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Charge order and antiferromagnetic order in the Hubbard model with nearest-neighbor Coulomb interaction: Weak coupling

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The half-filled-band Hubbard model with an added Coulomb repulsion between electrons on nearest-neighbor sites is studied. We investigate the existence of Hartree-Fock self-consistent solutions which break the symmetry between even and odd sites: these are of the antiferromagnetic and charge-order type. Emphasis is put on the large-bandwidth (weak-coupling) regime where we find BCS-like gap equations and critical temperatures for the order parameters. At zero temperature, as the parameters of the Hamiltonian are altered, the system exhibits a first-order phase transition from an antiferromagnetic to a charge-ordered state. The two kinds of order never coexist.

I. INTRODUCTION

The half-filled-band Hubbard Hamiltonian[1] with an added nearest-neighbor Coulomb-repulsion term (besides the band term and the on-site Coulomb repulsion) has been studied since Bari[2] first analyzed its properties in the narrow-band limit. The more recent work,[3–5] restricted to one-dimensional systems, has been aimed at making contact with experiments on NMP-TCNQ (N-methylphenazinium-tetracyanoquinodimethane).[6] The Hubbard model alone was shown[7] to be inadequate to explain the magnetic susceptibility of NMP-TCNQ, especially the much reduced Curie constant. The hope was[4] that the additional term in the Hamiltonian (nearest-neighbor Coulomb repulsion) could improve the theoretical picture. The reason for this, as mentioned in Ref. 4, was that a large enough nearest-neighbor interaction actually induces a transition to a charge-ordered state (at least when the bandwidth is zero[2]), a state in which the average $\langle S_{iz}^2\rangle = 0$ (S_{iz} is the spin operator at site i). This fact was expected to lead to a reduction of the number of Bohr magnetons in χ^{-1} in the Curie-Weiss region of temperature for small but not negligible nearest-neighbor repulsion. Unfortunately, the results for χ were negative. One concludes that at zero bandwidth,[2–4] or for very small bandwidth[5] (with respect to Coulomb energy), the inclusion of the nearest-neighbor Coulomb term in the Hamiltonian fails to bring theory closer to experiment.

There are good reasons to look at the weak-coupling region, besides its intrinsic interest. The kinetic energy tends to spread to charge and spin densities uniformly, reducing the amount of ordering. Cabib and Kaplan,[7] in an exact calculation for small one-dimensional systems, showed that the bandwidth does not reduce the paramagnetic susceptibility enough to bring agreement with experiment, even when it is very large compared with the interaction. They included only on-site repulsion and there is as yet no study of the effect of the nearest-neighbor interaction in the weak-coupling case.

In this paper we allow for both spin order and charge order, and we calculate the spin-order–charge-order phase diagram, in the weak-coupling regime. We show that spin order and charge order do not coexist: Depending upon the ratio of on-site to nearest-neighbor Coulomb repulsion, the system is either spin ordered or charge ordered, but not both.

We decouple the Hamiltonian in the Hartree-Fock approximation. This would be impermissible in the strong-coupling regime, but for weak coupling it may be adequate. We assume solutions which break the symmetry between even and odd sites with respect to both the number of electrons on the sites and their spin. Both of these kinds of order open a gap at the Fermi momentum ($k_F = \pi/2a$) of the half-filled band, which is the only charge concentration we consider. Opening a gap of course lowers the energy of the ground state and creates an electronic insulator. Overhauser investigated[8] the instability of an electron system at metallic densities with respect to such charge- and spin-density waves. In the model Hamiltonian that we study we find similar waves and, furthermore, we look for the conditions of existence of the charge- and the spin-density waves in terms of the parameters of the Hamiltonian. We do not allow for solutions with a net magnetic moment, which *a priori* are not ruled out by our calculations. Our calculation is internally consistent. One starts by assuming that the moment is zero and then finds it to be zero self-consistently. This does not exclude ferromagnetism; it only means that our treatment does not self-destruct.

In Sec. II we show the formalism and the solution. In Sec. III we derive the gap equations, the phase diagram at zero temperature, and the equations defining the critical temperatures. In Sec. IV we discuss the results.

II. ORDER PARAMETERS AND ENERGY LEVELS

A half-filled band of electrons in one dimension, if it is unmagnetized, has a Fermi momentum $k_F = \pi/2a$. A periodic electronic disturbance of wave number $q = \pm 2k_F$ will then create gaps at the Fermi surface, lower the energy of the occupied states (and raise that of the empty states), lower the energy of the electrons, and thereby be self-sustaining. A disturbance of this wave number will double the unit cell: even-numbered sites will be different from odd-numbered sites. Because of spin there are then four variables to be considered, $n_{e\uparrow}$, $n_{e\downarrow}$, $n_{o\uparrow}$, and $n_{o\downarrow}$ (e, even; o, odd; $\uparrow$, $\downarrow$ are the spin states). These variables are not all independent: They are subject to the charge-conservation constraint

$$2A = \langle n_{e\uparrow} + n_{e\downarrow} + n_{o\uparrow} + n_{o\downarrow} \rangle . \qquad (2.1)$$

The three order parameters are then the magnetization (per site):

$$2m = \langle n_{e\uparrow} - n_{e\downarrow} + n_{o\uparrow} - n_{o\downarrow} \rangle ; \qquad (2.2)$$

the charge order parameter (per site):

$$2c = \langle n_{e\uparrow} + n_{e\downarrow} - n_{o\uparrow} - n_{o\downarrow} \rangle ; \qquad (2.3)$$

and the antiferromagnetic order parameter (per site):

$$2s = \langle n_{e\uparrow} - n_{e\downarrow} - n_{o\uparrow} + n_{o\downarrow} \rangle . \qquad (2.4)$$

Throughout our paper we will choose $A = 1$ (half-filled band) and $m = 0$. If the band is not exactly half-filled or if $m \neq 0$ the proper theoretical approach is not obtained by simply setting $A \neq 1$ or $m \neq 0$ in Eqs. (2.1) and (2.2): In fact, the size of the unit cell and the order parameter must also be changed, because they are intimately related to $2k_F$. For the time being we keep A and m general to show the logic of the treatment.

Our Hamiltonian is

$$H = -t \sum_{i\sigma} (c^\dagger_{i\sigma} c_{i+1\,\sigma} + c^\dagger_{i+1\,\sigma} c_{i\sigma}) + U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_i n_i n_{i+1} . \qquad (2.5)$$

The three terms of (2.5) are, respectively, the band energy, the intra-atomic Coulomb repulsion, and the nearest-neighbor Coulomb repulsion; this is just the Hubbard Hamiltonian[1] plus an additional nearest-neighbor term. The on-site U term is spin dependent, discouraging two electrons of antiparallel spin from occupying the same site if U is positive. There is no need for a term discouraging parallel electrons from occupying the same site, since the orbitals are assumed to be nondegenerate, and the fermion commutation rules already forbid such occupation.

U is ordinarily due to Coulomb repulsion, and is therefore usually assumed to be a positive quantity.

It has been suggested[9] that in some quasi-one-dimensional systems {for example, tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) and $\mathrm{K_2Pt(CN)_4Br_{0.3}} \cdot n\mathrm{H_2O}$ (KCP)[10]} the origin of the large peaks of the dc conductivity is electron coupling to a soft lattice mode. As it is argued in recent literature[2,3] one can imagine electron-phonon interaction to give rise to effective electron-electron interactions of the kind we have in our model Hamiltonian, after summing over phonon coordinates. Positive and negative values of the parameters U and V could result and therefore be of interest.

We take the nearest-neighbor Coulomb repulsion to be spin independent. In a later section we show that in the Hartree-Fock (HF) approximation the only effect of the inclusion of exchange terms is a nonessential redefinition of coefficients. There is an interesting competition between the different terms of (2.5). The kinetic energy is least when each of the N electrons is spread smoothly over all N sites. The U term (when positive) prefers to bunch up electrons on different sites, one on each site. The V term prefers to bunch two electrons on one site (with antiparallel spins), say an even numbered site, and none on the adjacent odd-numbered sites, so that

$$\langle n_i n_{i+1} \rangle = 0 .$$

When the Coulomb terms are dominant, particularly the on-site term, correlation is so strong that one must give it special consideration. But in the weak-coupling regime the band energy dominates and it may be adequate to decouple in the Hartree-Fock approximation. It is certainly instructive to do so because the method is transparent. So doing, the Hamiltonian becomes

$$\begin{aligned} H = {} & -t \sum_{i\sigma} (c^\dagger_{i\sigma} c_{i+1\,\sigma} + c^\dagger_{i+1\,\sigma} c_{i\sigma}) \\ & + [-\tfrac{1}{2}U(m+s) + (\tfrac{1}{2}U - 2V)c] \sum_i n_{2i\uparrow} \\ & + [-\tfrac{1}{2}U(m-s) - (\tfrac{1}{2}U - 2V)c] \sum_i n_{2i-1\,\uparrow} \\ & + [\tfrac{1}{2}U(m+s) + (\tfrac{1}{2}U - 2V)c] \sum_i n_{2i\downarrow} \\ & + [\tfrac{1}{2}U(m-s) - (\tfrac{1}{2}U - 2V)c] \sum_i n_{2i-1\,\downarrow} . \end{aligned}$$

There is also an additive constant in each square parenthesis, $(\frac{1}{2}U + 2V)A$, which we have dropped. The summations now go over $i = 1$ to $\frac{1}{2}N$.

To diagonalize the kinetic energy one transforms to momentum space:

$$c^{\dagger}_{j\sigma}=\frac{1}{\sqrt{N}}\sum_{k} c^{\dagger}_{k\sigma}e^{ikja}, \qquad c_{j\sigma}=\frac{1}{\sqrt{N}}\sum_{k} c_{k\sigma}e^{-ikja}.$$

The summations are over N sites, or over the N states of the original zone. Some summations one needs are

$$\sum_{i=1}^{N}(c^{\dagger}_{i}c_{i+1}+c^{\dagger}_{i+1}c_{i})=2\sum_{k}c^{\dagger}_{k}c_{k}\cos ka, \tag{2.6}$$

$$\sum_{i=1}^{N/2}c^{\dagger}_{2i}c_{2i}=\frac{1}{2}\sum_{k}c^{\dagger}_{k}c_{k}+\frac{1}{2}\sum_{k}c^{\dagger}_{k}c_{k+\pi/a}, \tag{2.7}$$

$$\sum_{i=1}^{N/2}c^{\dagger}_{2i-1}c_{2i-1}=\frac{1}{2}\sum_{k}c^{\dagger}_{k}c_{k}-\frac{1}{2}\sum_{k}c^{\dagger}_{k}c_{k+\pi/a}. \tag{2.8}$$

Each state k is coupled to the state $k+\pi/a$. It is convenient to transform to a reduced zone $-\pi/2a \leqslant k \leqslant \pi/2a$, and label the states by a band index, l and u. The transformation is illustrated in Fig. 1. In this representation the Hamiltonian is written as

$$H=-2t\sum_{k\sigma}c^{l\dagger}_{k\sigma}c^{l}_{k\sigma}\cos ka+2t\sum_{k\sigma}c^{u\dagger}_{k\sigma}c^{u}_{k\sigma}\cos ka-\frac{Um}{2}\sum_{k}(c^{l\dagger}_{k\uparrow}c^{l}_{k\uparrow}+c^{u\dagger}_{k\uparrow}c^{u}_{k\uparrow})+\frac{Um}{2}\sum_{k}(c^{l\dagger}_{k\downarrow}c^{l}_{k\downarrow}+c^{u\dagger}_{k\downarrow}c^{u}_{k\downarrow})$$
$$+[-\tfrac{1}{2}Us+(\tfrac{1}{2}U-2V)c]\sum_{k}(c^{l\dagger}_{k\uparrow}c^{u}_{k\uparrow}+c^{u\dagger}_{k\uparrow}c^{l}_{k\uparrow})+[\tfrac{1}{2}Us+(\tfrac{1}{2}U-2V)c]\sum_{k}(c^{l\dagger}_{k\downarrow}c^{u}_{k\downarrow}+c^{u\dagger}_{k\downarrow}c^{l}_{k\downarrow}). \tag{2.9}$$

We introduce a few convenient symbols. Let

$$\epsilon_{k}=2t\cos ka, \tag{2.10}$$

$$\Delta_{-}=\tfrac{1}{2}Us-(\tfrac{1}{2}U-2V)c, \tag{2.11}$$

$$\Delta_{+}=\tfrac{1}{2}Us+(\tfrac{1}{2}U-2V)c, \tag{2.12}$$

$$x_{k-}=(\epsilon^{2}_{k}+\Delta^{2}_{-})^{1/2}, \tag{2.13}$$

$$x_{k+}=(\epsilon^{2}_{k}+\Delta^{2}_{+})^{1/2}. \tag{2.14}$$

The Hamiltonian now separates into $H_{\uparrow}$ and $H_{\downarrow}$, but the two bands l, u, are coupled at each k. To diagonalize at each k let us define new operators $a_{k\sigma}$, $b_{k\sigma}$ and their adjoints as follows:

$$c^{l}_{k\sigma}=\cos\theta_{k\sigma}a_{k\sigma}-\sin\theta_{k\sigma}b_{k\sigma}, \tag{2.15a}$$

$$c^{u}_{k\sigma}=\sin\theta_{k\sigma}a_{k\sigma}b_{k\sigma}+\cos\theta_{k\sigma}b_{k\sigma}, \tag{2.15b}$$

where $\theta_{k\sigma}$ are real parameters. $a^{\dagger}_{k\sigma}$ and $b^{\dagger}_{k\sigma}$ are defined by taking the adjoints of (2.15).

Substitution of Eqs. (2.15) into the Hamiltonian (2.9) gives diagonal terms in $a^{\dagger}a$, $b^{\dagger}b$ and off-diagonal terms proportional to $a^{\dagger}b+b^{\dagger}a$. The parameters $\theta_{k\sigma}$ corresponding to the transformations which make the coefficients of the nondiagonal terms vanish, are given by

$$\tan 2\theta_{k\uparrow}=\Delta_{-}/\epsilon_{k}, \quad \tan 2\theta_{k\downarrow}=-\Delta_{+}/\epsilon_{k}. \tag{2.16}$$

Then one has

$$\sin 2\theta_{k\uparrow}=\Delta_{-}/x_{k-}, \quad \cos 2\theta_{k\uparrow}=\epsilon_{k}/x_{k-},$$
$$\sin 2\theta_{k\downarrow}=-\Delta_{+}/x_{k+}, \quad \cos 2\theta_{k\downarrow}=\epsilon_{k}/x_{k+}. \tag{2.17}$$

The Hamiltonian is now fully diagonalized:

$$H_{k\uparrow}=(-\tfrac{1}{2}Um-x_{k-})a^{\dagger}_{k\uparrow}a_{k\uparrow}+(-\tfrac{1}{2}Um+x_{k-})b^{\dagger}_{k\uparrow}b_{k\uparrow}, \tag{2.18a}$$

$$H_{k\downarrow}=(\tfrac{1}{2}Um-x_{k+})a^{\dagger}_{k\downarrow}a_{k\downarrow}+(\tfrac{1}{2}Um+x_{k+})b^{\dagger}_{k\downarrow}b_{k\downarrow}, \tag{2.18b}$$

with

$$H=\sum_{k}(H_{k\uparrow}+H_{k\downarrow})$$
$$=\sum_{k\sigma}(E^{a}_{k\sigma}a^{\dagger}_{k\sigma}a_{k\sigma}+E^{b}_{k\sigma}b^{\dagger}_{k\sigma}b_{k\sigma}), \tag{2.18c}$$

(2.18a)–(2.18c) define the one particle energies $E^{a}_{k\sigma}$, $E^{b}_{k\sigma}$. From (2.18) one sees that the two lower bands, with positive curvature, are the a bands. The upper bands, curving downward, are the b bands.

Let us now discuss the order parameters and the one-particle energy levels. There are four operators whose expectation values in the a, b basis are the four order parameters

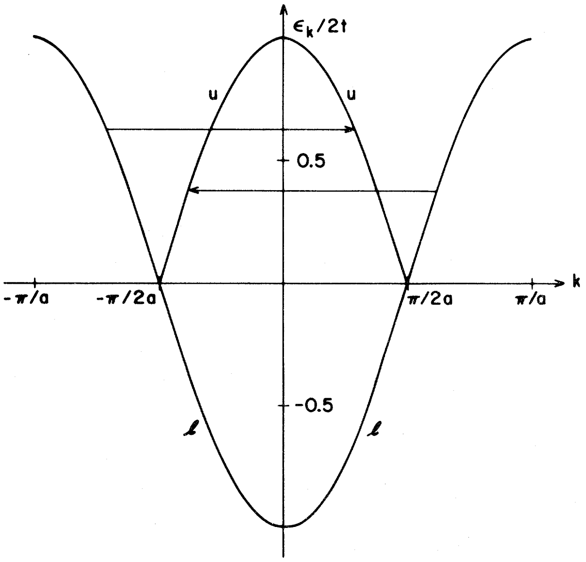

FIG. 1. Translation of momentum states into the reduced zone.

$$A_{\mathrm{op}}=\frac{1}{N}\sum_{k\sigma}(a^\dagger_{k\sigma}a_{k\sigma}+b^\dagger_{k\sigma}b_{k\sigma})\,, \tag{2.19}$$

$$m_{\mathrm{op}}=\frac{1}{N}\sum_{k}(a^\dagger_{k\uparrow}a_{k\uparrow}+b^\dagger_{k\uparrow}b_{k\uparrow}-a^\dagger_{k\downarrow}a_{k\downarrow}-b^\dagger_{k\downarrow}b_{k\downarrow})\,, \tag{2.20}$$

$$s_{\mathrm{op}}=\frac{\Delta_-}{N}\sum_k\frac{1}{x_{k-}}(a^\dagger_{k\uparrow}a_{k\uparrow}-b^\dagger_{k\uparrow}b_{k\uparrow})+\frac{\Delta_+}{N}\sum_k\frac{1}{x_{k+}}(a^\dagger_{k\downarrow}a_{k\downarrow}-b^\dagger_{k\downarrow}b_{k\downarrow})\,, \tag{2.21}$$

$$c_{\mathrm{op}}=\frac{\Delta_-}{N}\sum_k\frac{1}{x_{k-}}(a^\dagger_{k\uparrow}a_{k\uparrow}-b^\dagger_{k\uparrow}b_{k\uparrow})-\frac{\Delta_+}{N}\sum_k\frac{1}{x_{k+}}(a^\dagger_{k\downarrow}a_{k\downarrow}-b^\dagger_{k\downarrow}b_{k\downarrow})\,. \tag{2.22}$$

Using Fermi statistics and (2.18), we have

$$\langle a^\dagger_{k\sigma}a_{k\sigma}\rangle=(e^{\beta(E^a_{k\sigma}-\mu)}+1)^{-1}\,,$$

and similarly for $\langle b^\dagger_{k\sigma}b_{k\sigma}\rangle$, where μ is the Fermi level.

First we note that when $s\to s$

$$\Delta_+\rightleftarrows-\Delta_-\,,\quad x_{k+}\rightleftarrows x_{k-}\,, \tag{2.23}$$

and when $c\to-c$

$$\Delta_+\rightleftarrows\Delta_-\,,\quad x_{k+}\rightleftarrows x_{k-}\,. \tag{2.24}$$

Therefore Eqs. (2.21) and (2.22) are invariant under change of sign of either s or c. This was expected because the symmetry breaking is arbitrary as to even sites and odd sites, and as to spin up and spin down. We can arbitrarily pick s and c to be positive quantities.

As for $\langle A_{\mathrm{op}}\rangle$, at each temperature, and for each value of t, U and V, one must adjust the Fermi level μ to make $\langle A_{\mathrm{op}}\rangle=1$. Later we will see that $\mu=0$ at all temperatures and independent of t, U, V. Let us now discuss the significance of the ferromagnetic order parameter.

Lieb and Wu[11] show the ground state of the Hubbard model to be a singlet and the V term of our Hamiltonian (2.5) discourages the onset of magnetization. We take this as a suggestion that $m=0$. At the stage of the present paper we cannot rule out that $m\neq0$, but we have now a proof that $m=0$ within the HF approximation, which will be published separately.

III. GAP EQUATIONS AND PHASE DIAGRAM

First we show that exchange terms in the Hamiltonian can be treated within the present formalism. If the Hamiltonian is

$$H=E_{\mathrm{kin}}+U\sum_i n_{i\uparrow}n_{i\downarrow}+V\sum_i n_in_{i+1}-J\sum_{i\sigma}n_{i\sigma}n_{i+1\,\sigma}$$

and one pulls out averages as before, the appropriate Hamiltonian becomes

$$\begin{aligned}H=E_{\mathrm{kin}}&+[-(\tfrac{1}{2}U+J)m-(\tfrac{1}{2}U-J)s+(\tfrac{1}{2}U-2V+J)c]\sum_i n_{2i\uparrow}+[-(\tfrac{1}{2}U+J)m+(\tfrac{1}{2}U-J)s-(\tfrac{1}{2}U-2V+J)c]\sum_i n_{2i-1\,\uparrow}\\&+[(\tfrac{1}{2}U+J)m+(\tfrac{1}{2}U-J)s+(\tfrac{1}{2}U-2V+J)c]\sum_i n_{2i\downarrow}+[(\tfrac{1}{2}U+J)m-(\tfrac{1}{2}U-J)s-(\tfrac{1}{2}U-2V+J)c]\sum_i n_{2i-1\,\downarrow}\,.\end{aligned}$$

If J is positive, encouraging ferromagnetism, one can obtain a magnetization, and should start by assuming it. A ferromagnetic J is also seen to discourage both spin order and charge order, and an antiferromagnetic J to encourage both of these. In any case, inclusion of exchange terms in the mean-field approximation requires only a redefinition of constants. The coefficient of m is replaced by $\frac{1}{2}U+J$, that of s by $\frac{1}{2}U-J$, and that of c by $\frac{1}{2}U-2V+J$. Exchange interactions can change the state of the system, causing magnetization, antiferromagnetism, or charge ordering, by tipping the balance in favor of one state over another, but this is merely a matter of the sizes of the various coefficients.

Let us assume that J is either negative or not large enough to induce ferromagnetism, and absorb J into U and V, so that the redefined constant $\frac{1}{2}U$ is $\frac{1}{2}U-J$ and the redefined $-2V$ is $-2V+J$. To proceed we must now fix the Fermi level. Since the energies $E^a_{k\sigma}$, $E^b_{k\sigma}$ defined in Eq. (2.18) are now $-x_{k-}$, x_{k-}, $-x_{k+}$, and x_{k+} and they are symmetric around zero, the Fermi level is zero at all temperatures and independent of t, U, V.

The self-consistent equations for the spin and charge order at finite temperature are obtained from Eqs. (2.21) and (2.22) by averaging both sides:

$$s=\frac{\Delta_-}{N}\sum_k\frac{1}{x_{k-}}\tanh\frac{\beta x_{k-}}{2}+\frac{\Delta_+}{N}\sum_k\frac{1}{x_{k+}}\tanh\frac{\beta x_{k+}}{2}\,, \tag{3.1}$$

$$c=\frac{\Delta_-}{N}\sum_k\frac{1}{x_{k-}}\tanh\frac{\beta x_{k-}}{2}-\frac{\Delta_+}{N}\sum_k\frac{1}{x_{k+}}\tanh\frac{\beta x_{k+}}{2}\,. \tag{3.2}$$

Let us examine (3.1) and (3.2) in detail at $T=0$ °K. At this temperature $\tanh\frac{1}{2}\beta x_k=1$. Transforming the summations in (3.1) and (3.2) into integrations over k space, we have

$$s+c=\frac{\Delta_-a}{2\pi}\int_{-\pi/2a}^{\pi/2a}\frac{dk}{x_{k-}}\,, \tag{3.3}$$

$$s-c=\frac{\Delta_+ a}{2\pi}\int_{-\pi/2a}^{\pi/2a}\frac{dk}{x_{k+}}\,. \tag{3.4}$$

We shall perform these integrals by two methods. First we do them exactly. Let

$$I=\frac{a}{2\pi}\int_{-\pi/2a}^{\pi/2a}\frac{dk}{x_k}\,, \tag{3.5}$$

with $x_k = x_{k+}$ or x_{k-} and

$$\nu=[1+(\Delta/2t)^2]^{-1}, \tag{3.6}$$

with $\Delta = \Delta_+$ or Δ_-. Then

$$I=(\sqrt{\nu}/2\pi t)K(\nu)\,, \tag{3.7}$$

where

$$K(\nu)=\int_0^{\pi/2}\frac{dx}{(1-\nu^2\sin^2 x)^{1/2}} \tag{3.8}$$

is the complete elliptic integral of the first kind. $K(\nu)$ has the asymptotic form

$$K(\nu)\cong\tfrac{1}{2}\ln[1/(1-\nu)]\,. \tag{3.9}$$

Thus at $T=0$ °K

$$|\Delta_-|\cong 2t\,e^{-\pi t(s+c)/\Delta_-}\,, \tag{3.10a}$$

$$|\Delta_+|\cong 2t\,e^{-\pi t(s-c)/\Delta_+}\,. \tag{3.10b}$$

If either s or c are 0, Eqs. (3.10a) and (3.10b) reduce to

$$s(0)=\frac{4t}{U}\,e^{-2\pi t/U}\quad(U>0) \tag{3.11a}$$

or

$$c(0)=[4t/(4V-U)]\,e^{-2\pi t/(4V-U)}\,. \tag{3.11b}$$

In the above form the result depends upon the particular shape of the energy bands. A somewhat more general and conventional approach is to integrate on energy:

$$s+c=\Delta_-\int_{-2t}^{2t}\frac{\rho(\epsilon)\,d\epsilon}{x_-}\,, \tag{3.12}$$

$$s-c=\Delta_+\int_{-2t}^{2t}\frac{\rho(\epsilon)\,d\epsilon}{x_+}\,. \tag{3.13}$$

Letting $\epsilon/\Delta=\sinh z$ and taking the density of states out of the integral sign, we obtain the usual BCS-like result when we approximate the hyperbolic sine by the exponential:

$$|\Delta_-|=4t\exp\{-(s+c)/[2\rho(\mu)\Delta_-]\}, \tag{3.14}$$

$$|\Delta_+|=4t\exp\{-(s-c)/[2\rho(\mu)\Delta_+]\}. \tag{3.15}$$

Equations equivalent to (3.11a) and (3.11b) are readily obtained from (3.14) and (3.15) in the event that either s or c is zero. The pair of coupled equations (3.10) and (3.11) or (3.14) and (3.15) must be solved as function of U/t and V/t to obtain the spin-order–charge-order phase diagram. For $U>4V$, $c=0$: only s is nonzero. When $U=0$, $s=0$: only c is nonzero. Along the line $U=2V$ there are three nontrivial solutions: either $s=0$ and there is charge order, or $c=0$ and there is spin order, or $s=c\neq 0$. To choose the correct solution we must solve the equations for each case, and find which one corresponds to the lowest energy. So doing, we find that the $s=c$ solution has higher energy than the other two. The result is that in this simple problem one never has the two order parameters simultaneously. In more complicated situations, and in three dimensions, one can obtain several order parameters simultaneously, as for example in magnetite.[12]

The spin-order–charge-order phase diagram is shown in Fig. 2. The straight line $U=2V$ is the boundary of a first-order transition from the antiferromagnetic phase to the charge-ordered phase. When $U<2V$, the system charge orders.

Thus, returning to the energies of Eq. (2.22), we conclude that the two a bands are degenerate, the b bands are degenerate, and the gap at the zone boundary is either Us or $(4V-U)c$, depending upon whether U is greater or less than $2V$. [The other solution with s and c simultaneously $\neq 0$ would give nondegenerate bands with a gap $|Us-(U-4V)c|$.]

From Eqs. (3.1) and (3.2) we can find the Curie points. When there is spin order the critical temperature kT_s is given implicitly by the equation

$$\frac{1}{U}=\frac{1}{N}\sum_k\frac{1}{\epsilon_k}\tanh\frac{\epsilon_k}{2kT_s}\quad(U>0). \tag{3.16}$$

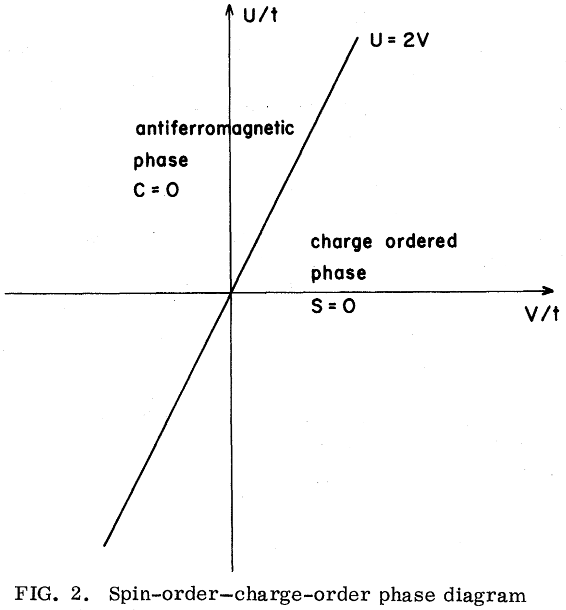

FIG. 2. Spin-order–charge-order phase diagram in the $U/t-V/t$ plane at all temperatures below the critical temperatures. The line $U=2V$ is the boundary of a first-order phase transition between an antiferromagnetic and a charge-ordered state, when U/V is varied.

When there is charge order we have for the critical temperature kT_c

$$\frac{1}{4V-U}=\frac{1}{N}\sum_k \frac{1}{\epsilon_k}\tanh\frac{\epsilon_k}{2kT_c}\ . \tag{3.17}$$

These are integrated as in BCS theory to give, for s

$$kT_s=2.28t\exp\left(-\frac{1}{\rho U}\right)\quad (U>0), \tag{3.18}$$

and for c

$$kT_c=2.28t\exp\left(-\frac{1}{\rho(4V-U)}\right). \tag{3.19}$$

Equation (3.16) has been obtained by Langer, Plischke, and Mattis[13] in the simple Hubbard model.

IV. DISCUSSION

In this paper we have studied the effect of small on-site and nearest-neighbor Coulomb repulsion on a half-filled one-dimensional band of electrons. In our calculation we have looked for solutions with antiferromagnetic and charge order within the Hartree-Fock approximation. We have obtained a phase diagram at zero temperature of the following sort: (i) the antiferromagnetic order and the charge order never coexist for any values of U/t and V/t; (ii) the line $U=2V$ is the boundary of a first-order phase transition between the two phases; (iii) the antiferromagnetic phase is stable for $U>2V$ and the charge-ordered phase is stable for $U<2V$; (iv) on the line $U=2V$ the two phases are degenerate. It is easy to see that on the line $U=2V$ the two phases remain degenerate as the temperature is increased and they have the same critical temperature. On this line there is another solution with $s=c$ which has higher energy at 0 °K and a smaller critical temperature than the two degenerate solutions. This higher-energy solution also exists off the line $U=2V$ with s and $c\neq 0$ and $s\neq c$. Furthermore for $U>2V$ ($U<2V$) the charge (antiferromagnetic) order does not turn on with increasing temperature, so that the phase diagram of Fig. 2 remains valid at all temperatures below the critical temperatures.

Among the motivations for performing the present calculation are the discrepancies between the theoretical and experimental magnetic susceptibilities, both as to magnitude and temperature dependence. One's first thought is that the susceptibility should be thermally activated, with a gap equal to the conductivity gap. This follows from the argument that the lower spin-up and spin-down subbands are filled, with a gap at the Fermi surface. In this picture, to induce a moment one must excite and flip a spin-down valence electron into the empty spin-up conduction band. But on second thought, one recognizes the possibility of first transferring electrons, in a magnetic field, from the spin-down to the spin-up subbands, and then creating (reduced) gaps at the two Fermi surfaces. The resolution as to which approach is correct turns out to be a delicate matter, and the calculation is detailed enough to merit severance from the present paper. Another aspect of the problem, and one closely related to the above, is the effect of deviation from the half-filled band. In NMP about 0.9 electrons are transferred per molecule unit, and in TTF-TCNQ about 0.7 electrons are transferred, so the deviations (from one extra electron per TCNQ ring) are considerable and are worthy of attention. This too shall be treated in a forthcoming paper.

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[1] J. Hubbard, Proc. R. Soc. A 276, 238 (1963).

[2] R. A. Bari, Phys. Rev. B 3, 2662 (1971).

[3] G. Beni and P. Pincus, Phys. Rev. B 9, 2963 (1974).

[4] R. S. Tu and T. A. Kaplan, Phys. Status Solidi B 63, 659 (1974).

[5] D. Cabib, Phys. Rev. B 12, 2189 (1975).

[6] A. J. Epstein *et al.*, Phys. Rev. B 5, 952 (1972).

[7] D. Cabib and T. A. Kaplan, AIP Conf. Proc. 10, 1504 (1973).

[8] A. W. Overhauser, Phys. Rev. 167, 691 (1968).

[9] B. Horovitz *et al.* report (unpublished).

[10] R. Comes, M. Lambert and H. R. Zeller, Phys. Status Solidi B, 58, 587 (1973).

[11] E. Lieb and F. Wu, Phys. Rev. Lett. 20, 1445 (1968).

[12] J. R. Cullen and E. Callen, Phys. Rev. B 7, 397 (1973).

[13] W. Langer, M. Plischke, and D. Mattis, Phys. Rev. Lett. 23, 1448 (1969).