Metal-insulator transition and local moments in a narrow band: A simple thermodynamic theory

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A theory of metal-insulator transition (MIT) and of the localized moments in a narrow band is given both at temperature $T=0$ and $T\neq 0$. In this approach the ratio η of doubly occupied sites is expanded in a power-expansion parameter of the ground-state energy. The coefficients of the expansion are determined from known expressions for the energy and η in certain limiting situations, while the optimal value of η is found by minimizing the energy (at $T=0$) or the free energy ($T\neq 0$). At $T=0$ the present theory reproduces the results for η and the energy obtained with the Gutzwiller method. Also, we decompose the system into localized moments and the Fermi liquid, and provide a precise meaning to the former. At $T\neq 0$ a simple expression for the entropy is proposed which contains both fermionic and localized-moment parts, each with an appropriate weighting factor. The entropy reproduces correctly both the metallic and paramagnetic-insulator limits. The coefficient γ of the linear electronic specific heat is found to be strongly enhanced close to the MIT. Additionally, we show that the insulating system (at $T=0$) behaves at $T\neq 0$ as a semiconductor with a Mott-Hubbard band gap. Our theory is based on the single-site approximation; in this paper only the paramagnetic phase is analyzed.

I. INTRODUCTION

Although the Mott-Hubbard transition[1] continues to receive widespread attention a full microscopic treatment of this transition is still lacking. Well-established theories are based on the perturbation expansions either close to the Hartree-Fock state[2] or close to the atomic limit.[3] For the intermediate range it has been necessary to resort to an interpolation scheme[4] that correctly extrapolates to the above limiting situations.

In this paper we set up a simple phenomenological approach which represents the single-site approximation to the correct analysis both for zero and nonzero temperatures. Namely, we expand the ground-state energy E_G in terms of the fraction η of doubly occupied sites and determine the expansion coefficients from a study of limiting cases. We set up also an expression for the entropy of the correlated electrons as composed of two parts. The first part deals with quasiparticles moving in a band narrowed by correlations. The narrowing effect is quite prominent for the stronger correlations and greatly reduces the degeneracy temperature. Secondly, the increased number of singly occupied sites gives rise to a localized-moment contribution $k_B \ln 2$ per extra moment in the paramagnetic phase (the only phase we consider). Both these contributions have appropriate weighting factors; combined together they correctly reproduce both the band and the atomic limits.

The principal characteristics of the present approach are the derivation of the entropy and of the specific-heat enhancement in the narrow-band system as well as the demonstration that for sufficiently strong correlations the system can behave thermodynamically as a semiconductor even though we start from the one-band description.

The paper is organized as follows. In Sec. II we formulate the problem based on both intuitive and formal grounds. The definition of the localized moments is also provided in Sec. II. In Sec. III we generalize our theory to nonzero temperatures, $T\neq 0$, and derive there the enhancement of the electronic specific heat near the metal-insulator transition. Also, in Sec. III we discuss the localized-moment regime at finite temperatures. We show that the Hubbard gap appears naturally in the activation energy for carriers in the semiconducting phase. The relation of the present treatment to earlier theories and to the nature of the underlying approximations are described in Sec. IV.

II. FORMULATION OF THE PROBLEM AT $T=0$

A. Definitions and phenomenological approach

For a quantitative formulation of the metal-insulator transition we begin with the conventional model Hamiltonian[5] in the site representation

$$H=\sum_{i,j,\sigma}{}'t_{ij}a_{i\sigma}^{\dagger}a_{j\sigma}+U\sum_{i}n_{i\uparrow}n_{i\downarrow}\ , \tag{2.1}$$

in which t_{ij} is the transfer integral between sites i and j (the case $i=j$ is excluded from the sum), $a_{i\sigma}^{\dagger}a_{j\sigma}$ represent the creation and annihilation operators for particles of spin σ on sites i and j, respectively, U is the on-site interaction energy between two electrons with opposite spins, and $n_{i\sigma}$ is the number operator for occupation of site i by particle with spin σ.

Our immediate aim is to obtain an approximate relation for the ground-state energy E_G for the N-site system. If interactions are restricted to nearest-neighbor hops,

$$\frac{E_G}{N}=\frac{t}{N}\sum_{i,j(i),\sigma}{}'\langle a_{i\sigma}^{\dagger}a_{j(i)\sigma}\rangle+U\eta\ , \tag{2.2}$$

in which $j(i)$ enumerates z sites that are nearest neighbors to site i, $t\equiv t_{ij(i)}$, and $\eta\equiv\langle n_{i\uparrow}n_{i\downarrow}\rangle$ is the expectation value of double occupancy at site i; the lattice is assumed to be translationally invariant so that η is actually independent of i.

Since ηN increases as U/W diminishes (here $W=2z\,|\,t\,|$ is the bandwidth in the tight-binding approximation) one must optimize η for each value of U/W. For this purpose it is expedient to introduce a representation that explicitly distinguishes between singly and doubly occupied states through the identity

$$n_{i\sigma}\equiv n_{i\sigma}(1-n_{i-\sigma})+n_{i\sigma}n_{i-\sigma}\equiv\nu_{i\sigma}+\eta_i\ , \tag{2.3}$$

in which the number operator $n_{i\sigma}$ for occupation of site i by electron of spin σ is expressed in terms of the number operators $\nu_{i\sigma}$ and η_i for single and double occupancy of site i. The factor $1-n_{i-\sigma}$ ensures nonoccupancy of site i by a second electron of reversed spin $-\sigma$; also, $\eta_i=n_{i\sigma}n_{i-\sigma}$.

The number operators just introduced are not independent since the sum of their expectation values must be equal to the average degree of band filling n which is a fixed quantity:

$$n\equiv\sum_{\sigma}\langle n_{i\sigma}\rangle=\sum_{\sigma}\langle\nu_{i\sigma}\rangle+2\langle\eta_i\rangle\equiv\nu+2\eta\ , \tag{2.4}$$

where translational invariance was invoked to render the expectation values site independent. Consistent with translational invariance we restrict ourselves to the paramagnetic case only.

We turn now to a consideration of the various hopping processes in the evaluation of $\sum_{\sigma}\langle a_{i\sigma}^{\dagger}a_{j\sigma}\rangle$ in Eq. (2.2) by writing

$$\begin{aligned}\sum_{\sigma,i,j}{}'a_{i\sigma}^{\dagger}a_{j\sigma}&\equiv\sum_{\sigma,i,j}{}'a_{i\sigma}^{\dagger}(1-n_{i-\sigma}+n_{i-\sigma})a_{j\sigma}(1-n_{j-\sigma}+n_{j-\sigma})\\&=\sum_{\sigma,i,j}{}'[a_{i\sigma}^{\dagger}(1-n_{i-\sigma})a_{j\sigma}(1-n_{j-\sigma})+a_{i\sigma}^{\dagger}n_{i-\sigma}a_{j\sigma}n_{j-\sigma}+a_{i\sigma}^{\dagger}(1-n_{i-\sigma})a_{j\sigma}n_{j-\sigma}+a_{i\sigma}^{\dagger}n_{i-\sigma}a_{j\sigma}(1-n_{j-\sigma})]\ .\end{aligned} \tag{2.5}$$

Taking expectation values on both sides of the above equation one obtains the following interpretations. (i) $\langle a_{i\sigma}^{\dagger}(1-n_{i-\sigma})a_{j\sigma}(1-n_{j-\sigma})\rangle$ represents the probability of transferring a particle with spin σ from a singly occupied site j to a previously empty site i. This quantity can be represented by $\nu_{\sigma}(1-n)$ since, according to the earlier definitions, $\nu_{\sigma}\equiv\langle\nu_{i\sigma}\rangle$ represents the probability of encountering a typical site in a singly occupied state, and $1-n=1-\langle n_{i\uparrow}\rangle-\langle n_{i\downarrow}\rangle$ represents the probability of finding a typical site empty. Briefly, (i) specifies the joint probability of finding site i empty and site $j(i)$ singly occupied by an electron with spin σ. The remaining terms in (2.5) are represented and interpreted in a similar manner. Namely, (ii) $\langle a_{i\sigma}^{\dagger}n_{i-\sigma}a_{j\sigma}n_{j-\sigma}\rangle=\eta\nu_{-\sigma}$ specifies the joint probability of finding site i singly occupied by an electron of spin $-\sigma$ and site $j(i)$ doubly occupied. Furthermore, we note that (iii) $\langle a_{i\sigma}^{\dagger}(1-n_{i-\sigma})a_{j\sigma}n_{j-\sigma}\rangle=\eta(1-n)$ specifies the joint probability of finding site j doubly occupied and site i empty. (iv) $\langle a_{i\sigma}^{\dagger}n_{i-\sigma}a_{j\sigma}(1-n_{j-\sigma})\rangle=\nu_{\sigma}\nu_{-\sigma}$ specifies the joint probability of encountering both sites i and $j(i)$ in a singly occupied state.

The expectation values (iii) and (iv) as written in the preceding paragraph present a problem because they should be equal; it is not obvious whether this requirement is met. Therefore, we choose to represent these terms as follows:

$$\begin{aligned}&\langle a_{i\sigma}^{\dagger}(1-n_{i-\sigma})a_{j\sigma}n_{j-\sigma}\rangle+\langle a_{i\sigma}^{\dagger}n_{i-\sigma}a_{j\sigma}(1-n_{j-\sigma})\rangle\\&\qquad=A_0+B_0\eta+C_0\eta^2\ ,\end{aligned} \tag{2.6}$$

which is suggested by the interrelations between $\eta(1-n)$ and $\nu_{\sigma}\nu_{-\sigma}$ [see Eqs. (2.3) and (2.4)]; the above equation is the central *ansatz* of the present variational treatment. The coefficients A_0, B_0, and C_0 will be determined from the known expression for E_G in several limiting cases. The coefficients are assumed to depend on the degree of band filling n and not on U/W.

We collect items (i)—(iv), applying Eq. (2.6), and substitute in the expectation value $\langle H\rangle$ derived from Eq. (2.1). We restrict t_{ij} to nearest-neighbor sites: then $t_{ij}=t$; otherwise $t_{ij}=0$. Summing first over $j(i)$ one obtains the factor z; on subsequently summing over i one obtains N. Setting $W=2z\,|\,t\,|$, the expectation value for the ground-state energy may be written as

$$\begin{aligned}\frac{E_G}{N}&=\frac{1}{N}\langle H\rangle\\&=-\frac{W}{2}[\nu(1-n)+\eta\nu+A_0+B_0\eta+C_0\eta^2]+U\eta\\&\equiv-\frac{W}{2}(A+B\eta+C\eta^2)+U\eta\ ,\end{aligned} \tag{2.7}$$

in which the parameters A, B, and C have been defined in

an obvious manner. An equation of the form (2.7) for $T=0$ will be rederived in a more formal fashion in the next section. From the derivation one can see how to generalize this procedure and the condition under which it is applicable. The present approach is in fact a single-site method since the averages (i)—(iv) are calculated assuming that the intersite correlations can be expressed in terms of single-site characteristics.

B. Systematic approach for $T=0$

The preceding discussion suggests the following, more systematic approach: It is expedient to replace the quantity

$$(t/N)\sum_{\sigma,i,j(i)}{}' \langle a_{i\sigma}^{\dagger}a_{j(i)\sigma}\rangle$$

by the function[6] $\Phi(\eta)\bar{\epsilon}$, with

$$\bar{\epsilon}=\sum_{|\vec{k}|<|\vec{k}_F|}\epsilon_{\vec{k}} \tag{2.8}$$

and

$$\epsilon_{\vec{k}}=t\sum_{j(i)}\exp[i\vec{k}\cdot(\vec{R}_{j(i)}-\vec{R}_i)] . \tag{2.9}$$

In the above equations $|\vec{k}_F|$ is the modulus of the Fermi wave vector, $\vec{R}_i$ and $\vec{R}_{j(i)}$ are the position vectors for sites i and $j(i)$, respectively. Here, and within the single-site approach, Φ is a function of the single variable η [recall Eq. (2.7)]. For the range of band filling $0\le n\le 1$ we have $0\le\eta\le\frac{1}{4}n^2\le\frac{1}{4}$. It is assumed that in this range of n, Φ may be expanded in a Taylor series in η as follows:

$$\Phi(\eta)=\Phi(0)+\left.\frac{d\Phi}{d\eta}\right|_{\eta=0}\eta+\left.\frac{d^2\Phi}{d\eta^2}\right|_{\eta=0}\eta^2+\cdots$$

$$\equiv f_0+f_1\eta+f_2\eta^2+\cdots . \tag{2.10}$$

Then, Eq. (2.7) is replaced by (we limit ourselves to order η^2 in the expansion)

$$E_G/N=\Phi(\eta)\bar{\epsilon}+U\eta=(f_0+f_1\eta+f_2\eta^2)\bar{\epsilon}+U\eta . \tag{2.11}$$

The optimal degree of double occupancy may be found by minimizing E_G: From $\partial(E_G/N)/\partial\eta=0$ one finds

$$\eta_0=-(1/2f_2)(f_1+U/\bar{\epsilon}) . \tag{2.12}$$

The coefficients f_0, f_1, and f_2 may now be determined by imposing the following special sets of conditions: (i) When $U=0$,

$$\left.\frac{E_G}{N}\right|_{U=0}\equiv\bar{\epsilon}=-\frac{W}{2}n(1-n/2) , \tag{2.13}$$

and $\eta=n^2/4$. This is so because Eq. (2.2) then reduces to the first term representing the expectation value for encountering an electron on site $j(i)$ with spin σ and transporting it to site i. For $U=0$, the probability of having an electron at site j is $n/2$, and the probability of locating a hole with given spin on site i is $(1-n/2)$. Hence, we obtain (2.13). Similarly,

$$\eta_0|_{U=0}=n^2/4 . \tag{2.14}$$

(ii) When $\eta=0$ one has $\nu=n$. Now $\langle a_{i\sigma}^{\dagger}a_{j\sigma}\rangle$ of Eq. (2.2) is given by $\frac{1}{2}n(1-n)$, the joint probability that site j is occupied by one electron and site i is empty.

Combining these conditions yields

$$\eta_0|_{U=0}=-\frac{f_1}{2f_2}=\frac{n^2}{4} , \tag{2.15a}$$

$$(E_G/N)|_{U=0}=\bar{\epsilon}=\bar{\epsilon}(f_0+f_1\eta+f_2\eta^2) , \tag{2.15b}$$

$$(E_G/N)|_{\eta=0}=-\frac{W}{2}n(1-n)=f_0\bar{\epsilon} , \tag{2.15c}$$

which may be solved for

$$f_0=(1-n)(1-n/2)^{-1} , \tag{2.16a}$$

$$f_1=4/n(1-n/2) , \tag{2.16b}$$

$$f_2=-8/n^3(1-n/2) . \tag{2.16c}$$

When Eqs. (2.16) are introduced into Eq. (2.12) we obtain

$$\eta_0=\frac{n^2}{4}\left[1-\frac{U}{2W}\right] , \tag{2.17}$$

and Eq. (2.11) becomes

$$E_G/N=-\Phi(\eta_0)(W/2)n(1-n/2)+U\eta_0 , \tag{2.18}$$

in which the coefficients of the function Φ are specified by Eqs. (2.16), and (2.17) is to be used to replace η_0.

The above results have points in common with earlier work: Equations (2.17) and (2.18) have been derived on a microscopic basis by Brinkman and Rice[7] for $n=1$ and for a rectangular density of states (DOS) for which case

$$\eta_0=\tfrac{1}{4}\left[1-\frac{U}{2W}\right] \tag{2.19a}$$

and

$$\frac{E_G}{N}=-\frac{W}{4}\left[1-\frac{U}{2W}\right]^2 . \tag{2.19b}$$

Their general result is obtained by retaining $\bar{\epsilon}$ in the equation for η. We see that factor $(1-U/2W)^2$ plays the role of a band-narrowing factor, which diminishes the effective bandwidth (band energy) toward zero with increasing U/W. For $n=1$ the critical value occurs at $U/W=2$. This ratio is considerably larger than the critical value $U/W=0.87$ obtained by Hubbard.[8] However, one should point out that while our approach is valid for a rather structureless form of the bare DOS (presumably rectangular), Hubbard[8] derived his results for a semielliptical DOS.

According to the present approach, the probability η of double occupation of a site vanishes at the critical ratio $U/W=2$, for any value $n\le 1$. A similar result is obtained by the methodology of Fulde *et al.*[9] (cf. Appendix). By contrast, in earlier approaches[10] based on the Gutzwiller variational principle,[5] η_0 does not approach zero for

any finite U/W and $n\neq 1$. The origin of the strong difference in η as a function of U/W for the cases $n=1$ and $n\neq 1$ within the Gutzwiller approach is not evident to us.

A more general argument concerning band narrowing involves the DOS function of electrons treated as a Fermi fluid for which $\vec{k}$ is a well-defined quantum number. Designate the single-particle energies by $E_{\vec{k}}=\tilde{\Phi}\epsilon_{\vec{k}}$ where $\epsilon_{\vec{k}}$ are the available energy states for noninteracting electrons. If $\rho(E)$ and $\rho_0(E)$ are the corresponding DOS it is readily established that

$$\rho(E)=\tilde{\Phi}^{-1}\rho_0(E/\tilde{\Phi}) , \tag{2.20}$$

which shows that the DOS for a set of bare band states is narrowed by the factor $\tilde{\Phi}$ when the electronic interactions are turned on. The internal energy for quasiparticles is given by

$$\frac{E_B}{N}=\int_{-\infty}^{\infty}E\rho(E)f\left[\frac{E-\mu}{k_BT}\right]dE$$
$$=\tilde{\Phi}\int_{-\infty}^{\infty}\epsilon\rho_0(\epsilon)f\left[\frac{\tilde{\Phi}(\epsilon-\mu_1)}{k_BT}\right]d\epsilon , \tag{2.21}$$

in which $f(x)$ is the Fermi-Dirac function, μ is the chemical potential, and μ_1 is the corresponding one for bare electrons ($\mu=\tilde{\Phi}\mu_1$).

If one compares Eq. (2.21) for $T=0$ with the band energy given before

$$\Phi\bar{\epsilon}\equiv\frac{t}{N}\sum_{\sigma,i,j(i)}{}'\langle a_{i\sigma}^{\dagger}a_{j(i)\sigma}\rangle=\Phi(\eta)\sum_{|\vec{k}|<|\vec{k}_F|}\epsilon_{\vec{k}}$$
$$=\Phi(\eta)\int_{-\infty}^{\mu_1}\epsilon\rho_0(\epsilon)d\epsilon , \tag{2.22}$$

one sees that $\tilde{\Phi}=\Phi$; the quasiparticle band narrowing obtained by the present line of reasoning coincides with that obtained by the more elementary arguments. However, it should be emphasized that since the variational approach considers only the ground-state or equilibrium configuration this approach does not specify excited states. In particular, the Hubbard subband structure derived from the Green-function formalism[8] is not directly available from the variational approach. Nonetheless, the existence of the Hubbard gap will be evident from the thermodynamic properties considered in Sec. IV. On the basis of the foregoing discussion the following conclusions may be established:

(1) At $T=0$ and for $n=1$ the results obtained here reduce to those of Brinkman and Rice.[7] However, we also find that for arbitrary $n\leq 1$, η vanishes at the critical ratio $U/W=2$.

(2) One may interpret the quantity Φ as a band-narrowing factor or alternatively as the fraction of electrons in an itinerant state for an assembly of charge carriers in a restricted hopping regime. The Fermi surface is well defined at $T=0$, even for the fraction $(1-\Phi)$ of charge carriers that reside in singly occupied states. Since electrons are indistinguishable, singly and doubly occupied states should have a common Fermi surface, in agreement with our quasiparticle description.

(3) Although a fraction Φ of electrons is itinerant one cannot point out specific sites at which the remaining ones are localized. Rather, the assembly of particles in the translationally invariant system represents a fluid in a ground state with an average number of singly and doubly occupied sites in the stationary state of the whole system.

(4) Here we have regarded $(1-\Phi)N$ electrons as effectively localized because they do not contribute to the band energy. However, the fact that $\Phi(\eta=n^2/4)=1$, while $\Phi(\eta=0)=(1-n)/(1-n/2)$ may be interpreted as follows: Firstly, for $U=0$ all electrons are itinerant ($\Phi=1$). Secondly, it has been shown earlier[11] that for $U=\infty$ (for which certainly $\eta_0=0$) and for a rectangular DOS we have

$$S_\sigma\equiv\langle a_{i\sigma}^{\dagger}a_{j(i)\sigma}\rangle=n_\sigma\frac{1-n}{1-n/2} .$$

In our notation, $\sum_\sigma S_\sigma=n\Phi$. Hence Φ represents the conditional probability that hopping will take place if an electron is present on a given site; thus the correspondence with our key suggestion for interpreting Φ is established once again.

C. Definition of localized moments

Since the number of double occupancies decreases as U/W increases the quantity $\nu\equiv\sum_\sigma\langle n_{i\sigma}(1-n_{i-\sigma})\rangle$ contains information concerning the increased number of localized moments. To put it more formally we note that the spin operator in second-quantized form is

$$\vec{S}_i=(S_i^+,S_i^-,S_i^z)\equiv(a_{i\uparrow}^{\dagger}a_{i\downarrow},a_{i\downarrow}^{\dagger}a_{i\uparrow},\tfrac{1}{2}(n_{i\uparrow}-n_{i\downarrow})) . \tag{2.23}$$

Equivalently, one can represent $\vec{S}_i$ in the terms of the following operators which are projected onto the subspace of singly occupied sites[12]:

$$\vec{S}_i=(b_{i\uparrow}^{\dagger}b_{i\downarrow},b_{i\downarrow}^{\dagger}b_{i\uparrow},\tfrac{1}{2}(\nu_{i\uparrow}-\nu_{i\downarrow})) , \tag{2.24}$$

where

$$b_{i\sigma}^{\dagger}\equiv a_{i\sigma}^{\dagger}(1-n_{i-\sigma}),\quad b_{i\sigma}\equiv a_{i\sigma}(1-n_{i-\sigma})$$

and

$$\nu_{i\sigma}=b_{i\sigma}^{\dagger}b_{i\sigma} .$$

Therefore,

$$\langle(\vec{S}_i)^2\rangle\equiv\langle\vec{S}_i\cdot\vec{S}_i\rangle=\tfrac{3}{4}\nu=\tfrac{1}{2}(\tfrac{1}{2}+1)\nu . \tag{2.25}$$

Thus, ν specifies the reduction of the magnitude of the spin due to the presence of doubly occupied sites (recall that $\nu=n-2\eta$). In other words, the observed length is $\frac{1}{2}$ times the probability of finding a given site singly occupied.

For $U=0$, $\nu=n(1-n/2)$. Therefore, we can define the degree of localization of moments as

$$\delta\equiv\frac{\langle(\vec{S}_i)^2\rangle-\frac{3}{4}n(1-n/2)}{\frac{3}{4}n-\frac{3}{4}n(1-n/2)}=\frac{2}{n^2}[\nu-n(1-n/2)] . \tag{2.26}$$

If $\delta=1$ the system can be regarded as a Heisenberg magnet which, in this case, coincides with the Mott insulator.

III. GENERALIZATION TO NONZERO TEMPERATURES

A. Free-energy functional

At nonzero temperature the entropy contribution must be adjoined to the internal energy of the particles, E_B/N, as given by Eq. (2.21). We recognize two such contributions. The first is due to the fraction Φ of electrons which are itinerant: With the use of the Fermi-Dirac distribution $f(E_k)\equiv f[(E_k-\mu)/k_BT)]$ for quasiparticles, these electrons contribute to the entropy an amount

$$\frac{S_i}{N}=-\Phi k_B\{f(E_{\vec{k}})\ln f(E_{\vec{k}}) +[1-f(E_{\vec{k}})]\ln[1-f(E_{\vec{k}})]\}\ , \tag{3.1}$$

which has the same form as that used by Chao and Berggren[13] except that we introduce[14] the quasiparticle energy $E_{\vec{k}}=\Phi\epsilon_{\vec{k}}$ in place of the bare particle energy $\epsilon_{\vec{k}}$. It is in this manner that the effect of band narrowing is included in the process of accounting for the thermal excitation of itinerant electrons. The effect is important close to the metal-insulator transition, where Φ is small [cf. also Eq. (2.21)].

The second contribution to the entropy arises from the fraction $(1-\Phi)$ of electrons regarded here in terms of their localized moments. There is no corresponding contribution to the internal energy because we neglect such effects as, for example, the second-order effects leading to the kinetic exchange interactions[12] which are important in the insulating phase. To set up this contribution to the entropy we consider the various configurations and their corresponding probabilities $\{p_i\}$. They are listed in Table I. Then the entropy within the single-site approximation may be written as

TABLE I. Single-site configurations and the corresponding probabilities.

Configuration $\{i\}$	Average probability of occurrence
Electron with $\sigma=\uparrow$	$\nu_\uparrow$
Electron with $\sigma=\downarrow$	$\nu_\downarrow$
Empty site	$1-\nu-\eta$
Doubly occupied site	η

$$S_l/N=-(1-\Phi)k_B\sum_{i=1}^{4}p_i\ln p_i\ , \tag{3.2}$$

or, equivalently,

$$S_l/N=-(1-\Phi)k_B[\nu\ln\nu-\nu\ln 2+\eta\ln\eta +(1+\eta-n)\ln(1+\eta-n)]\ , \tag{3.3}$$

in which we have set $\nu_\sigma=\nu_{-\sigma}=\nu/2$ since we consider here only the paramagnetic case.

The free energy of the system is specified by

$$\frac{F}{N}=\frac{1}{N}\sum_{\vec{k}\sigma}E_{\vec{k}}f(E_{\vec{k}})+\frac{k_BT\Phi}{N}\sum_{\vec{k}}\{f(E_{\vec{k}})\ln f(E_{\vec{k}})+[1-f(E_{\vec{k}})]\ln[1-f(E_{\vec{k}})]\} +k_BT(1-\Phi)[\eta\ln\eta+\nu(\ln\nu-\ln 2)+(1+\eta-n)\ln(1+\eta-n)]\ . \tag{3.4}$$

Next, recall Eqs. (2.20) and (2.21) and introduce the definitions

$$\bar{\epsilon}^*(T)\equiv\int_{-W/2}^{W/2}\rho_0(\epsilon)\epsilon f^*(\epsilon)d\epsilon\ , \tag{3.5a}$$

$$s^*(T)\equiv\int_{-W/2}\rho_0(\epsilon)\{f^*(\epsilon)\ln f^*(\epsilon)+[1-f^*(\epsilon)]\ln[1-f^*(\epsilon)]\}d\epsilon\ , \tag{3.5b}$$

with $f^*(\epsilon)\equiv f((\epsilon-\mu_1)/k_BT^*)$ and $T^*\equiv T/\Phi$. With the use of these definitions Eq. (3.4) may be rewritten as

$$\frac{F}{N}=\Phi\bar{\epsilon}^*(T)-k_BTs^*(T)-k_BT(1-\Phi)[-(n-2\eta)\ln(n-2\eta)+(n-2\eta)\ln 2-\eta\ln\eta-(1-n+\eta)\ln(1-n+\eta)]\ . \tag{3.6}$$

One should note that $T^*=T/\Phi$ plays the role of an effective temperature; as Φ decreases with decreasing η the thermal activation of the carriers across the Fermi surface is enhanced. Thus, the degeneracy temperature defined through the conditions

$$\left|\frac{\mu_1-(W/2)}{k_BT_D}\right|=\left|\frac{\mu-(W/2)\Phi}{k_BT_D^*}\right|=1 \tag{3.7}$$

is much lower than the corresponding temperature for noninteracting electrons. The situation is shown schematically in Fig. 1.

Equation (3.6) must now be minimized with respect to η; for this purpose it is necessary to specify $\rho_0(\epsilon)$. In accordance with previous considerations we select the rectangular DOS for the bare band,

$$\rho_0(\epsilon)=\begin{cases}2/W\text{for } |\epsilon|\le W/2\\ 0\ ,\ \text{otherwise}\ .\end{cases} \tag{3.8}$$

Upon inserting (3.8) into (3.5) and noting that for this

$\rho_0(\epsilon)$ $\mu=\mu_1=0$ for all temperatures, one obtains

$$\bar{\epsilon}^*(T)=-2k_BT^*\ln\cosh(W/4k_BT^*)+\frac{4k_BT^*}{W}\int_0^{W/2}d\epsilon\ln\cosh(\epsilon/2k_BT^*)\ . \quad (3.9)$$

The condition $\partial F/\partial\eta=0$ leads then to the following equation determining $\eta=\eta(T)$ for the most interesting case of $n=1$:

$$\frac{2k_BT}{W}\frac{\Phi'}{\Phi}(1-\Phi)\ln\cosh\left[\frac{W\Phi}{4k_BT}\right]-\frac{2k_BT}{W}\frac{\Phi'}{\Phi}J(\Phi)-\tfrac{1}{2}\Phi'(1-\Phi)\tanh\left[\frac{W\Phi}{4k_BT}\right]-\frac{2k_BT}{W}\Phi'\ln 2$$
$$+\frac{2k_BT}{W}(1-\Phi)\ln\left[\frac{2\eta}{1-2\eta}\right]+\frac{k_BT}{W}\Phi'\left[(1-2\eta)\ln\left[\frac{2}{1-2\eta}\right]-2\eta\ln\eta\right]+\frac{U}{W}=0\ , \quad (3.10)$$

where $\Phi=8\eta(1-2\eta)$, $\Phi'\equiv d\Phi/d\eta=8(1-4\eta)$, and

$$J(\Phi)\equiv\int_0^1 dx\ln\cosh\left[\frac{x\Phi W}{4k_BT}\right]\ . \quad (3.11)$$

Equation (3.10) will be analyzed separately in detail. Here we discuss only the most interesting special cases through minimization of the free energy (3.6) by solving Eq. (3.10).

B. Low-temperature specific heat for a half-filled band

The low-temperature specific heat of the itinerant-electron system is of intrinsic interest and also serves to determine the entropy of this system. We proceed with the Sommerfeld expansion[15] for the internal energy of the system which is applicable to a correlated narrow band under the condition $W\Phi/k_BT\gg1$, not too close to the metal-insulator transition. The energy is given by

$$E_B/N=\Phi\bar{\epsilon}+\tfrac{1}{2}\gamma_0\Phi(T^*)^2+U\eta=\Phi\bar{\epsilon}+\tfrac{1}{2}(\gamma_0/\Phi)T^2AU\eta\ , \quad (3.12)$$

in which γ_0 is the coefficient (per site) of the linear specific heat for bare electrons,

$$\gamma_0=\pi^2\rho_0(\mu_1)(k_B^2/3)=2\pi^2k_B/3W\ , \quad (3.13)$$

and $\bar{\epsilon}$ is, as before (see Fig. 1),

$$\bar{\epsilon}\equiv\int_{-W/2}^0\epsilon\rho_0(\epsilon)d\epsilon\ . \quad (3.14)$$

We assume that the specific heat has the form $C_v=\gamma T$ (where γ will be determined later), in which case $S=\gamma T=C_v$.

The free-energy trial function of the system with $n=1$ is thus given by

$$\frac{F}{N}=\Phi\bar{\epsilon}+\tfrac{1}{2}\frac{\gamma_0}{\Phi}T^2+U\eta-k_BT(1-\Phi)\left[(1-2\eta)\ln\left[\frac{2}{1-2\eta}\right]-2\eta\ln\eta\right]\ . \quad (3.15)$$

This quantity must be minimized with respect to the variable η. The relation $\partial F/\partial\eta=0$ in the low-temperature limit corresponding to (3.10) yields for $n=1$

$$\eta-\eta_0-\frac{1}{8}\frac{\gamma_0T^2}{2W}\frac{\Phi'}{\Phi^2}+\frac{k_BT}{8W}\Phi'\left[(1-2\eta)\ln\left[\frac{2}{1-2\eta}\right]-2\eta\ln\eta\right]+\frac{k_BT}{4W}(1-\Phi)\ln\left[\frac{2\eta}{1-2\eta}\right]=0\ . \quad (3.16)$$

The specific heat is then found according to

$$C_v=\left[\frac{\partial E_B}{\partial T}\right]_\eta+\left[\frac{\partial E_B}{\partial\eta}\right]_T\frac{\partial\eta}{\partial T}\ . \quad (3.17)$$

The leading terms in T as $T\to0$ in $\partial\eta/\partial T$ are obtained from Eq. (3.16) as follows:

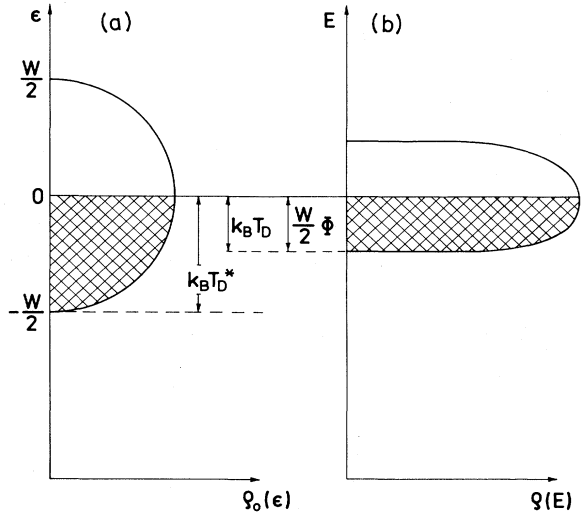

FIG. 1. Schematic representation of the effective degeneracy temperature T_D^* for (a) the bare-band electrons which plays the same role as the true T_D does for (b) the quasiparticle states. Narrowed quasiparticle band is also shown in (b). Situation drawn here corresponds to the half-filled case ($n=1$) for which one can choose $\mu=\mu_1=0$.

$$\left[\frac{\partial\eta}{\partial T}\right]_{T\to 0}=\frac{1}{8}\frac{\gamma_0 T}{W}\frac{\Phi'}{\Phi}-\frac{k_B}{8W}\Phi_0'\left[(1-2\eta_0)\ln\left[\frac{2}{1-2\eta_0}\right]-2\eta_0\ln\eta_0\right]$$
$$-\frac{k_B}{4W}(1-\Phi_0)\ln\left[\frac{2\eta_0}{1-2\eta_0}\right], \tag{3.18}$$

in which $\Phi_0\equiv\Phi(\eta_0)$, $\Phi_0'\equiv\Phi'(\eta_0)$, and η_0, as before, is the optimized number of double occupancies per site. The internal energy E_B is given by (3.12); thus,

$$\left[\frac{\partial E_B}{\partial T}\right]_\eta=\frac{\gamma_0 T}{\Phi}, \tag{3.19a}$$

$$\left[\frac{\partial E_B}{\partial \eta}\right]_T=\bar{\epsilon}\Phi'-\frac{\gamma_0 T^2\Phi'}{2\Phi^2}+U. \tag{3.19b}$$

The procedure now calls for substitution of (3.19) and (3.18) into (3.17), followed by an elimination of the term $\gamma_0 T^2\Phi'/2\Phi^2$ via Eq. (3.16). We neglect terms in T^2 and identify the multiplier of T with the linear coefficient in the specific heat, namely

$$\gamma=\frac{\gamma_0}{\Phi_0}+\frac{k_B^2}{2W}\left\{\frac{\Phi_0'}{2}\left[(1-2\eta_0)\ln\left[\frac{2}{1-2\eta_0}\right]-2\eta_0\ln\eta_0\right]\right.$$
$$\left.-(1-\Phi_0)\ln\left[\frac{2\eta_0}{1-2\eta_0}\right]\right\}^2. \tag{3.20}$$

Thus, the coefficient γ of the specific heat is enhanced by two factors. One is the band-narrowing effect (the first term); the other one arises from the localized moments which are placed below or at the Fermi surface and contribute to the thermal excitations over the Fermi surface since the electrons are indistinguishable.

One should note that many experimental cases are known[16] for which γ exceeds the normal Sommerfeld contribution γ_0 to the specific heat by a factor of the order of 10^2. To obtain such large enhancements it is sufficient to require that $\Phi_0=8\eta_0(1-2\eta_0)\simeq 10^{-2}$; here $\eta_0=(\frac{1}{4})\times(1-U/2W)$. Thus one must demand that $\eta_0\approx 10^{-3}$ or that $U/2W$ be very close to unity. For the strongly correlated band the conductivity at low temperatures is mainly due to the doubly occupied sites. Thus, for systems for which the specific heat is enhanced by a factor Φ^{-1} with respect to normal metals, the conductivity drops by a factor of at least Φ^2. This is so because both the bandwidth as well as the carrier concentrations drop by the factor Φ.

The band-energy change caused by a transition from the insulating phase ($\Phi=0$) to the correlated metallic phase ($\Phi\simeq 10^{-2}$) involves a change in band energy of the order of 10^{-2} eV since the band energy is given by $E_B\simeq-\Phi W/4+2W\eta$. The corresponding degeneracy temperature is of the order of $T_D=100$ K, beyond which the term γT in the specific heat is unimportant with respect to the remaining contributions to C_v.

The change of band energy of the order of 0.01 eV ≈ 100 K for the transition to the metallic phase (as estimated from the enhancement γ/γ_0) points to the importance of the magnetic contribution and/or the lattice effects in driving the transition in actual systems since both the magnetic and lattice parts of the internal energy can be of this order of magnitude.

Small values of Φ_0 and η_0 also contribute to C_v from the second term in Eq. (3.20), in which the dominant term is given by $(k_B^2/2W)(\ln\eta_0)^2$. The role of the localized electrons is a minor one under conditions described here.

C. Localized-moment regime (semiconducting phase)

We now turn our attention to the localized moment regime, in which $U\geq 2W$ and for which $\Phi=0$ at $T=0$. At low temperatures we can neglect the band part of entropy, i.e., set $S_i=0$. Then, the trial free energy has the form

$$\frac{F}{N}=\Phi\bar{\epsilon}+U\eta+k_BT[\eta\ln\eta-(n-2\eta)\ln 2$$
$$+(n-2\eta)\ln(n-2\eta)$$
$$+(1-n+\eta)\ln(1+\eta-n)]. \tag{3.21}$$

Consider the semiconducting phase in detail by minimizing Eq. (3.21) and setting $n=1$. The equation for $\eta=\eta(T)$ is given by

$$\eta-\eta_0+(k_BT/4W)\ln[2\eta/(1-2\eta)]=0. \tag{3.22}$$

The variation of η with k_BT/W is shown in Fig. 2, for various values of U/W as a parameter. We have also plotted $\eta(T)$ for $U/W<2$ for comparison with the results of Chao and Berggren[13] who considered the opposite limit: They neglected the part S_l of the entropy and disregarded the band-narrowing factor in the Fermi-Dirac distribution for particles. Thus, their results apply to the metallic limit $U\ll 2W$, while those based on (3.21) are complementary, being valid for $U\geq 2W$. As may be seen, the free-energy functional (3.4) interpolates correctly between those limits. When comparing the curves drawn in Fig. 2 and those presented in Fig. 2 of Ref. 13 one notices a similar qualitative trend, although there are substantial numerical differences. Furthermore, within the previous approach[13] it is impossible to obtain the specific-heat enhancement γ/γ_0 calculated above.

At this point it is expedient to define an effective Coulomb interaction parameter $U_{\rm eff}(T)$ for $n=1$ through the relation [compare with Eq. (2.17)],

$$\eta(T)=\tfrac{1}{4}[1-U_{\rm eff}(T)/2W]. \tag{3.23}$$

Plots of $U_{\rm eff}(T)/W$ are provided in Fig. 3 as a function of k_BT/W for several values of $\eta_0(U/W)$. One notes a steep decline in $U_{\rm eff}/W$ as k_BT/W increases, which is consistent with intuition: With increasing temperature $U_{\rm eff}/W$ approaches zero because the number of double occupancies per site increases and eventually reaches the

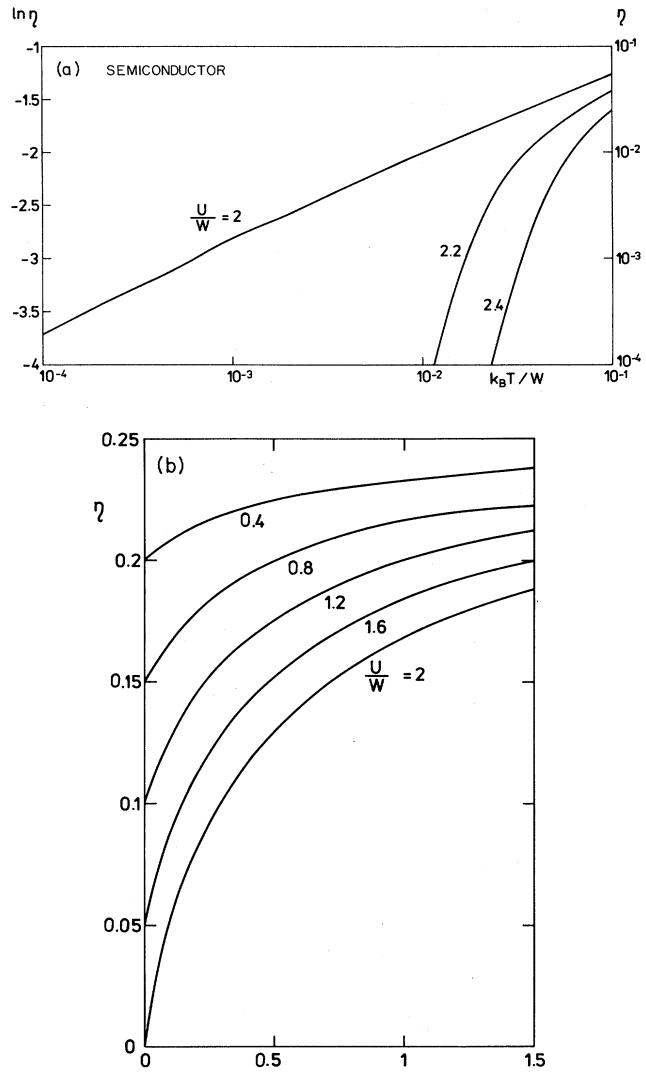

FIG. 2. Number of double occupancies η per site as a function of reduced temperature k_BT/W. (a) specifies $\eta(T)$ in the semiconducting phase ($U>2W$) while (b) shows $\eta(T)$ for $U\leq 2W$. Latter family of curves is drawn for comparison with Ref. 13. Note the logarithmic scales on (a).

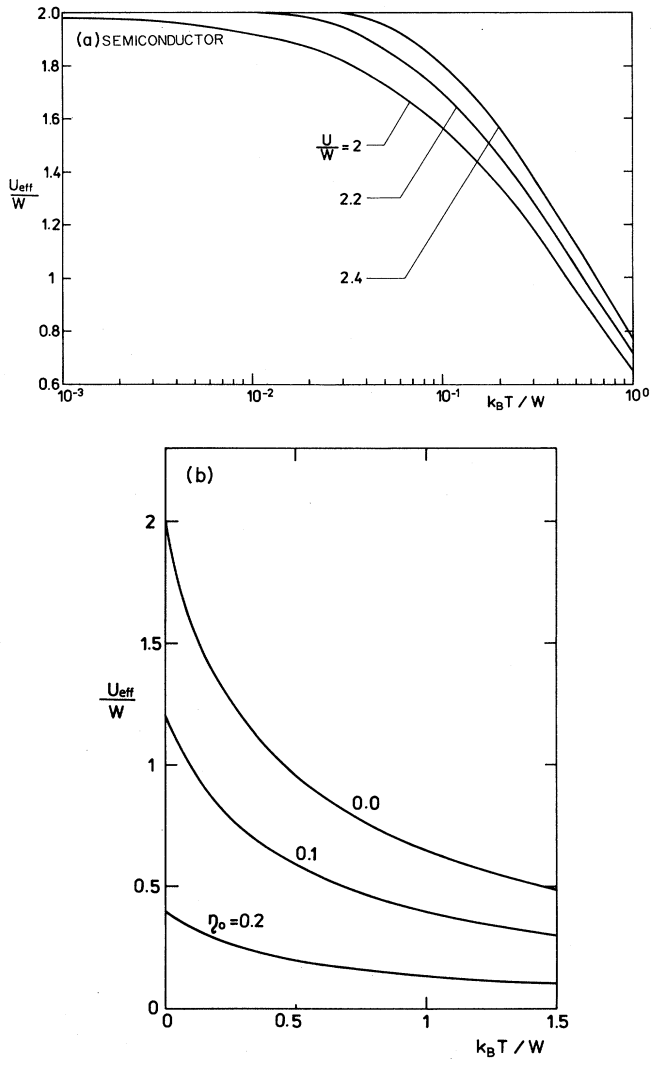

FIG. 3. Effective Coulomb integral $U_{\text{eff}}(T)/W$ as a function of reduced temperature k_BT/W, for (a) $U>2W$ and (b) $U\leq 2W$. Note the logarithmic scale on the abscissa of (a).

asymptotic value $\frac{1}{4}$.

The main reason for considering the limit $U>2W$ is to prove the existence of the Hubbard gap in the semiconducting phase. For this purpose we solve Eq. (3.22) analytically for η in the low-temperature range with $U/W>2$. For $T\to 0$, $\eta\to 0$, and then $\ln(1-2\eta)\simeq -2\eta$; thus, Eq. (3.22) has the form

$$\eta\left[1+\frac{k_BT}{2W}\right]-\eta_0+\frac{k_BT}{4W}\ln(2\eta)=0\ . \tag{3.24}$$

For $T\to 0$ we can neglect the first term in the above equation and obtain the solution

$$\eta(T)=\tfrac{1}{2}\exp(-\epsilon_a/2k_BT)\ . \tag{3.25}$$

Thus, $\eta(T)$ exhibits an activated behavior, with activation energy $\epsilon_a=U-2W$, i.e., the value of the Hubbard gap. Thus, although our approach does not explicitly specify the Hubbard-split subbands,[8] their existence shows up in the thermal-promotion properties of charge carriers in the semiconducting phase $U>2W$ for $n=1$.

From Eq. (3.21) one can now separate out the contributions associated with the energy of the system. One can then use Eq. (3.23) in conjunction with Fig. 3(a) to evaluate the variation of η with k_BT/W, and thence, the dependence of the energy on k_BT/W. Numerical differentiation then yields the heat capacity curves shown in Fig. 4 for $U/W=2$, 2.2, 2.4; one should note the steep rise in C_v/k_B as k_BT/W is decreased.

Returning to Eq. (3.21) one can also identify the entropy terms. On using Fig. 3(a) again, one obtains the variation of the entropy with k_BT/W as shown in Fig. 5. One

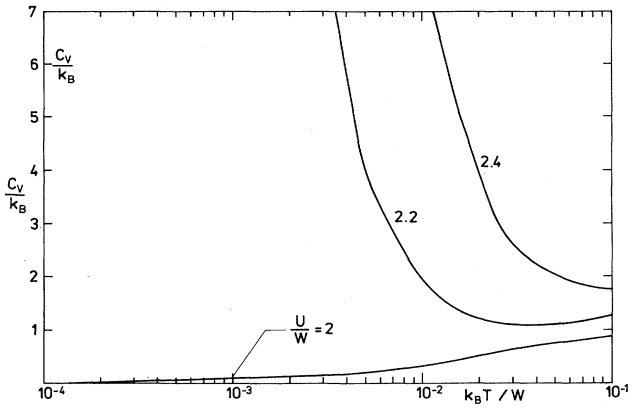

FIG. 4. Specific heat as a function of reduced temperature for $U>2W$ as a parameter. Curve for $U=2W$ is drawn for comparison.

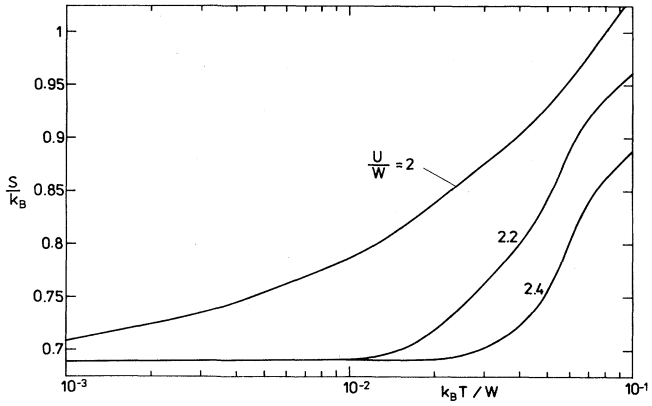

FIG. 5. Temperature dependence of the total entropy per site (in units of k_B) with $U>2W$ as parameter. Curve for $U=2W$ is drawn for comparison.

observes a far slower rise in S/k_B with k_BT/W for $U/W>2$ than for the case $U/W=2$.

IV. DISCUSSION

In this paper we have formulated a simple single-site theory based on the expansion of the ground-state energy with respect to $\eta=\langle n_{i\uparrow}n_{i\downarrow}\rangle$. The same parameter is involved in the Gutzwiller variational method.[5,7] This approach differs from the phenomenological expansion of March *et al.*[17] who used the value of the Fermi-Dirac distribution discontinuity at the Fermi level as a variational parameter. Besides, March *et al.*[17] did not determine the expansion parameters; hence, the values of the energy for a given U/W cannot be determined and their results cannot be compared with ours.

We did not study in detail the nature of the transition at finite temperatures; it is planned to solve this problem separately at a later stage.[19] The present formulation deals only with the paramagnetic phase, so that a direct comparison with the phase diagram obtained earlier (cf. Cyrot[4] and Moriya and Hasegawa[4]) is not possible. We plan to extend the present theory to the antiferromagnetic case, since the enhancement of the linear specific heat derived here (cf. Sec. III B) shows that the basic ingredients of the correlated state have already been included.

The enhancement factor Φ^{-1} of the specific heat in the metallic phase is associated with the band narrowing factor Φ; the paramagnetic susceptibility will be enhanced to the same extent. This result is in contrast to paramagnon theory where the paramagnetic susceptibility χ is exchange enhanced and γ is mass enhanced, so that χ/γ grows strongly with the correlation ratio (U/W).[18] It has been pointed out (cf. Moriya[1]) that as U/W grows and approaches the metal-insulator boundary the spin and charge fluctuations become more and more localized; eventually, the local nature of the charge fluctuations in real space becomes dominant near the transition to the insulating phase, in which the moments are described by atomic spins.

In conclusion, we summarize the work by pointing out the specific physical points of the method developed here. First, the entire approach is based on the assumption that the long-range correlations $\langle n_{i\sigma}n_{j\sigma'}\rangle$ for $i\neq j$ are not very important in describing the behavior of the insulating phase (for $n=1$) because they would greatly increase the energy of the system.

Second, we have interpreted the band narrowing Φ for the optimized number of double occupancies η as an averaged contribution of itinerant electrons in the system of $N_e=N$ electrons. This is a characteristic of a macroscopic ground state; hence, one should not draw the conclusion that the $(1-\Phi)N$ electrons localized on given sites are not involved in the band motion. The electrons are indistinguishable; therefore, one cannot point to specific sites with electrons residing on them. Nevertheless, the ground state and free energies contain contributions which do not originate from either the band-energy or Fermi-Dirac statistics. In other words, there arises a nonfermionic contribution[20] to the fundamental macroscopic quantities such as entropy or free energy[21] [cf., e.g., Eq. (3.3)].

Third, starting with the concept of local moments which are well defined in the metallic phase on a macroscopic scale only, we have derived an expression for their contribution to the entropy S_l in explicit form. This expression again involves the single-site approximation and is widely used in similar situations.[22] As one can see from the expression contributing to S_l and given in Table I the approximation is also valid for the magnetically ordered state (then $\nu_\sigma=\nu/2+\sigma\langle S^z\rangle$, where $\langle S^z\rangle$ is the average moment per site). However, the full treatment of magnetic phases calls for an expression for the band narrowing $\Phi(\eta\langle S^z\rangle)$, which is valid in the ordered state. This is a challenging problem which, if solved and introduced in the present approach, would yield a self-consistent solution for the magnetic phases and the metal-insulator transition at the same time.

APPENDIX: COMPARISON WITH THE FULDE VARIATIONAL APPROACH

In the approach of Ref. 9 the optimal parameter $\eta=\eta_0$ at $T=0$ is given by

$$\eta_0=\frac{n^2}{4}-\frac{2\langle OH\rangle^2}{\langle OHO\rangle}\ , \tag{A1}$$

where in the paramagnetic phase and for a rectangular DOS,

$$\langle OH\rangle=U(n/2)^2[1-(n/2)]^2 \tag{A2}$$

and

$$\langle OHO\rangle=[W+U(1-n)^2](n/2)^2[1-(n/2)]^2\ . \tag{A3}$$

Thus

$$\eta_0=\frac{n^2}{4}\left[1-\frac{2U}{W+U(1-n)^2}\left[1-\frac{n}{2}\right]^2\right]\ . \tag{A4}$$

Thus, $\eta_0=0$ only if $U\geq U_c=W[1-(n^2/2)]^{-1}$. In particular, for $n=1$ one obtains $U=2W$. The value U_c coincides with ours only for $n=1$. However, both methods have in common the fact that U for $\eta_0=0$ is finite. This is in contrast to the Gutzwiller method for which $\eta_0\neq 0$ for any value of U and $n\neq 1$ (cf. Ref. 10).

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[6]Strictly speaking, the function generally should have the form $\sum_{|\vec{k}|<|\vec{k}_F|}\Phi_{\vec{k}}(\eta)\epsilon_{\vec{k}}$. However, it is easy to prove following the argument presented below in that section, that one has $\Phi_{\vec{k}}(\eta)\equiv\Phi(\eta)$, i.e., that Φ does not depend on $\vec{k}$.

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[14]The derivation of the entropy in Ref. 13 is based on the thermodynamic relation $(\partial E_B/\partial T)|_\eta=T(\partial S_i/\partial T)|_\eta$ which must be fulfilled for any entropy functional for itinerant electrons. Our quantities (2.21) and (3.1) fulfill the relation $(\partial E_B/\partial T^*)|_\eta=T(\partial S_i/\partial T^*)|_\eta$, with $T^*=T/\Phi$. This equation is equivalent to the previous one for any $\Phi\neq 0$.

[15]Cf., e.g., A. H. Wilson, *The Theory of Metals* (Cambridge University Press, London, 1958), pp. 14—16.

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[20]The same conclusion has been reached through a different approach by T. Arai [Phys. Rev. B 21, 3320 (1980)]. However, since there is no limitation on the states in $\vec{k}$ space within our approach [cf. Eqs. (2.20)—(2.22)] we conclude that the volume within the Fermi surface does not change in the metallic phase. For $\Phi\equiv 0$, i.e., in the insulating phase ($U>2W$) the concept of the Fermi surface has no well-defined meaning because the band-energy contribution to E_G vanishes at $T=0$.

[21]There is no contribution of localized moments to the ground-state energy because considering the paramagnetic phase only we have ignored the kinetic exchange contribution (cf. Ref. 12.)

[22]See, e.g., K. A. Penson, S. Ghatak, and K. H. Bennemann, Phys. Rev. B 20, 4665 (1979).