

Theory of itinerant antiferromagnetism: Zero-temperature properties*

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The method of Gutzwiller is extended to include antiferromagnetism in a s -band Hubbard model. A first-order paramagnetic (PM) to antiferromagnetic (AFM) transition is obtained with increasing U/W ratio. The AFM ground state in the phase diagram is restricted between the electron density $n_1 < 1$ and $n_2 = 2 - n_1$. It is also bounded from below by a critical value of U/W . The complete AFM ordering appears only for $n = 1$. As n approaches n_1 or n_2 along the phase boundary, the AFM ordering gradually disappears. The AFM ordering is essentially due to virtual electron hopping, and the values of n_1 , n_2 , and critical U/W depend on the bare density of states and the coordination number. The probability of having antiparallel-spin nearest-neighbor pair is computed. The result is consistent with the phase diagram. We also found a region in the phase diagram where the PM and the AFM states coexist. The AFM ground state at $n = 1$ is insulating. Depending on the value of U/W , the present theory predicts either an AFM insulating—PM metallic or an AFM insulating—PM insulating—PM metallic transition as the temperature is raised. Therefore, the V_2O_3 -type phase diagram follows from the present theory.

I. INTRODUCTION

The s -band Hubbard model,¹ as one of the simplest and most tractable models of a many-fermion system, is of intrinsic theoretical interest regarding the metal-insulator (M - I) transition² and the appearance of magnetic ordering³ in strongly correlated electron systems. In their pioneering works Hubbard, Gutzwiller, and Kanamori have used different approaches to solve this model Hamiltonian.¹ The Green's-function decoupling scheme due to Hubbard and the Gutzwiller variational method have been improved and generalized by many authors.^{4,5} For sufficiently strong correlation, criteria for the M - I transition and for ferromagnetism were obtained in terms of the density of electrons and the electronic density of states.

At the atomic limit, where the interatomic separation is very large, the ground state of the Hubbard Hamiltonian should be antiferromagnetic (AFM) insulating in accordance with experiment. However, as Mott² and Herring³ have pointed out, the M - I transition and the AFM ordering are due to different mechanisms. Consider an insulator with one electron per atom and near the M - I transition. In this case the hopping terms $t_{gg'}$ for $g \neq g'$ in the Hubbard Hamiltonian

$$H = \sum_{gg'\sigma} t_{gg'} a_{g\sigma}^\dagger a_{g'\sigma} + U \sum_g n_{g\uparrow} n_{g\downarrow} \quad (1)$$

can be treated as a perturbation. The ground state of the unperturbed Hamiltonian is just a collection of noninteracting atoms. Owing to the random distribution of electronic spins, this ground state is highly degenerate. The second-order perturba-

tion will lift the degeneracy, and is interpreted as due to virtual electron hoppings. If we include only the nearest-neighbor hopping t , the energy correction per electron is simply $\Delta E_1 = -Zt^2/U$, 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 , the virtual hopping invariably provides AFM coupling in the Hubbard model.

On the other hand, the metallic conductivity requires the formation of polar states. It needs an activation energy $\Delta E_2 \approx U$. For strong correlation, $\Delta E_2 > -\Delta E_1$. Consequently, in this model the M - I transition temperature should be higher than the Néel temperature. This conclusion agrees with the experimental evidence that lower Néel temperatures are more usual for materials exhibiting M - I transitions.⁶ Although the s -band Hubbard model does not include the orbital degeneracy which is crucial for the magnetic ordering, the more general model will not change this conclusion qualitatively.

The AFM state of the s -band Hubbard model has been investigated by Penn,⁷ Caron and Pratt,⁸ Johansson and Berggen,⁹ Brinkman and Rice,¹⁰ Arai,¹¹ and Bernasconi.¹² The importance of electron virtual hopping near the M - I transition was emphasized by Caron and Pratt. Recently Ogawa, Kanda, and Matsubara¹³ have tried to extend the Gutzwiller variational method to include the AFM state. Nevertheless, owing to their approximating algebraic manipulation, they obtain some unphysical results, which will be discussed in Sec. IV.

In Gutzwiller's variational approach^{1,5} the basis for the many-electron wave functions is a set of Slater determinants $\{\Phi\}$ from Wannier states. For

a given value of correlation energy U , one finds that it is sufficient to consider only a subset $\{\Phi(\nu)\}$ where all the $\Phi(\nu)$'s have the same optimum number ν of doubly occupied atoms. Approaching the M - I transition from the metallic side, ν decreases monotonically to zero if the band is half-filled. Therefore, Gutzwiller's trial function is ideal for incorporating the AFM virtual hopping coupling to the M - I transition.

The purpose of this paper is to extend the Gutzwiller method along this line in order to investigate the AFM ordering in the s -band Hubbard model. In view of previous work⁵ our method can be easily generalized to cope with the orbital degeneracy. In Sec. II, we will construct the proper trial function, which will be used to calculate the energy in Sec. III. We then perform a model calculation using a parabolic density of states. The results are discussed in Sec. IV. A concluding remark will follow in Sec. V.

II. TRIAL FUNCTION

In order to cope with the AFM ordering, our trial function will contain a parameter in terms of which we can determine the probability of having antiparallel-spin nearest neighbors. To avoid ambiguity in the following presentation, we separate the lattice of L sites into two interpenetrating sublattices $L(\uparrow)$ and $L(\downarrow)$. However, our method is general enough to deal with the lattices which do not have interpenetrating sublattices. We will consider in this section only the special case of a half-filled band with equal numbers of up- and down-spin electrons, $N(\uparrow) = N(\downarrow) = \frac{1}{2}L$. The general case of less or more than one electron per atom will be left to the appendix.

Consider the single-particle creation operator

$$d_{k\uparrow}^\dagger = \cos \theta_k a_{k\uparrow}^\dagger + \sin \theta_k a_{k+Q\uparrow}^\dagger, \quad (2)$$

where θ_k is a parameter. $a_{k\uparrow}^\dagger$ is the creation operator for the k Bloch state with up spin. Q is so chosen that

$$e^{iQg} = \begin{cases} 1 & \text{for site } g \in L(\uparrow) \\ -1 & \text{for site } g \in L(\downarrow). \end{cases} \quad (3)$$

Using the transformation

$$a_{k\sigma}^\dagger = L^{-1/2} \sum_g e^{ikg} a_{g\sigma}^\dagger \quad (4)$$

we have

$$\begin{aligned} (\cos \theta_k + \sin \theta_k)^{-1} d_{k\uparrow}^\dagger &= L^{-1/2} \sum_{g \in L(\uparrow)} e^{ikg} a_{g\uparrow}^\dagger \\ &+ \zeta_k L^{-1/2} \sum_{g \in L(\downarrow)} e^{ikg} a_{g\uparrow}^\dagger, \end{aligned} \quad (5)$$

where $\zeta_k = (\cos \theta_k - \sin \theta_k) / (\cos \theta_k + \sin \theta_k)$.

Let $k = (k_1, k_2, \dots, k_{L/2})$ be the set of vectors in the inner half of the first Brillouin zone. This set of vectors define a many-electron wave function

$$\Psi_\uparrow = \prod_{k \in K} d_{k\uparrow}^\dagger |0\rangle, \quad (6)$$

where $|0\rangle$ is the vacuum. The many-electron wave functions in the localized picture can be similarly constructed by first defining $G = (g_1, g_2, \dots, g_{L/2})$, a set of lattice sites to be occupied by up-spin electrons. Then the localized many-electron wave function can be expressed as

$$\Phi_\uparrow(G) = \prod_{g \in G} a_{g\uparrow}^\dagger |0\rangle. \quad (7)$$

When Eq. (5) is substituted into Eq. (6), it becomes

$$\Psi_\uparrow = \sum_{\text{all } G} A_\uparrow(G) \Phi_\uparrow(G) \quad (8)$$

except for a normalization constant. The coefficient $A_\uparrow(G)$ can be conveniently expressed as a determinant:

$$A_\uparrow(G) = \begin{vmatrix} g_1 g_2 \cdots g_{L/2} \\ k_1 \\ k_2 \\ \zeta_{\uparrow k}(g) L^{-1/2} e^{ikg} \\ \vdots \\ k_{L/2} \end{vmatrix}. \quad (9)$$

The elements of the determinant are $\zeta_{\uparrow k}(g) L^{-1/2} e^{ikg}$, and the rows (or columns) are labeled by k_i (or g_i). $\zeta_{\uparrow k}(g)$ is defined as

$$\zeta_{\uparrow k}(g) = \begin{cases} 1 & \text{for } g \in L(\uparrow) \\ \zeta_k & \text{for } g \in L(\downarrow). \end{cases} \quad (10)$$

For down-spin electrons we can similarly define

$$d_{k\downarrow}^\dagger = \cos \theta_k a_{k\downarrow}^\dagger - \sin \theta_k a_{k+Q\downarrow}^\dagger \quad (11)$$

and

$$\Psi_\downarrow = \prod_{k \in K} d_{k\downarrow}^\dagger |0\rangle. \quad (12)$$

Let $F = (f_1, f_2, \dots, f_{L/2})$ be a set of lattice sites to be occupied by down-spin electrons, and define

$$\Phi_\downarrow(F) = \prod_{f \in F} a_{f\downarrow}^\dagger |0\rangle. \quad (13)$$

Ψ_\downarrow can then be rewritten as

$$\Psi_{\uparrow} = \sum_{\text{all } F} A_{\uparrow}(F) \Phi_{\uparrow}(F), \quad (14)$$

where

$$A_{\uparrow}(F) = \begin{matrix} f_{\uparrow} f_2 \cdots f_{L/2} \\ \left. \begin{array}{c} k_1 \\ k_2 \\ \vdots \\ k_{L/2} \end{array} \right| \zeta_{\uparrow k}(f) L^{-1/2} e^{ikf} \end{matrix} \quad (15)$$

and

$$\zeta_{\uparrow k}(f) = \begin{cases} 1 & \text{for } f \in L(\uparrow) \\ \zeta_k & \text{for } f \in L(\downarrow). \end{cases} \quad (16)$$

We now define

$$A(GF) = A_{\uparrow}(G) A_{\uparrow}(F),$$

$$\Phi(GF) = \Phi_{\uparrow}(G) \Phi_{\uparrow}(F),$$

and the uncorrelated many-electron wave function

$$\Psi = \Psi_{\uparrow} \Psi_{\downarrow} = \sum_{\text{all } G, F} A(GF) \Phi(GF). \quad (17)$$

The Gutzwiller projection operator¹ is defined as

$$P = \prod_{\text{all } g} [1 - (1 - \xi) n_{g\uparrow} n_{g\downarrow}], \quad (18)$$

where ξ is a variational parameter. Applying to Ψ we obtain the trial function for the ground state of a correlated system

$$\Psi_c = P \sum_{\text{all } G, F} A(GF) B(GF) \Phi(GF). \quad (19)$$

The factor $B(GF)$ is introduced to count for the less-important interatomic correlation. In Gutzwiller's variational scheme he has proposed a quasichemical approximation (QCA)^{1,5} to determine $B(GF)$. Note that the parameter ξ in Eq. (18) is different from the parameter η which Gutzwiller used in his original formulation. The relation between ξ and η will be given later.

For given G and F , let $\nu(\sigma)$ be the number of doubly occupied atoms in sublattice $L(\sigma)$, and $\mu(\sigma)$ be the number of σ -spin electrons in $L(-\sigma)$ sublattice. Also define $\nu = \nu(\uparrow) + \nu(\downarrow)$ and $\mu = \mu(\uparrow) + \mu(\downarrow)$. Then

$$\langle \Psi_c | \Psi_c \rangle = \sum_{\nu, \mu} \xi^{2\nu} \sum_{\mu(\uparrow), \nu(\uparrow)} \sum'_{G, F} |A(GF) B(GF)|^2, \quad (20)$$

where the primed sum runs over only those G and F which have the same number of $\mu(\uparrow)$, $\mu(\downarrow)$, $\nu(\uparrow)$, and $\nu(\downarrow)$. This primed sum can be calculated with QCA. However, in doing so one should be aware of the possibility that the function $\zeta_{\sigma k}$ in Eqs. (9) and (15) may affect the validity of QCA if the fluctuation of $\zeta_{\sigma k}$ is large.

Ogawa *et al.*¹³ have obtained the Slater split-band model from the Hubbard Hamiltonian with Hartree-Fock approximation. They find from there an expression for $\zeta_{\sigma k}$ and use it in the trial function. So $\zeta_{\sigma k}$ are no longer variational parameters. However, their $\zeta_{\sigma k}$ varies rapidly near the Slater split gap⁹ and, therefore, most likely make the QCA a very bad approximation in their calculation. This is the reason why they have obtained some unphysical results, which we will discuss later.

In this paper we assume that $\zeta_{\sigma k}$ depends on the electron hopping probability and the correlation energy U , but not on k . Hence, we have reduced a large number of variational parameters into a single one to measure the AFM ordering. This is also necessary in order to be mathematically manageable. This approximation does not affect the nonmagnetic state where all the $\zeta_{\sigma k}$ are equal to one. On the other hand, the restriction on the variational parameters $\zeta_{\sigma k}$ 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.

We then have a second variational parameter $\zeta_{\sigma k} = \zeta$ for all k and σ . For paramagnetic state $\zeta = 1$ while $\zeta = 0$ specifies a complete AFM state. With the notation

$$\{a|b\} = a! / b! (a-b)!,$$

the QCA result is readily obtained:

$$\begin{aligned} \langle \Psi_c | \Psi_c \rangle^{\text{QCA}} = & \sum_{\nu, \mu} \xi^{2\nu} \zeta^{2\mu} \sum_{\nu(\uparrow), \mu(\uparrow)} \left\{ \frac{1}{2} N | \mu - \mu(\uparrow) |^2 \left[\frac{1}{2} N - \mu + \mu(\uparrow) | \nu(\uparrow) \right] \right. \\ & \times \left. \left[\mu - \mu(\uparrow) | \mu(\uparrow) - \nu(\uparrow) \right] \left[\mu - \mu(\uparrow) | \nu - \nu(\uparrow) \right] \left[\frac{1}{2} N - \mu + \mu(\uparrow) | \frac{1}{2} N - \mu(\uparrow) + \nu(\uparrow) - \nu \right] \right\}. \end{aligned} \quad (21)$$

The right-hand side of the above equation has the form of a hypergeometric function. It is highly

peaked and the sum can be well approximated by the peak term. For given ξ and ζ , the peak term

is easily determined by the optimum value ν_0 and μ_0 which satisfy the conditions

$$\begin{aligned}\mu(\dagger) &= \mu(\ddagger) = \frac{1}{2}\mu_0, \\ \nu(\dagger) &= \nu(\ddagger) = \frac{1}{2}\nu_0, \\ (\mu_0 - \nu_0)/(L - \mu_0 - \nu_0) &= \zeta^2,\end{aligned}$$

and

$$\nu_0^2/(L - \mu_0 - \nu_0)(\mu_0 - \nu_0) = \xi^2.$$

These conditions agree with the symmetry requirement.

The product $\eta = \xi\zeta$ with $0 \leq \eta \leq 1$ is just the variational parameter originally defined in Gutzwiller's projection operator.^{1,5} Let us relabel ν_0 and μ_0 , respectively, as ν and μ for the peak term in Eq. (21). The ground-state trial function becomes

$$\Psi_c(\nu\mu) = \eta^\nu \zeta^{\mu-\nu} \sum'_{G,F} B(GF)A(GF)\Phi(GF), \quad (22)$$

where

$$\nu = \eta L / (1 + 2\eta + \zeta^2), \quad \mu = (\eta + \zeta^2)L / (1 + 2\eta + \zeta^2). \quad (23)$$

The primed sum in Eq. (22) is restricted to the G and F which have the same values ν and μ . Note that for $\zeta = 1$, Eqs. (22) and (23) reduce to the correct nonmagnetic results.

III. ENERGY CRITERION FOR ANTIFERROMAGNETISM

The trial function Eq. (22) is characterized by two parameters ν and μ . Their values for the ground states are obtained from the minimization conditions $\partial E_0(\nu\mu)/\partial\nu = 0$ and $\partial E_0(\nu\mu)/\partial\mu = 0$, where

$$E_0(\nu\mu) = \langle \Psi_c(\nu\mu) | H | \Psi_c(\nu\mu) \rangle / \langle \Psi_c(\nu\mu) | \Psi_c(\nu\mu) \rangle.$$

However, this approach originally proposed by Gutzwiller^{1,5} has neglected the contribution of the electron virtual hopping to the total energy. Since the virtual hopping provides an AFM coupling in the itinerant theory of antiferromagnetism, we will extend the Gutzwiller method to include this effect.

The conventional approach is second-order perturbation theory. In our case, the zeroth-order wave functions are specified by a pair of parameters (ν, μ) as indicated by Eq. (22). In the strong correlation limit where the electron hopping is a perturbation, the expectation value of the Hamiltonian Eq. (1) to the second-order correction is

$$\begin{aligned}E(\nu\mu) &= E_0(\nu\mu) \\ &+ \sum'_{\omega,\gamma} \frac{|\langle \Psi_c(\omega\gamma) | \sum'_{g'g''} t_{g'g''} a_{g''}^\dagger a_{g'} | \Psi_c(\nu\mu) \rangle|^2}{(\Delta E) \langle \Psi_c(\nu\mu) | \Psi_c(\nu\mu) \rangle \langle \Psi_c(\omega\gamma) | \Psi_c(\omega\gamma) \rangle}.\end{aligned} \quad (24)$$

Here the first-order correction, i.e., the real hopping energy is included in $E_0(\nu\mu)$. The primed sum excludes the term $(\omega, \gamma) = (\nu, \mu)$.

Substituting Eq. (22) into Eq. (24), the hopping matrix elements are reduced to the form $\langle \Phi(WR) | a_{g''}^\dagger a_{g'} | \Phi(GF) \rangle$. Since the configurations (GF) and (WR) are characterized by two different pairs of parameters (ν, μ) and (ω, γ) , respectively, these matrix elements are nontrivial only if $\omega = \nu \pm 1$ and γ differs from μ by no more than 1.

For large U the only important electron hoppings are between nearest neighbors. Let t be the nearest-neighbor hopping integral. Then the energy factor in the second term of Eq. (24) has the simple form t^2/U , which is valid for large U . For numerical computation in the next section, we have to treat U as a variable between the atomic limit and the band limit. Therefore, for convenience we will express this energy factor as $V(U)$. At the limit of strong correlation, $V(U)$ approaches asymptotically to t^2/U . The exact form of $V(U)$ will be discussed in Sec. IV.

The total energy Eq. (24) can now be readily computed in the quasicheical approximation. The reader is referred to the original work^{1,5} for the details of QCA. Let us normalize E , ν , and μ as E/L , ν/L , and μ/L , and then relabel them by the same symbols E , ν , and μ respectively. The QCA result for the average energy per electron can be expressed as

$$E = \frac{4\eta(1+\zeta)^2}{(1+2\eta+\zeta^2)^2} \bar{\epsilon} + \nu U - (1-2\mu-2\nu+2\mu^2)ZV(U), \quad (25)$$

where Z is the number of nearest neighbors. $\bar{\epsilon}$ is the average band energy per electron in an uncorrelated system. If we normalize the band energy to make the energy of a full band zero, then $\bar{\epsilon} \leq 0$. We should point out that the ν and the μ in Eq. (25) are the optimum numbers which characterize the zeroth-order wave function under the influence of the electron virtual hopping. This is unambiguously shown in Eq. (24). The number of doubly occupied atoms in the total wave function which includes the higher-order corrections fluctuates around this optimum number ν . This concept is quite essential to the M - I transition to be discussed below.

It is convenient to work with the dimensionless quantities $\mathcal{E} = E/4|\bar{\epsilon}|$, $\alpha = U/4|\bar{\epsilon}|$, and $\beta = ZV(U)/4|\bar{\epsilon}|$. Substituting Eq. (23) into Eq. (25), we have

$$\begin{aligned}\mathcal{E} &= -[\eta(1+\zeta)^2 - \eta(1+2\eta+\zeta^2)\alpha + (1-2\eta^2+\zeta^2)\beta] \\ &\times (1+2\eta+\zeta^2)^{-2}.\end{aligned} \quad (26)$$

The next step is to minimize \mathcal{E} with respect to the variational parameters η and ζ . The resulting formula is so complicated that the minimum of \mathcal{E}

can be obtained only numerically. Before presenting the results, we will first investigate a simpler case in order to get an analytical solution. This will enable us to demonstrate the essential features of our model.

For large U , the major contribution to the virtual hopping energy is from the singly occupied antiparallel-spin nearest neighbors. If we only consider the contributions from such processes to the virtual hopping energy in Eq. (24), then Eq. (26) can be approximated as

$$\mathcal{E} = -\frac{\eta(1+\zeta)^2}{(1+2\eta+\zeta^2)^2} + \frac{\eta\alpha - \beta}{1+2\eta+\zeta^2}. \quad (27)$$

The optimum number η_0 for the condition $\partial\mathcal{E}/\partial\eta=0$ is

$$\eta_0 = \left(\frac{1+\zeta^2}{2}\right) \frac{(1+\zeta)^2 - \alpha(1+\zeta^2) - 2\beta}{(1+\zeta)^2 + \alpha(1+\zeta^2) + 2\beta}. \quad (28)$$

Substituting this in Eqs. (23) and (27), we get

$$\nu = [(1+\zeta)^2 - \alpha(1+\zeta^2) - 2\beta]/4(1+\zeta)^2, \quad (29)$$

$$\mathcal{E} = -[2(1+\zeta)^2\nu^2 + \beta]/(1+\zeta^2). \quad (30)$$

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

$$U_0(\zeta) = [4(1+\zeta)^2|\bar{\epsilon}| - 2ZV(U_0)]/(1+\zeta^2), \quad (31)$$

ν vanishes. [This conclusion also holds if the exact energy Eq. (26) is used.] Note that ν is only the number of doubly occupied atoms in the zeroth-order wave function. The total wave function still contains a finite number of doubly occupied sites owing to the electron virtual hopping. It has been proved⁵ that in the Gutzwiller variational scheme, a vanishing ν is equivalent to the non-existence of a Fermi surface. Therefore, the condition $\nu=0$ indicates a M - I transition. Under this condition the energy contains only the virtual hopping energy

$$\mathcal{E} = -\beta/(1+\zeta^2). \quad (32)$$

It is clearly seen that the minimum value of \mathcal{E} corresponds to $\zeta=0$. Hence the ground state for large U is AFM insulating.

At the other limit, U small, $V(U)$ can be neglected. We can then set $\beta=0$ and Eqs. (26) and (27) are identical. For $\beta=0$ and for fixed value of U , the ν of Eq. (29) increases monotonically with increasing ζ . It is easy to see from Eq. (30) that the energy is less for larger value of ζ . Consequently in this region the ground state is paramagnetic metallic.

The details of the transition from the paramagnetic metallic to the AFM insulating state depend on the form of $V(U)$. The form $V(U)=t^2/U$ derived

from the second-order perturbation is valid only for large U . Since for small U the wave functions are sufficiently delocalized, $V(U)$ must approach zero very rapidly. In this region the exact form of $V(U)$ is no longer important as long as it is small enough to guarantee a paramagnetic ground state. Hence we can join t^2/U smoothly to a smooth function which vanishes at $U=0$ (in fact we have tried different functions and obtained similar qualitative results). Without further information except $V(U) \rightarrow 0$ as $U \rightarrow 0$, we assume the following form for numerical calculation

$$V(U) = \begin{cases} W^2/4Z^2U & \text{for } U \geq U_0(\zeta=1) = 8|\bar{\epsilon}| \\ W^2U(12|\bar{\epsilon}| - U)/1024Z^2|\bar{\epsilon}|^3 & \text{for } U \leq 8|\bar{\epsilon}|, \end{cases} \quad (33)$$

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

IV. RESULTS AND DISCUSSIONS

The minimization of \mathcal{E} given by Eq. (26) with respect to η yields the relation

$$\eta = \frac{(1+\zeta^2)(1+\zeta)^2 - (\alpha+2\beta)(1+\zeta^2)^2 - 2\beta(1-\zeta^2)^2}{2(1+\zeta)^2 + 2(\alpha+2\beta)(1+\zeta^2)}. \quad (34)$$

Substituting this relation into Eq. (26) the energy \mathcal{E} becomes a function of U , Z , W , and ζ . For the electron density $n \neq 1$ the \mathcal{E} has been derived in the Appendix. Hence, in general, the energy is a function of U , Z , W , ζ , and n . The condition $\partial\mathcal{E}/\partial\zeta=0$ will determine the optimum value of ζ for the ground state as a function of U , Z , W , and n . However, the equation $\partial\mathcal{E}/\partial\zeta=0$ is too complicated to be solved analytically. Therefore we will use a parabolic density of states of width W to determine the optimum value $\zeta(U, Z, W, n)$.

The general scheme is the following: For given values of Z , n , and the ratio U/W , we find the optimum value of ζ , which gives the minimum of \mathcal{E} . Since U/W is proportional to the $\alpha=U/4|\bar{\epsilon}|$, we can then plot this optimum value of ζ for the ground state against α . For $Z=6$ the results are shown in Fig. 1. The numbers inserted in the dotted lines are the electron density n . For fixed electron density there is a first-order transition from the paramagnetic ($\zeta=1$) to the AFM state ($\zeta<1$) as α increases. Only for one electron per atom, $n=1$, there is complete AFM ordering $\zeta=0$ for $\alpha>1.425$. As n gets smaller the degree of AFM spin polarization decreases continuously until at a critical electron density $n_c=0.9548$ it disappears entirely.

Ogawa *et al.*¹³ and Takano and Uchinami¹⁴ have

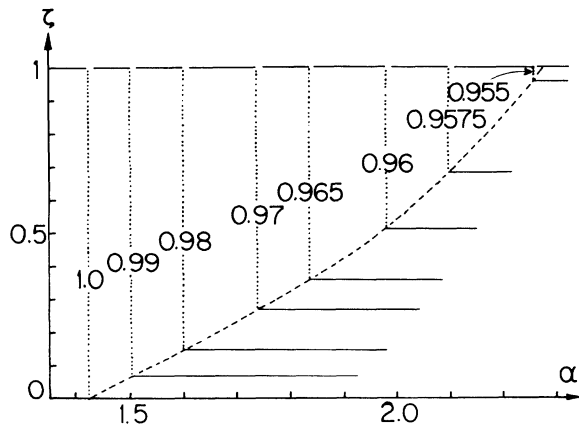


FIG. 1. Optimum number of ζ for the ground state versus the normalized intra-atomic correlation energy α . The inserted numbers are the electron density. The coordination number is 6.

extended the Gutzwiller variational method with different approximation to study the criterion of antiferromagnetism. These authors also found a critical electron density n_c such that for $n \geq n_c$ AFM ordering can occur for sufficiently large U . However, their AFM ground state has complete spin polarization $\zeta = 0$ for all values of $n \geq n_c$. This is certainly incorrect for $n \neq 1$ because of the existence of spin diffusion among the holes. Furthermore, our minimum value of α for the occurrence of AFM ordering is $\alpha = 1.425$ (for $n = 1$) in contrary

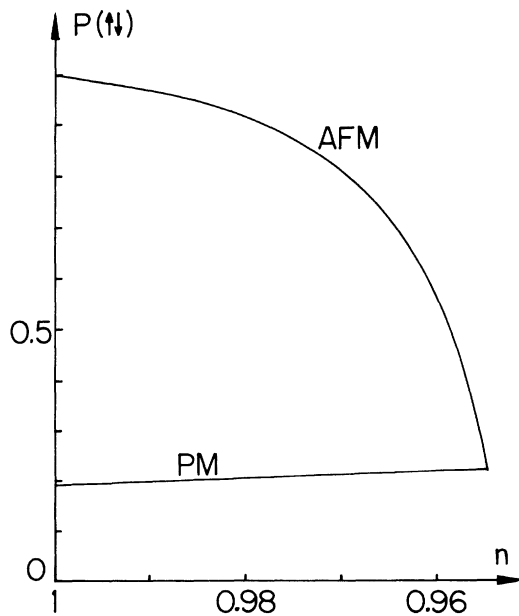


FIG. 2. Probability of having singly occupied antiparallel-spin nearest-neighbor pair. AFM and PM correspond, respectively, to the states specified by the bottom and the top points of the dotted lines in Fig. 1.

to Matsubara and Takano's minimum values around $\alpha = 0.7-0.9$. Judging from the critical value $\alpha = 2$ for the $M-I$ transition,¹⁰ and from the fact that the AFM state for $n = 1$ is insulating, Matsubara and Takano's values of $\alpha = 0.7-0.9$ are too low.

To demonstrate the degree of AFM spin polarization under various conditions, it is clearer to compute the probability of having singly occupied antiparallel-spin nearest-neighbor pair:

$$P(\uparrow\downarrow) = \langle \Psi_c | n_{g\uparrow}(1 - n_{g\downarrow})n_{g'\downarrow}(1 - n_{g'\uparrow}) | \Psi_c \rangle / \langle \Psi_c | \Psi_c \rangle.$$

For a given value of n and at the critical value of α where the first-order paramagnetic to antiferromagnetic transition occurs, we compute the $P(\uparrow\downarrow)$ for both the paramagnetic and the AFM states. The result for $Z = 6$ is shown in Fig. 2. The $P(\uparrow\downarrow)$ for the AFM state is greater than the $P(\uparrow\downarrow)$ for the paramagnetic state as it should be as long as $n \geq 0.9548$. Note that the $P(\uparrow\downarrow)$ for the paramagnetic state does not equal to the Hartree-Fock value because here we have $U \neq 0$.

The magnetic phase diagram in terms of α and n is given in Fig. 3. For the s -band Hubbard model, ferromagnetic ordering is possible only at $U \rightarrow \infty$ and therefore does not appear in Fig. 3. Our model contains the assumption of the existence of interpenetrating sublattices. $Z = 12$ corresponds to a face-center-cubic structure, which does not have such sublattices. Since our method can be easily generalized to all kinds of lattices, we include the

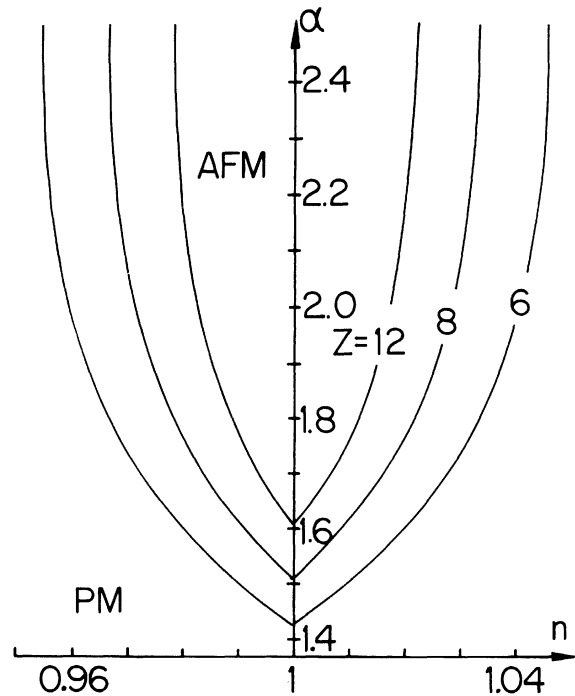


FIG. 3. Magnetic phase diagrams for different coordination numbers.

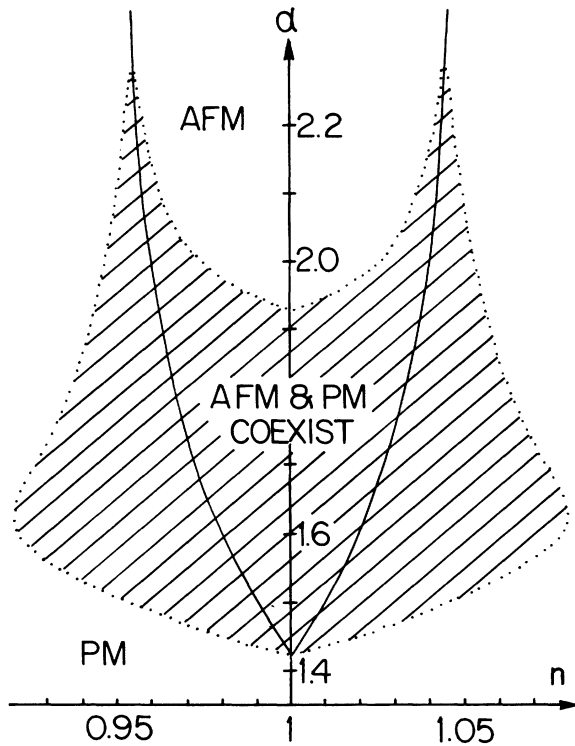


FIG. 4. AFM and PM states coexist in the shaded region. The coordination number is 6.

$Z=12$ case here to illustrate the influence of coordination number on the phase diagram. We see that it requires stronger correlation to stabilize the AFM state in lattices with larger coordination number Z . The reason is as follows: The direct hoppings favor the nonmagnetic state while the AFM state is caused by the virtual hoppings. The direct hopping is a first-order effect as compared to the second-order virtual hopping. Hence, an increase of the coordination number will stabilize the paramagnetic state. Nevertheless, in a more general degenerate-band Hubbard model our conclusion may not hold.

In a system exhibiting a first-order paramagnetic-AFM transition it is possible that the system is in an inhomogeneous state in which the two phases coexist.¹⁵ The coexistence region is determined by the common tangent of the two \mathcal{E} vs $1/n$ curves, one for the paramagnetic state and the other for the AFM state. Figure 4 shows the coexistence region for $Z=6$ by a shaded area. At fixed value of n , the coexistence region has both a lower and an upper bounds. Ogawa *et al.*¹³ do not find the upper bound; their coexistence region extends to infinite α . Since the AFM state becomes more stable for larger α , such upper bound must exist. As n approaches the limit 0.9548 or 1.0452 along the phase boundary (the solid curve), the coexis-

tence region gradually disappears. This is in accordance with the diminishing of the AFM ordering at this limit, as indicated by Figs. 1 and 2.

Another striking difference between our phase diagram and those of Ogawa *et al.* and of Penn⁷ is illustrated in Fig. 5. In order to be consistent with their works we have recomputed our phase boundary using a rectangular density of states. Penn's phase boundary, curve C, obtained from the Hartree-Fock approximation does not show critical values of both α and n for the occurrence of AFM state. Curve A is from the present theory while curve B is Matsubara's phase boundary. Between $n=1.045$ (or 0.9555) and $n=1.065$ (or 0.935) the behavior of curve B is unphysical. If we increase α along a line of fixed n in these ranges, the system goes through a para-antiferro-paramagnetic transition. The second AFM-paramagnetic transition with increasing correlation is definitely wrong. The reason for their unphysical result is obvious: They have compared the energy of the paramagnetic state in the Gutzwiller scheme with that of the AFM state in the Hartree-Fock approximation. We will have further discussion on this later. The similar incorrect result also shows up in the phase diagram of Takano and Uchinami.¹⁴

The V_2O_3 -type phase diagram⁶ follows naturally from the present theory. In Fig. 6 we plot the energies of the AFM state and the paramagnetic state against α for $n=1$ and $Z=6$. The paramagnetic-AFM transition occurs at $\alpha = \alpha_{PA}$. From Eq. (23)

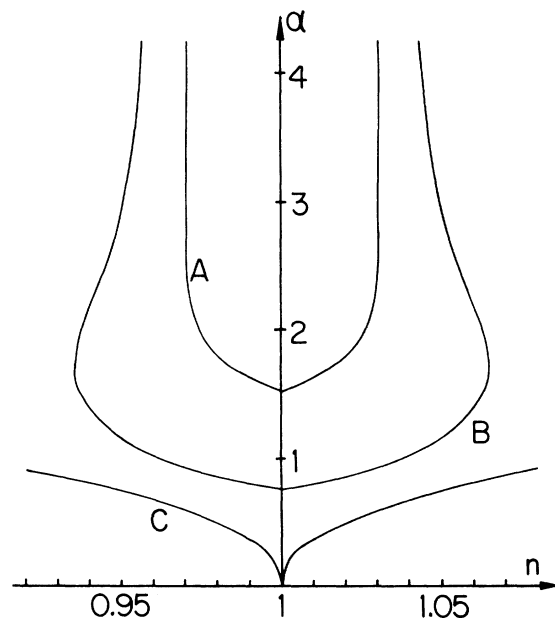


FIG. 5. Comparison of the magnetic phase diagrams: curve A is the present theory, curve B is from Ogawa, Kanda, and Matsubara (Ref. 13), and curve C is from Penn (Ref. 7).

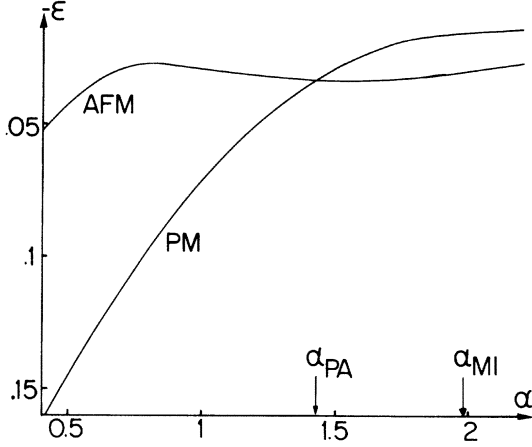


FIG. 6. The normalized energy per electron versus the normalized intra-atomic correlation energy. The electron density $n = 1$ and the coordination number is 6.

we found $\nu = 0$ for the AFM ground state. Hence the AFM ground state is insulating. Within the paramagnetic state $\nu = 0$ when $\alpha \geq \alpha_{MI}$. Since the paramagnetic state has more entropy than the AFM state, a AFM insulating 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 insulating to the paramagnetic insulating, and then to the paramagnetic metallic as the temperature is raised. In the region $\alpha > 1.6$ the energy difference between the two curves is almost constant. This indicates a constant Néel temperature in this range of α . Such behavior has been observed in V_2O_3 .

V. CONCLUSION

Owing to its emphasis on the localized properties of electrons, the Gutzwiller variational scheme is particularly useful in investigating the AFM ordering under strong correlation. However, an AFM trial function is rather difficult to construct. Ogawa *et al.* used the Slater's split-band model to incorporate the AFM ordering to the Gutzwiller method. Hence, they did not introduce a new variational parameter. Let $\epsilon^*(k)$ be the split-band energy and $n_{k\sigma}^*$ be the corresponding number operator. Furthermore, let the associated number operator in the Wannier representation be $n_{g\sigma}^*$. Then the result of Ogawa *et al.*¹³ can be obtained by applying the Gutzwiller scheme to the Hamiltonian

$$H^* = \sum_{k\sigma} \epsilon^*(k) n_{k\sigma}^* + U \sum_{g\uparrow} n_{g\uparrow}^* n_{g\downarrow}^*. \quad (35)$$

However, $\epsilon^*(k)$ already contains a large portion of the intra-atomic correlation energy in the Hartree-Fock approximation. This is the reason why

they failed to obtain the AFM state with the energy lower than the paramagnetic state in extending the method of Gutzwiller.

The AFM state of Ogawa *et al.* for $n = 1$ is not necessarily insulating. Whether it is insulating depends on the existence of a band gap in Slater split-band model. Takano and Uchinami¹⁴ obtained an AFM ground state by another extension of the Gutzwiller method. Their AFM state is always metallic. Besides, it is not clear if the transition obtained by Takano and Uchinami is of first or of second order. All of these ambiguities are clarified in the present work.

The crucial assumption in the present theory is the use of a single variational parameter ζ to measure the AFM ordering. Herring¹⁶ pointed out that in this case it may be better to use the probability of having antiparallel-spin nearest-neighbor pair $P(\uparrow\downarrow)$ as the variational parameter. Comparing Figs. 1 and 2, we see that the role of ζ and the role of $P(\uparrow\downarrow)$ are actually equivalent. The present theory will be much improved if we can treat each $\zeta_{\sigma k}$ as an individual variational parameter. However, how to handle these 10^{24} variational parameters mathematically is a real challenge.

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APPENDIX

We will derive the energy expression to be used in Sec. IV for the numerical computation. Consider the general case that the electron $n \leq 1$. For $n \geq 1$ the same results apply owing to the electron-hole symmetry. The description and the definitions in Sec. II are valid except that the number of electrons for each spin is now $\frac{1}{2}N$ instead of $\frac{1}{2}L$. The sets K , G , and F should be redefined as $K = (k_1, k_2, \dots, k_{N/2})$, $G = (g_1, g_2, \dots, g_{N/2})$, and $F = (f_1, f_2, \dots, f_{N/2})$. Furthermore, instead of Eq. (23) we found it more convenient to use the relations

$$\mu = [(1 + \zeta^2)\nu + N\zeta^2/2] / (1 + \zeta^2), \quad (A1)$$

$$\eta = (1 + \zeta^2) [\nu(L - N/2 + \nu)]^{1/2} / (N - 2\nu). \quad (A2)$$

With these modifications, the energy per electron in Eq. (25) becomes

$$E = (1 + \zeta)^2 (n - 2\nu) [\nu^{1/2} + (1 - n + \nu)^{1/2}]^2 (1 + \zeta^2)^{-1} \bar{\epsilon}(n) + \nu U / N - [(1 + \zeta^4)(n - 2\nu)^2 (1 + \zeta^2)^{-2} - 2\nu(1 - n + \nu)] Z V(U) / n, \quad (A3)$$

where $\bar{\epsilon}(n) = 2 \sum_{k \in K} \epsilon(k)/N$ is the average band energy per electron. If we define the dimensionless quantities $\mathcal{G} = E/4 |\bar{\epsilon}(n=1)|$, $\alpha = U/4 |\bar{\epsilon}(n=1)|$, and $\beta = ZV(U)/4 |\bar{\epsilon}(n=1)|$, then the normalized energy per electron \mathcal{E} corresponding to Eq. (26) is given by

$$n\mathcal{E} = -(1+\zeta)^2 (n-2\nu) [\nu^{1/2} + (1-n+\nu)^{1/2}]^2 / 4(1+\zeta^2) + \alpha\nu - \beta [(1+\zeta^4)(n-2\nu)^2(1+\zeta^2)^{-2} - 2\nu(1-n+\nu)]. \quad (\text{A4})$$

To obtain the above equation, we have used the approximation $n\bar{\epsilon}(n) = \bar{\epsilon}(n=1)$, which is correct to the order $(1-n)^2$ for symmetric density of states.

The minimization of \mathcal{E} with respect to ν , $\partial\mathcal{E}/\partial\nu$

= 0 yields the condition

$$(A^2 - 64n^2)\nu^4 + (A^2D - 2AB - 96n^2 + 128n^3)\nu^3 \times [B^2 + 2(8n^3 - AB)(1-n) - 4n^2(3-4n)^2]\nu^2 + (1-n)(B^2 + 12n^3 - 16n^4)\nu - (1-n)^2n^4 = 0, \quad (\text{A5})$$

where

$$A = 8n - 16n^2\beta(1-\zeta)^2/(1+\zeta^2), \\ B = 2n[2n - 1 - 4n^2\beta(1-\zeta)^2(1+\zeta^2)^{-1}] - 4(\alpha n + 2\beta n^2)(1+\zeta^2)(1+\zeta)^{-2}. \quad (\text{A6})$$

Giving the values of α , β , and n , Eqs. (A4) and (A5) are then solved simultaneously for \mathcal{E} as a function of ζ .

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¹J. Hubbard, Proc. R. Soc. A 276, 238 (1963); 281, 401 (1964); M. C. Gutzwiller, Phys. Rev. Lett. 10 159 (1963); Phys. Rev. 137, A 1726 (1965); J. Kanamori, Prog. Theor. Phys. 30, 275 (1963).
²N. F. Mott, *Metal-Insulator Transition* (Taylor and Francis, London, 1974).
³C. Herring, *Magnetism*, edited by G. T. Rodo and H. Suhl (Academic, New York, 1966), Vol. IV.
⁴For Green's-function techniques see Rev. Mod. Phys. 40, No. 4 (1968).
⁵For the Gutzwiller variational scheme, see K. A. Chao, Phys. Rev. B 4, 4034 (1971), 8, 1088 (1973); J. Phys. C 7, 127 (1974); 7, 2269 (1974); W. F. Brinkman and

T. M. Rice, Phys. Rev. B 2, 4302 (1970); K. A. Chao and K. F. Berggren, Phys. Rev. Lett. 34, 880 (1975).
⁶D. B. McWhan and J. P. Remeika, Phys. Rev. B 2, 3734 (1970).
⁷D. R. Penn, Phys. Rev. 142, 350 (1966).
⁸L. G. Caron and G. W. Pratt, Rev. Mod. Phys. 40, 802 (1968).
⁹B. Johansson and K.-F. Berggren, Phys. Rev. 181, 855 (1969).
¹⁰W. F. Brinkman and T. M. Rice, Phys. Rev. B 2, 1324 (1970).
¹¹T. Arai, Phys. Rev. B 4, 216 (1971).
¹²J. Bernasconi, Phys. Kondens. Mater. 14, 225 (1972).
¹³T. Ogawa, K. Kanda, and T. Matsubara, Prog. Theor. Phys. 53, 614 (1975).
¹⁴F. Takano and M. Uchinami, Prog. Theor. Phys. 53, 1267 (1975).
¹⁵P. B. Visscher, Phys. Rev. B 10, 932 (1974); 10, 943 (1974).
¹⁶C. Herring (private communication).