrons in the highest occupied b_{2g} (D_{2h}) π orbital.[7]

A complete structure determination for $\mathrm{TTFCuS_4C_4(CF_3)_4}$ has not been done, but a study of single crystals with the x-ray precession technique shows that the Cu compound is isostructural with the corresponding Pt derivative for which a full structure determination[8] has been made. Their space groups are the same and their lattice parameters and diffraction intensities of corresponding reflections are quite similar. The true space group is $P\bar{1}$, with one formula unit per unit cell, but it is convenient to describe the structure in terms of a face-centered cell with $Z=4$ and space group $F\bar{1}$. With that description for the Cu compound, $a=23.1$ Å, $b=13.2$ Å, $c=7.80$ Å, $\alpha=92.7°$, $\beta=101.8°$, and $\gamma=90°$.

The molecular arrangement is shown in Fig. 1. There occurs an alternate stacking of the two kinds of ions along c axis, as well as alternation along the a and b axes. The molecular planes of both kinds of ions are nearly parallel to the (001) planes, and the protrusion of π orbitals from these planes strongly favors electronic interaction along the c axis. The alternate stacking arrangement of oppositely charged ions and their