Charge-ordered ground state of a half-filled Hubbard model with strong intra-atomic attraction

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With a canonical transformation, the antiferromagnetic ground state and the electron-hole excitation energy gap of the conventional Hubbard model are transferred to describe the charge-ordered ground state and the similar excitation energy of a half-filled Hubbard model with negative U. The band-structure effect is also considered.

Since Little[1] suggested the possibility of superconductivity in one-dimensional organic chains, the problem of ordering in one-dimensional metallic chains has been discussed extensively. The central theme of the investigations is the role of an attractive on-site interaction, which can be derived from the coupling between the electrons and molecular vibrations or electronic excited states.[1-3] Two models have been considered: an extension of the Luttinger or Tomonaga model has been studied by many authors[4-8]; and a modified Hubbard model by the others.[2,3,9-15] While the former is mostly restricted to the one-dimensional systems, the latter can be easily generalized to the cases of three dimensions. Furthermore, the Hubbard model with attractive intra-atomic interaction has been used by Anderson[16] and Street and Mott[17] to interpret the electrical and optical properties of amorphous semiconductors. In ordered systems, mean-field approximation[18] and solution derived from the functional integral method[19] yield charge-ordered state solutions for such case. On the other hand, Brouers[20] has shown the absence of the charge-ordered solution in the Hubbard-III Green's-function decoupling scheme (see Ref. 21).

For the attractive Hubbard model

$$H = \sum_{ij\sigma} t_{ij} a_{i\sigma}^{\dagger} a_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} \tag{1}$$

With $U < 0$, Shiba[10] has pointed out that at the strong-coupling limit $|U| >> t_{ij}$ the ground state of a half-filled band corresponds to a charge-density wave with every second site doubly occupied. The charge-ordered state was explored further by Emery[12] by elementary degenerate perturbation theory. In this short note we will use the symmetry of the Hubbard Hamiltonian under $U \rightarrow -U$ plus an appropriate canonical transformation to show that the transition from the charge-ordered to the disordered states can be obtained simply from the transition between the antiferromagnetic and the paramagnetic states of the conventional Hubbard model with $U > 0$. Such transition was derived earlier with the Gutzwiller scheme.[22,23]

Let us briefly outline the Gutzwiller treatment on the antiferromagnetic-paramagnetic transition in the conventional Hubbard model with $U > 0$ and a half-filled band.[23] Following Slater's suggestion of sublattices with split subbands,[24] we separate the lattice of L sites into two interpenetrating sublattices $L(\uparrow)$ and $L(\downarrow)$. The number of electrons with up-spins and down-spins are equal, namely, $N(\uparrow) = N(\downarrow) = L/2 = N/2$. We also split each Brillouin zone into an inner and an outer subzone of equal volume, and so each energy band into two subbands. For convenience, we will call the inner (or the outer) subzone of the first Brillouin zone the first (or the second) magnetic zone, and the corresponding split subband the lower (or the upper) subband.

For each k vector in the first magneitc zone K we define two sets of single-particle creation operators $d_{k\sigma}^{\dagger}$ and $\tilde{d}_{k\sigma}^{\dagger}$ as

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

and

$$\tilde{d}_{k\sigma}^{\dagger} = S_k \left(-\zeta_k \sum_{g \in L(\sigma)} e^{ikg} a_{g\sigma}^{\dagger} + \sum_{g \in L(-\sigma)} e^{ikg} a_{g\sigma}^{\dagger} \right) , \tag{3}$$

where $a_{g\sigma}^{\dagger}$ creates a σ-spin electron in the Wannier state localized at site g. S_k is a normalization constant and ζ_k is a variational parameter to be deter-

mined later. The operators $d_{k\sigma}^{\dagger}$ and $\tilde{d}_{k\sigma}^{\dagger}$ are associated, respectively, to the states in the lower and the upper subbands.

To construct the trial function for the ground state, we must specify the occupied states in both the lower and the upper subbands. Let Σ_σ (or Γ_σ) be a set of $\gamma(\sigma)N$ k vectors in the second (or the first) magnetic zone such that the corresponding Bloch states in the upper (or the lower) subband are occupied (or unoccupied) by σ-spin electrons. The set k vectors in the first magnetic zone which specifies the set of Bloch states in the lower subband occupied by σ-spin electrons is then labeled as $K(\Gamma_\sigma)$. If we define the Gutzwiller projection operator[25]

$$P=\prod_{\text{all } g}[1-(1-\xi)n_{g\uparrow}n_{g\downarrow}] \ , \tag{4}$$

where ξ is a variational parameter, the trial function can be expressed as

$$\Psi(\Sigma_\sigma\Gamma_\sigma\{\zeta_k\}\xi)=P\prod_{\sigma}\prod_{k\in\Sigma_\sigma}\tilde{d}_{k\sigma}^{\dagger}\prod_{k\in K(\Gamma_\sigma)}d_{k\sigma}^{\dagger}|0\rangle \ . \tag{5}$$

For a most general mathematical treatment, one should choose Σ_σ and Γ_σ so as to minimize the energy. However, to be mathematically tractable, almost all authors assumed Σ_σ and Γ_σ as null set. In other words, they assumed that the first magnetic zone (K) boundary coincides with the Fermi surface. Although the variations of Σ_σ and Γ_σ are considered in the Gutwiller treatment,[23] to avoid further complication in mathematical manipulation, it has been assumed the the number of k vectors in Σ_σ (and Γ_σ) is small compared to the total number of electrons.

The calculation of the energy $E=\langle\Psi|H|\Psi\rangle/\langle\Psi|\Psi\rangle$ consists of two steps. The step is to use the quasichemical approximation [25] to calculate the energy E for given Σ_σ Γ_σ, $\{\zeta_k\}$, and ξ, and then minimize E with respect to these parameters. From Eq. (4) it is clear that the variation of ξ optimizes the number of doubly occupied atoms

$$\nu=\langle\Psi|\sum_g n_{g\uparrow}n_{g\downarrow}|\Psi\rangle/\langle\Psi|\Psi\rangle \ .$$

It has been shown[22,23] that ν decreases monotonically to zero as U/W, where W is the bare bandwidth, increases to a critical value $(U/W)_c$. For a correct treatment,[22,23,26] ν can be small but never vanishes. The reason for $\nu=0$ if $U/W\geq(U/W)_c$ is entirely due to the quasichemical approximation. Also as a result of the quasichemical approximation, the dependence of E on Σ_σ and Γ_σ is drastically simplified. Let $\gamma=\gamma(\uparrow)+\gamma(\downarrow)$ and $\epsilon(k)$ be the bare band energy. If we define the average energy of the γN bare-electron-hole pairs as

$$E_{B0}(\Sigma_\sigma\Gamma_\sigma)=\frac{1}{\gamma N}\sum_\sigma\left[\sum_{k\in\Sigma_\sigma}\epsilon(k)-\sum_{k\in\Gamma_\sigma}\epsilon(k)\right] \ , \tag{6}$$

then E depends on Σ_σ and Γ_σ only through $E_{B0}(\Sigma_\sigma\Gamma_\sigma)$ and $\gamma(\sigma)$.

It was first pointed out by Brinkman and Rice[27] that $\nu\to0$ indicates the metal-nonmetal transition. To illustrate the physical properties of the half-filled Hubbard Hamiltonian in the strong correlation regime, let us rewrite the Hamiltonian Eq. (1)

$$H=H_0+H_1 \ , \tag{7}$$

where

$$H_0=\sum_{ij\sigma}t_{ij\sigma}[n_{i-\sigma}a_{i\sigma}^{\dagger}a_{j\sigma}n_{j-\sigma}+(1-n_{i-\sigma})a_{i\sigma}^{\dagger}a_{j\sigma}(1-n_{j-\sigma})]+\frac{U}{2}\sum_i[n_{i\uparrow}n_{i\downarrow}+(1-n_{i\uparrow})(1-n_{i\downarrow})] \ , \tag{8}$$

and

$$H_1=\sum_{ij\sigma}t_{ij\sigma}[(1-n_{i-\sigma})a_{i\sigma}^{\dagger}a_{j\sigma}n_{j-\sigma}+n_{i-\sigma}a_{i\sigma}^{\dagger}a_{j\sigma}(1-n_{j-\sigma})] \ . \tag{9}$$

Here we have introduced the spin dependence in $t_{ij\sigma}$ for the convenience of future discussion, though it is clear that $t_{ij\sigma}=t_{ij}$. In rewriting Eq. (8) we have used the condition $N=L$, namely, one electron per atom.

The electron hopping processes in H_0 do not alter the number of doubly occupied atoms, while each hopping in H_1 changes the number of double occupancies by one. One characteristic feature of the ground state Ψ in the Gutzwiller variational method is that the probability $P(\mu)$ of having μ doubly occupied atoms in Ψ is a hypergeometric function of μ highly peaked at the optimum value ν_0 of double occupancies.[25] Consequently, one can approximate

$$\nu=\langle\Psi|\sum_g n_{g\uparrow}n_{g\downarrow}|\Psi\rangle/\langle\Psi|\Psi\rangle\simeq\nu_0 \ .$$

However, we must point out that Ψ still contains configurations with numbers of double occupancies $\mu\neq\nu_0$, although the occupation probabilities of such configurations are extremely small. In the following second step of calculating E, we will improve the result with respect to this aspect.

For a strongly correlated metal, the dominating contribution of electron hoppings to the total energy E is from H_0, while H_1 can be treated as a second-order process. It is not so for the special case of half-filled band with $U/W\geq(U/W)_c$ where the quasichemical approximation yields $\nu_0=0$, but actually

$$\nu=\langle\Psi|\sum_g n_{g\uparrow}n_{g\downarrow}|\Psi\rangle/\langle\Psi|\Psi\rangle\neq0 \ .$$

In this case we can consider H_0 as the unperturbed Hamiltonian and H_1 the perturbation. It is clear that the eigenstates of H_0 are characterized by the number of double occupancies being 0, 1, 2, $\cdots$, with no doubly occupied atom for the ground state. The hopping terms in H_0 thus contribute nothing to the ground-state energy of H_0. Since H_1 changes the number of double occupancies by one, the perturbation correction in energy starts from the second order. It is easy to see that such second-order processes provide an antiferromagnetic coupling between the unpaired spins localized on different atoms. As the intermediate state of the second-order process contains one doubly occupied atom, to the first-order correction in the wave function, it has been found that

$$\langle\Psi|\sum_g n_{g\uparrow}n_{g\downarrow}|\Psi\rangle/\langle\Psi|\Psi\rangle$$

is nonzero for the ground state of H.[22,23,26]

We therefore conclude that the quasichemical approximation treats H_1 incorrectly not only for $U/W \geq (U/W)_c$, but also for $U/W < (U/W)_c$ and very close to $(U/W)_c$. For the latter, the number of doubly occupied atoms (or of holes) is small and the number of nearest-neighbor pairs of unpaired spins in large. Hence, the net contribution from the first-order hoppings due to H_0 and from the second-order hoppings due to H_1 to the energy E are equally important. An improved energy calculation with more careful treatment of H_1 than the original quasichemical approximation was carried out in Ref. 23. Let us redefine E as the so-obtained energy including both the first- and the second-order hopping processes. This is the energy which should be minimized with respect to $\gamma(\sigma)$, E_{B0}, $\{\zeta_k\}$, and ξ. However, the minimization with respect to $\gamma(\sigma)$ and E_{B0} requires the detailed bare band structure. Without such information, parabolic density of states with nearest-neighbor hopping t was used in the actual calculation,

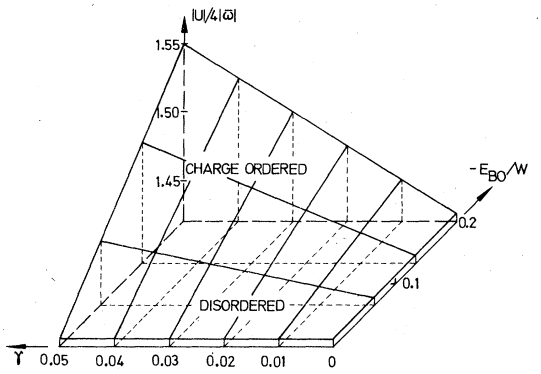

FIG. 1. The charge-ordered state for large $|U|$ is separated from the disordered state for small $|U|$ by a surface across which a first-order transition occurs. γ and E_{B0} measure the band-structure effect.

while $\gamma(\uparrow)=\gamma(\downarrow)=\frac{1}{2}\gamma$ and E_{B0} were treated as varying parameters.[22,23] Let $\bar{\epsilon}\leq 0$ be the average bare band energy per electron. For simple cubic structure, the antiferromagnetic-paramagnetic transition is shown in Fig. 1 (reproduced from the Fig. 4 of Ref. 23), provided that $\bar{\omega}$, charge-ordered and disordered are replaced, respectively, by $\bar{\epsilon}$, antiferromagnetic and paramagnetic. For given values of E_{B0}/W and γ, the ground state becomes antiferromagnetic when the intra-atomic Coulomb repulsion reaches a critical value.

Now we consider the Hubbard Hamiltonian with negative U. Let us first define $\tau_{ij\uparrow}=t_{ij\uparrow}=t_{ij}$, $\tau_{ij\downarrow}=-t_{ij\downarrow}=-t_{ij}$ and the canonical transformation

$$b_{i\uparrow}=a_{i\uparrow}\ ,\quad b_{i\downarrow}=a_{i\downarrow}^{\dagger}\ . \tag{10}$$

If we further define $m_{i\sigma}=b_{i\sigma}^{\dagger}b_{i\sigma}$, then we can transform the Hubbard Hamiltonian with $U<0$ to

$$\tilde{H}=H-\frac{N}{2}U=\tilde{H}_0+\tilde{H}_1\ , \tag{11}$$

where

$$\tilde{H}_0=\sum_{ij\sigma}\tau_{ij\sigma}[m_{i-\sigma}b_{i\sigma}^{\dagger}b_{j\sigma}m_{j-\sigma}+(1-m_{i-\sigma})b_{i\sigma}^{\dagger}b_{j\sigma}(1-m_{j-\sigma})]+\frac{|U|}{2}\sum_i[m_{i\uparrow}m_{i\downarrow}+(1-m_{i\uparrow})(1-m_{i\downarrow})]\ , \tag{12}$$

and

$$\tilde{H}_1=\sum_{ij\sigma}\tau_{ij\sigma}[(1-m_{i-\sigma})b_{i\sigma}^{\dagger}b_{j\sigma}m_{j-\sigma}+m_{i-\sigma}b_{i\sigma}^{\dagger}b_{j\sigma}(1-m_{j-\sigma})]\ . \tag{13}$$

This Hamiltonian has exactly the same structure as the previous one defined by Eqs. (7)–(9). The down-spin holes for $U<0$ then play the roles of the down-spin electrons for $U>0$. As a consequence, the antiferromagnetic ground state for $U>0$ corresponds to the charge-ordered ground state for $U<0$ with every second site doubly occupied. Since $\tau_{ij\downarrow}=-t_{ij\downarrow}$, it is convenient to define $\omega(k)$ as the bare band energy for up-spin electrons and $-\omega(k)$ as the bare band energy for down-spin holes. We can then define $\bar{\omega}$ as the average bare band energy for up-spin electrons and down-spin holes, and similarly define E_{B0} in terms of $\omega(k)$. The transition between the charge-ordered and the disordered ground states is simply obtained from the corresponding transition for $U>0$, as illustrated by Fig. 1.

For the case of $U > 0$, the electron-hole excitation energy of a stable antiferromagnetic ground state has been calculated in Ref. 23. Depending on the configuration of the final state, there are two types of excitations. In the Wannier representation, an electron-hole excitation can be described as a ω-spin electron hops from the singly occupied ith site to a nearest- neighbor jth site which is already occupied by a $-\sigma$-spin electron. An empty ith site and a doubly occupied jth site are then created, leaving the system in a conducting state. We call this the "frozen" final state and the corresponding excitation energy Δ_F measures the Mott-Hubbard gap. However, the final state can relax via the hopping of the $-\sigma$-spin electron from the jth site to the empty ith site. Such "relaxed" final state is just a magnetically excited state created by double spin flips at both the ith and the jth sites simultaneously. Thus the excitation energy Δ_R corresponds to the antiferromagnetic coupling strength. Δ_F and Δ_R are shown in Fig. 2 (reproduced from the Fig.6 of Ref. 23) in the energy unit of $4|\bar{\epsilon}|$, if we replace $\bar{\omega}$ by $\bar{\epsilon}$.

Similar excitations can be defined for the charge-ordered ground state for $U < 0$. The frozen final configuration is produced by the split of one doubly occupied atom into two singly occupied nearest-neighbor pair. If both electrons hop from one doubly occupied atom to an empty neareat-neighbor site, we have the relaxed final state. Therefore, Fig. 2 exhibits such excitation energies in the energy unit of $4|\bar{\omega}|$.

To close this short note, we make the following remarks. First, the Hartree-Fock result of Penn[28] for the antiferromagnetic ground state for $U > 0$ can also be transferred directly to describe the charge-ordered ground state for $U < 0$ and $n = 1$. Therefore, in Hartree-Fock approximation the charge-ordered ground state is stable even with infinitesimal $|U|$, in contrast to our result with a finite critical value of U.

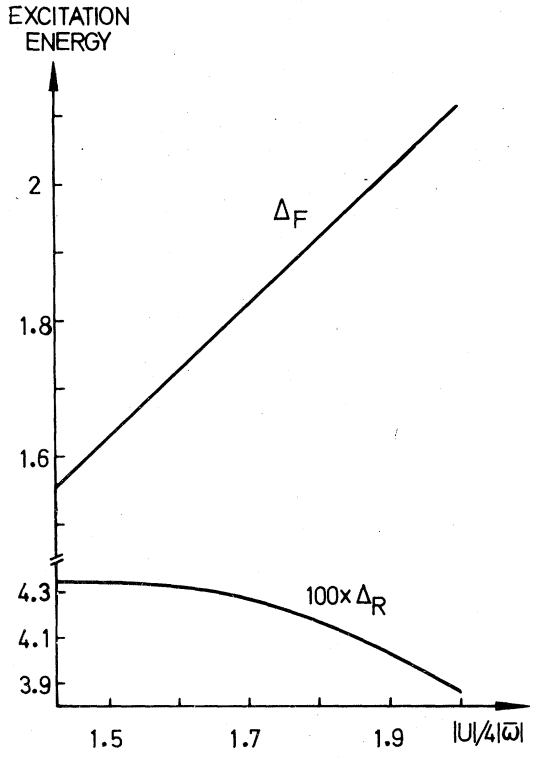

FIG. 2. Energy gaps for an electron-hole pair excitation in the charge-ordered state: Δ_F for frozen final configuration and Δ_R for relaxed final configuration.

Second, although the electron-hole symmetry used above to transfer the results of $U > 0$ to describe the case $U < 0$ breaks down when $n \neq 1$, the variational calculation for $U < 0$ and $N \neq 1$ is straightforward. Yet in this case one should also consider the stability of the charge-ordered state against the superconducting state.

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