Minimal charge gap in the ionic Hubbard model

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We study the ionic Hubbard model at temperature $T=0$ within the mean-field approximation, and show that the charge gap does not close completely at the ionic-band insulator to antiferromagnetic insulator transition, contrary to previous expectations. Furthermore, we find an intermediate phase for on-site repulsions $U>U_c$ for different lattices, and calculate the phase diagram for the ionic Hubbard model with alternating U, corresponding to a Cu-O lattice.

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I. INTRODUCTION

The generalization of the Hubbard model with different on-site energies on the neighboring sites has been named the ionic Hubbard model (IHM),

$$H=t\sum_{\langle i,j\rangle,\sigma} c^{\dagger}_{j,\sigma}c_{i,\sigma}+\frac{U}{2}\sum_{i,\sigma} n_{i,\sigma}n_{i,-\sigma}+E_0\sum_{i,\sigma}(-1)^{|i|}n_{i,\sigma}, \tag{1}$$

which is characterized by a nearest-neighbor hopping amplitude t, an on-site Coulomb-repulsion U, and a site-dependent on-site energy $\pm E_0$. Here $|i|=$even/odd respectively for A and B sites on a bipartite lattice.

The IHM is used in two contexts: (a) For a, description of the neutral-ionic transition (NIT) (Ref. 1) in organic mixed-stack charge-transfer (CT) crystals. The stacks in CT crystals form quasi-one-dimensional insulating chains with alternating donor and acceptor molecules. The charges on the acceptor ρ and on the donor $-\rho$ characterize the crystal state. For $\rho<0.5$ the crystal is said to be neutral-like, otherwise it is ionlike. The transition from one region to the other due to the change of temperature or pressure is called the NIT. (b) The IHM has also been used in the context of ferroelectrics and superconductivity in the transition-metal oxides.[2] It has been argued[2] that the influence of the underlying lattice on the electronic system could be large in the critical region, leading to a nonlinear electronic polarizability.

The phase diagram of Eq. (1) was discussed previously by several authors. Oritz *et al.* found a single phase transition in a mean-field study using a one-dimensional density of states.[3] The transition takes place between paramagnetic and antiferromagnetic states. The point where it takes place has a special role with respect to the electrical conductivity. Whereas the system is a semimetal at this point, at other points of the phase diagram it is an insulator. The possibility of a semimetallic transition point involving antiferromagnetism has also been discussed in a local density approximation study.[4]

Gidopoulos *et al.* performed a mean-field decoupling for two-dimensional bipartite square and honeycomb lattices.[5] They found two special values of U for a given energy alternation E_0. The first denotes the phase transition where magnetic order sets in, at the second special value of the one-site repulsion U, the charge gap for one spin species would presumably close. In what follows, we will show that there are actually two phase transitions in the mean-field decoupling scheme. Furthermore, it will be shown that the solution in which the gap for one spin species vanishes is thermodynamically unstable, the charge-gap consequently does not close at any point in the phase diagram.

II. ORDER PARAMETERS

Application of the mean-field decoupling

$$n_{i\uparrow}n_{i\downarrow}\rightarrow\sum_{\sigma}\langle n_{i,-\sigma}\rangle n_{i,\sigma}-\langle n_{i,\uparrow}\rangle\langle n_{i,\downarrow}\rangle \tag{2}$$

leaves us with the system of equations

$$\Delta_{\sigma}=-\int_0^{\infty}d\epsilon D(\epsilon)\frac{E_0+U\Delta-\sigma}{\sqrt{\epsilon^2+(E_0+U\Delta_{-\sigma})^2}} \tag{3}$$

for the two order parameters Δ_{σ} defined through the respective spin-densities $n_{A/B\sigma}=1/2\mp\Delta_{\sigma}$ on A and B sites. $D(\epsilon)$ is a free-particle density of states (DOS). In what follows, one-dimensional DOSs will be used, but qualitatively the same results have been obtained for flat and semicircular DOSs. Quasiparticle states are accommodated in four bands with a dispersion

$$\lambda_{\alpha\sigma}(\epsilon)=\frac{U}{2}+\alpha\sqrt{\epsilon^2+(E_0+U\Delta_{\sigma})^2},\quad \alpha=\pm 1. \tag{4}$$

In the ground-state the $\alpha=-1$ bands are filled. The thermodynamic stability of a possible self-consistent solution of Eq. (3) is determined, at $T=0$, by the total energy

$$\frac{E}{N}=\sum_{\alpha,\sigma}\int_0^{\infty}d\epsilon D(\epsilon)\lambda_{\alpha\sigma}(\epsilon)\Theta[\epsilon_F-\lambda_{\alpha\sigma}(\epsilon)] -(U/4+U\Delta_{\uparrow}\Delta_{\downarrow}.) \tag{5}$$

The above equations are valid for the half-filled system. Use of the particle-hole symmetry

$$c_{j\sigma}|\mathrm{FB}\rangle=(-1)^{|j+1|}d^{\dagger}_{j+1,-\sigma}|0\rangle_h \tag{6}$$

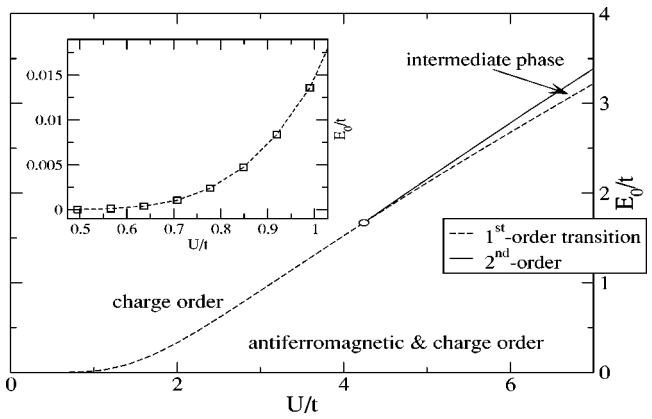

FIG. 1. Phase diagram for the one-dimensional DOS. For $U<U_c$ the intermediate phase (I) is thermodynamically not stable and the transition from the antiferromagnetic (AF+CO) to paramagnetic phase (CO) is of the first-order. The $U>U_c$ region has a stable I phase. The transition between the two magnetic phases (AF+CO and I) is of the first order; the I phase goes into the CO phase through the second order phase transition. The inset shows asymptotic behavior of the phase border for small U.

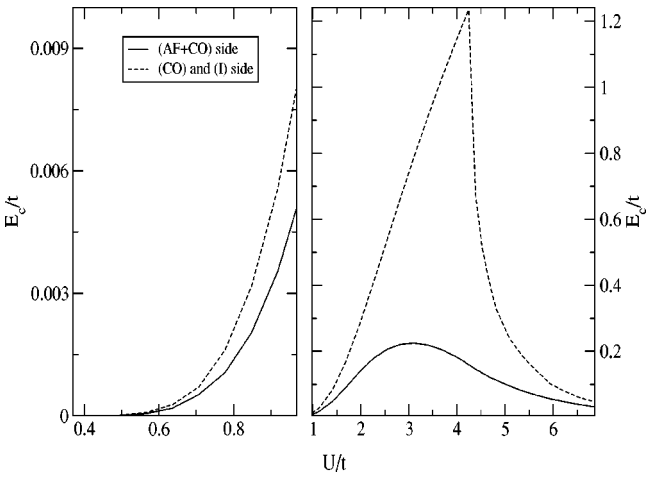

FIG. 3. Charge gap as a function of U on the first order transition point (AF+CO)→(I) for $U>U_c$ and (AF+CO)→(CO) for $U<U_c$. In the left plot we zoom in on the curves showing the behavior of the gaps in the region of the parameter space where the AF+CO phase shrinks rapidly.

where $|\mathrm{FB}\rangle$ denotes a full band and $|0\rangle_h$ a hole vacuum,[6] shows that $\epsilon_F=U/2$. Together with the dispersion of the bands, this implies that the number of each spin species is the same.

III. PHASE DIAGRAM

The phase diagram of the IHM is shown in Fig. 1. Regarding the U axis, it has two separate regions. For $U<U_c \approx 4.25t$ one finds two phases: the charge-ordered (CO) phase and a mixture of the charge ordered and the antiferromagnetic phase (AF+CO). In the $U>U_c$ region there are three phases. Beside the CO and the AF+CO phases, we find another phase which we will call the intermediate I phase. The I phase has the same order parameters as the AF+CO phase.

The phases shown in Fig. 1 can be observed clearly in the curves for the staggered magnetization $m_{st}=|\Delta_\downarrow-\Delta_\uparrow|$, shown in Fig. 2 as a function of E_0 and various values of U. We notice a jump in the curves for all values of U, indicative

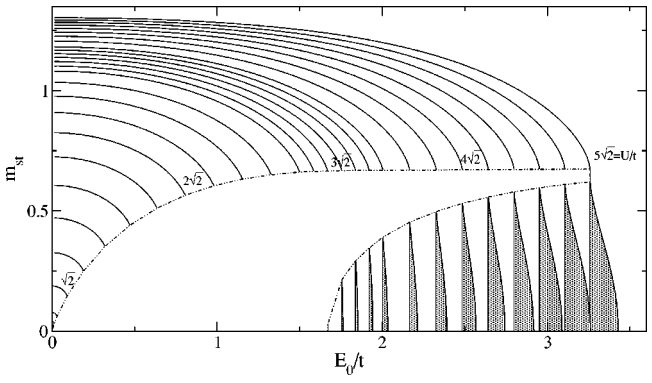

FIG. 2. Staggered magnetization curves for different U's. The blank, inclosed region contains jumps of the m_{st}. Shaded regions are placed under the magnetization curves of the I phase.

of a first order phase transition. The jumps define a region of m_{st} for which the system is unstable, illustrated by the light shaded area in Fig. 2. When $U>U_c$ there is no direct transition from the low-E_0 (AF+CO) phase to the high-E_0 (CO) phase which is characterized by $m_{st}=0$. The AF+CO phase now shares a border with the I phase. The jump in the staggered magnetization vanishes asymptotically as U becomes large. The transition from I to CO is, on the other hand, of the second order. From the magnetization curves it is also transparent that the width of I rises as one increases U (illustrated by the dark-shaded areas in Fig. 2).

The first-order nature of the transition between the AF+CO phase realized for low values of E_0 and the CO and I phases, respectively, shows up in a jump of the charge gap, as shown in Fig. 3. The discontinuity in the charge gap is manifested by two different curves of the gap as a function of U for the two sides of the transition, respectively.

A difference between I and AF+CO phases appears in the behavior of the charge gap as a function of E_0; see Fig. 4. The transition point between the AF+CO and I phases is characterized by a minimum in the charge gap; see Fig. 2. Even though the gap is close to zero, it remains finite. In the AF+CO phase [Fig. 4(a)], the charge gap, as a function of E_0, decreases while it increases in the I phase [Fig. 4(b)]. As expected, this increase proceeds in the CO phase [Fig. 4(c)].

IV. THERMODYNAMIC STABILITY

A self-consistent solution of Eq. (3) with finite values for the order parameters Δ_σ is not a guarantee that the corresponding phase is indeed realized in the system. The condition for the stability of a phase on $T=0$ is that it has a minimal energy with respect to the energies of the other phases. This fact is important in the case of the (AF+CO)-(I) transition. There, the AF+CO and I solutions show a hysteresis effect, and the ground state is determined on the basis of the minimum energy principle.

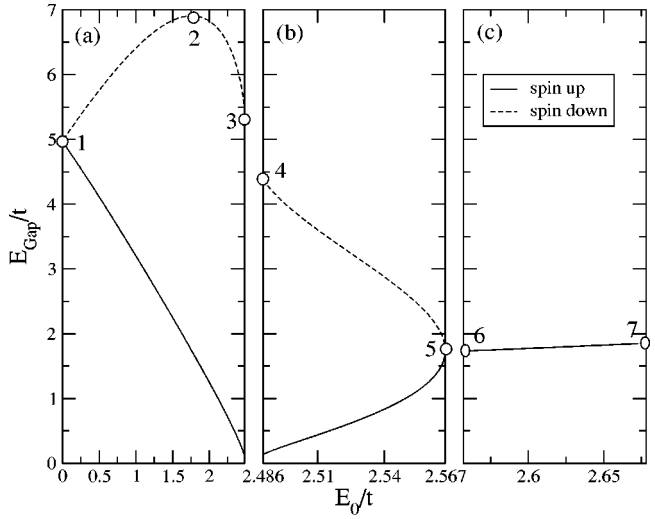

FIG. 4. Evolution of the gaps for each spin direction as a function of E_0, for fixed $U=4\sqrt{2}t$. The smaller gap is equivalent to the charge gap. (a) AF+CO phase; the charge gap decreases. (b) I state; the charge gap increases. (c) CO phase; the gap for both spin directions is the same.

The examination of the energy space for the case $U<U_c$ is shown on Fig. 5(a). On this figure one sees the energy [Eq. (5)] for the four different solutions which solve the self-consistency equation (3) for the order parameters Δ_σ. They are the three solutions (AF+CO,line), (CO, large filled circles) and intermediate phase (I, small filled circles) which we have already discussed, together with the fourth solution, which is always unstable (empty squares). The energy of the I phase is larger than the one of the AF+CO phase in the whole interval of its existence. The I phase is thus unstable. Crossing of the energy curves of AF+CO and CO phases discloses an underlying first order phase transition. The lower inset shows the energies of all phases in the whole E_0 interval.

For $U=3.2\sqrt{2}\ t>U_c$ the results are given in Fig. 5(b). Part of the I phase is now stable.

Stable solutions have been obtained by iterating Eq. (3) directly, and the unstable solutions by fixing one Δ_σ and allowing E_0 to change. The fixed order parameter Δ_σ has been chosen such that it is in the range which is not covered by the stable solutions. We have also tried to use a fixed U, but the self-consistency map, for the parameters we examined, did not turn out to be attractive and thus useful. Limiting cases: (1) $E_0=0$ and (2) $U=0$ assure us that in these limits we found all solutions. Thus, possible solutions with weakly attractive self-consistency map are a possibility in the intermediate range of parameters. We cannot exclude the possibility of their existence, but due to a few self-consistency arrangements we find them improbable.

The charge gap vanishes when $\Delta_\sigma=-E_0/U$ for one spin species and $\Delta_{-\sigma}=0$ for the other species. The energy of this solution is given in Figs. 5(a) and 5(b), and is denoted by an empty triangle. It turned out to be unstable in the calculations done. Furthermore, from the performed calculations (see Fig. 5) we see that the vanishing-gap solution always has AF+CO and CO companions with a smaller energy. This leads us to extend the conclusions obtained from our results to the whole parameter region, including an interval $U/t<0.5$ which we have not investigated numerically. Thus, the charge gap closes only in the point $E_0=U=0$.

Finally, we would like to mention that the three stable phases CO, I, and CO+AF are characterized by different distributions of the charge densities $n_{A/B\sigma}=1/2\mp\Delta_\sigma$ on A and B sites. We find $\Delta_\uparrow=\Delta_\downarrow$ for the CO phase, $\Delta_\uparrow\neq\Delta_\downarrow$ and $\Delta_\uparrow\Delta_\downarrow>0$ for the I phase, and $\Delta_\uparrow\Delta_\downarrow<0$ for the AF+CO phase.

V. ALTERNATING U IONIC HUBBARD MODEL (AIHM)

A natural generalization of the ionic Hubbard model is the model where the on-site Coulomb interaction on the atoms A

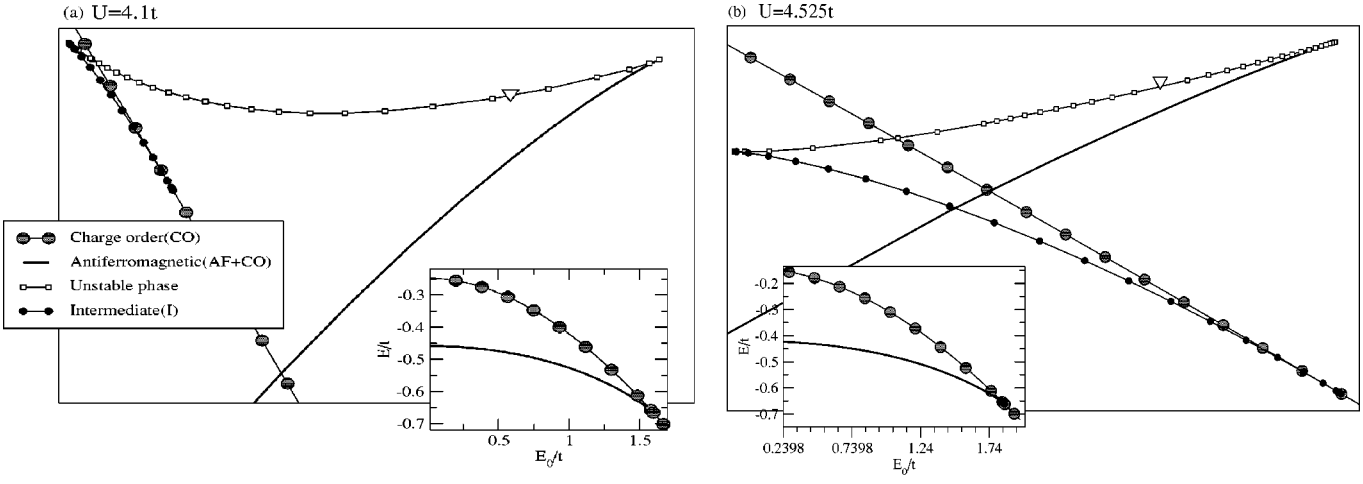

FIG. 5. (a) Energy of the various states as a function of E_0. $U=2.9\sqrt{2}t<U_c$ is chosen such that the I phase is unstable. The main panel is a blowup of the energies shown in the inset, transformed by the subtraction of a suitably chosen straight line so that the particular transitions can be more easily visualized. The large empty triangle denotes the position of the vanishing charge gap in the thermodynamically unstable solution. (b) $U=3.2\sqrt{2}t>U_c$, so that part of the I phase is stable.

and B is not the same. The Hamiltonian of the new system may be written as

$$H_{AIHM}=H_{IHM}+\sum_i dU(-1)^{|i|}n_{i\uparrow}n_{i\downarrow}. \tag{7}$$

For simplicity, here we consider the extreme case where the Coulomb interaction disappears on site A. This implies $dU=-U$ and a value of $2U$ for the Coulomb repulsion on site B. This model is than equivalent to the Cu-O lattice model[3] with correlated B sites (copper, lower on-site energy) and uncorrelated A sites (oxygen, higher on-site energy).

Let us write $E_0=U/2+e_0$ and $\mu=U/2+\mu'$, where μ is the chemical potential for the half-filled system. The transformations

$$E_0=U/2+e_0\rightarrow E_0'=U/2-e_0$$

and

$$\mu=U/2+\mu'\rightarrow\mu=U/2-\mu'$$

leave us with an equivalent Hamiltonian. This can be shown by performing a canonical particle-hole transformation $c_{j,\sigma}\rightarrow(-1)^{|j|}d^{\dagger}_{j,-\sigma}$. It yields

$$\begin{aligned}H=&\sum_{\langle i,j\rangle,\sigma} td^{\dagger}_{j,\sigma}d_{i,\sigma}+\sum_i U[1-(-1)^{|i|}]n^h_{i\uparrow}n^h_{i\downarrow}\\&+\sum_{i,\sigma}(-1)^{|i|}\left(\frac{U}{2}+e_0\right)n^h_{i,\sigma}\\&-\sum_{i,\sigma}(-1)^{|i|}\left(\frac{U}{2}+\mu'\right)n^h_{i,\sigma}+2N\mu'.\end{aligned} \tag{8}$$

The difference with respect to the original Hamiltonian (7) lies in the constant term $2N\mu'$. This, together with the fact that the order parameter operators preserve the same form in the hole picture, implies that the phase diagram of Eq. (7) is symmetric with respect to the line $E_0=U/2$ in the parameter E_0 and for $dU=-U$.

The self-consistency equation, derived under the assumption that the ferromagnetic order parameter vanishes, is given by

$$\Delta_\sigma=-\int_0^\infty d\epsilon D(\epsilon)\frac{B_\sigma}{\sqrt{\epsilon^2+B_\sigma^2}}, \tag{9}$$

where $B_\sigma=E_0+U\Delta_{-\sigma}+dU/2$.

The energy spectrum has a form $\lambda_{\pm,\sigma}(\epsilon)=A_\sigma\pm\sqrt{\epsilon^2+B_\sigma^2}$, where $A_\sigma=U/2+dU\Delta_{-\sigma}$.

In Fig. 6 we present the phase diagram of the AIHM. It contains the same phases as the IHM phase diagram. The dash-dotted line in Fig. 6 indicates the symmetry axis. On it the system is antiferromagnetic with a vanishing charge-order parameter (AF phase). In the region around the symmetry line the system is in the AF+CO phase which, for $U<U_c$, makes a transition into the pure charge-ordered state. For $U>U_c$ the transition takes place into the I phase and than into the CO phase.

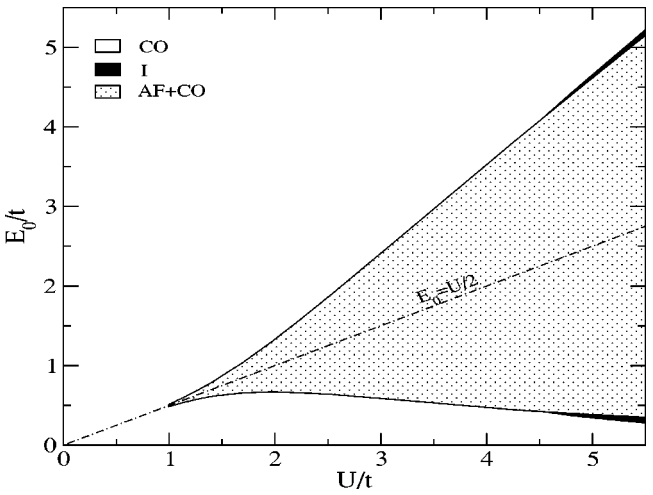

FIG. 6. Phase diagram of the half-filled AIHM with the one-dimensional, density of states. It contains three phases. The charge ordered (CO) phase is given by a white area. The dotted area represents a mixture of the antiferromagnetic and the charge ordered phase (AF+CO), and the black region covers a parameter range where the intermediate (I) phase appears. The symmetry of the phase diagram is denoted by the dash-dotted line.

Let us define a singlet gap as the minimal energy needed for a transfer of the electron in an empty state without a spin-flip and a triplet gap as the minimal energy of the transition where the spin is flipped and the total S_z changes. In the mean-field formulation these gaps are given by $\Delta_s=2|B_\sigma|$ and $\Delta_t=|A_\uparrow+|B_\uparrow|+|B_\uparrow|-A_\downarrow|$.

A distinct property of the AIHM is the closing of the triplet gap in the AF+CO phase. This is illustrated in Fig. 7. The IHM case with a uniform U is shown in Fig. 7(a). In Fig. 7(c) we see that the triplet gap vanishes for $U_A=0$ and $U_B=2U$. A necessary (but not sufficient) condition for the vanishing of the triplet gap can be derived from Eq. (9) and

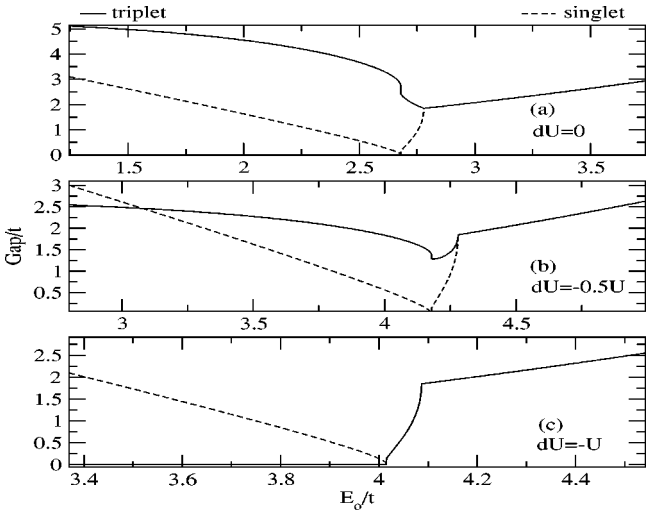

FIG. 7. Singlet (dashed curve) and triplet (full curve) gaps as a function of the on-site chemical potential amplitude E_0 for $U=6t$. (a) U is the same for both atom species. (b) $U_A<U_B$. (c) U on site A vanishes.

expressed in the form $\Delta_\uparrow\Delta_\downarrow<0$. This is the case in the CO+AF phase. $\Delta_\uparrow\Delta_\downarrow>0$, and the triplet gap is nonvanishing, as can be seen in Fig. 7. The exception to the condition $\Delta_\uparrow\Delta_\downarrow<0$ for the disappearance of the triplet gap is a solution $\Delta_\uparrow=\Delta_\downarrow=0$, which exists for $E_0=\frac{U}{2}$.

VI. DISCUSSION

Previous mean-field studies of the ionic Hubbard model found a vanishing charge gap at the transition point between antiferromagnetic and paramagnetic states,[3,5] in contrast to our result for a minimal charge gap. The presented data were obtained for a one-dimensional one-electron density of states. For comparison we have also carried out a calculation for the flat and semicircular densities of states. The results changed only quantitatively; all major features discussed previously remain valid.

It is interesting to compare with the one-dimensional ionic Hubbard model, which was studied by Resta and Sorella[7] using the boundary-condition-integration technique,[8] by Brune *et al.* using the density matrix renormalization group (DMRG),[9] and by Wilkins and Martin using the quantum Monte Carlo (QMC).[10] Fehske *et al.* considered the dynamical IHM coupled to phonons.[11]

Fabrizio *et al.*, in a bosonization study,[12] proposed the existence of a dimerized intermediate phase in the one-dimensional ionic Hubbard model. DMRG and QMC results indicate[9,10] that this bond-ordered (dimerized) insulating phase extends to arbitrarily large values of *U*, due to the instability of the one-dimensional Mott-Hubbard insulator towards dimerization. DMRG studies of the one-dimensional model,[9,13] found indications of a ''strange'' metallic point with a finite charge gap at the transition from the band insulator to the correlated insulating state. We may speculate that our mean-field result of two distinct phase transitions reflects the occurence of magnetic long-range order possible in dimensions larger than one. We note, in this context, that the intermediate phase (I) evidenced in Figs. 1 and 6 does not show a spontaneous dimerization.

VII. CONCLUDING REMARKS

The mean-field decoupling scheme is an approximation of a full evaluation of the Hamiltonian. Its validity is restricted to the small U limit and a large dimension where it is qualitatively correct.[14] We have found, however, that the stability analysis for the various solutions possible for the ionic Hubbard model is highly nontrivial. Here we have presented two results: (i) a nonvanishing charge gap for all parameters, and (ii) the existence of two distinct phase transitions for larger values of *U*.

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