

Charge ordering in the one-dimensional extended Hubbard model: Implication to the TMTTF family of organic conductors

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We study the charge ordering (CO) in the one-dimensional (1D) extended Hubbard model at quarter filling where the nearest-neighbor Coulomb repulsion and dimerization in the hopping parameters are included. Using the cluster mean-field approximation to take into account the effect of quantum fluctuations, we determine the CO phase boundary of the model in the parameter space at $T=0$ K. We thus find that the dimerization suppresses the stability of the CO phase strongly, and in consequence, the realistic parameter values for quasi-1D organic materials such as $(\text{TMTTF})_2\text{PF}_6$ are outside the region of CO. We suggest that the long-range Coulomb interaction between the chains should persist to stabilize the CO phase.

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I. INTRODUCTION

The charge-ordering (CO) phase transition has recently attracted much attention in physics of strongly correlated electron systems such as transition-metal oxides and organic charge-transfer salts. A possible mechanism of CO is the localization of electrons on a lattice due to long-range Coulomb repulsions, which is a lattice version of the Wigner crystallization. The spin degrees of freedom of the system of CO are yet active and can undergo an additional phase transition by lowering temperature, to result in a variety of magnetic ground states such as spin-Peierls (SP), spin-density wave (SDW), and antiferromagnetic (AF) states. One of the simplest models that allow for such CO is the one-dimensional (1D) Hubbard model with onsite (U) and nearest-neighbor (V) Coulomb repulsions, where the charge-density wave (CDW) with twofold periodicity, i.e., $4k_F$ -CDW with k_F being the Fermi momentum, is realized when the band filling is either $3/4$ or $1/4$ (quarter filling).

Bechgaard salts $(\text{TMTSF})_2X$ and their sulfur analogs $(\text{TMTTF})_2X$, where X is PF_6 , Br , ClO_4 , etc., offer a series of materials suitable for studying quasi-1D correlated electron systems at quarter filling.¹ It is known that the lattice dimerization of the systems causes an alternation of hopping integrals and makes the system a Mott insulator. The metal-insulator transition of the series is then controlled by the interchain hopping parameter t_\perp , i.e., by the dimensional crossover from 1D to 2D.²⁻⁴

Recently, clear evidence of the CO phase transition in $(\text{TMTTF})_2\text{PF}_6$ has been given by the measurements of dielectric response⁵ and NMR spectroscopy.⁶ This material has the smallest interchain coupling t_\perp in the series and is in the 1D confinement regime.^{1,2} The transition temperature of CO is reported to be $T_{\text{CO}} \approx 100$ K, which is very high for small energy scales of organic systems. An interesting research area for studying CO has thus been established.⁶

A number of theoretical studies have so far been made on the 1D extended Hubbard model at quarter filling,⁷⁻¹⁶ which provide useful information to consider the physics of CO. While some of them have not included the effect of lattice

dimerization,⁷⁻¹² recent mean-field calculations¹³⁻¹⁶ have taken into account the effect and explained how the $2k_F$ or $4k_F$ CDW coexists with $2k_F$ SDW in the ground state of the systems. We note, however, that the mean-field analyses usually overestimate the stability of the ordered phase. Coupling to the lattice degrees of freedom has also been argued to play an essential role.¹⁷

Motivated by such development in the field, we study in this paper the CO of the 1D extended Hubbard model with the dimerization of hopping parameters, and consider its implication to the observed CO in the TMTTF family of organic conductors. We use a method of calculating the long-range order in strongly correlated electron models, i.e., an extension of the so-called cluster mean-field approach¹⁸ to correlated fermion systems. Thus the amplitude of CO, rather than its correlation functions or exponents, can be calculated directly as in the standard mean-field theory. Moreover, critical interaction strength of the quantum phase transition can be evaluated with improved accuracy since the effect of quantum fluctuations is automatically taken into account. The CO phase boundary and its dimerization dependence of the model is thus determined in the parameter space (U, V) at $T=0$ K.

We will thereby show that the critical interaction strength V_c is much larger than the value obtained in the mean-field approximation, as expected, and also that the dimerization in the hopping integrals suppresses the stability of the CO phase strongly. Then, it follows that the present model does not have the CO ground state if we assume realistic values of the electronic parameters for quasi-1D organic materials $(\text{TMTTF})_2\text{PF}_6$ and $(\text{TMTSF})_2\text{ClO}_4$. This result suggests that the present framework of the model under the influence of weak three dimensionality (3D) is not sufficient for describing the CO observed in $(\text{TMTTF})_2\text{PF}_6$. Inclusion of any additional degrees of freedom, in particular the 3D long-range Coulomb interaction between the chains, may be essential for stabilizing the CO phase.

II. MODEL AND METHOD

The extended Hubbard model is defined by the Hamiltonian

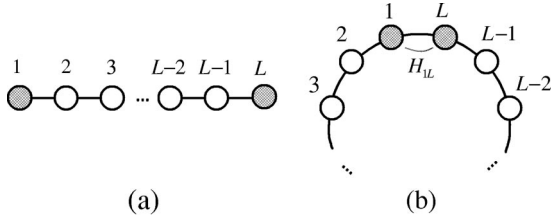


FIG. 1. Schematic representations of (a) the Hubbard chain and (b) the chain with the mean-field bond.

$$\begin{aligned}
 H = & -t_1 \sum_{i=1}^{L/2} \sum_{\sigma} (c_{2i-1,\sigma}^{\dagger} c_{2i,\sigma} + \text{H.c.}) \\
 & -t_2 \sum_{i=1}^{L/2-1} \sum_{\sigma} (c_{2i,\sigma}^{\dagger} c_{2i+1,\sigma} + \text{H.c.}) \\
 & + U \sum_{i=1}^L n_{i,\uparrow} n_{i,\downarrow} + V \sum_{i=1}^{L-1} n_i n_{i+1}
 \end{aligned} \quad (1)$$

on the 1D lattice of size L (even), where $c_{i,\sigma}^{\dagger}$ ($c_{i,\sigma}$) is the electron creation (annihilation) operator at site i and spin σ ($=\uparrow, \downarrow$), and $n_i = n_{i,\uparrow} + n_{i,\downarrow}$ is the number operator. We introduce a dimerization in the hopping parameters, $t_1 \geq t_2$. U and V are the onsite and nearest-neighbor Coulomb repulsions, respectively. We restrict ourselves to the case of quarter filling.

Our cluster mean-field method is the following: We first introduce an exactly solved finite-size system (or a cluster, see Fig. 1) and then assume the presence of the mean-field acting on the edges of the system. The value of the mean field is then determined self-consistently so as to minimize the total energy of the system. In the present case, we prepare an L -site chain treated exactly by a numerical method and assume that the mean field is applied on the edge sites 1 and L of the chain. We then replace the mean field by the “mean-field bond” connecting between the sites 1 and L ; i.e., we assume

$$n_1 n_L \approx n_1 \langle n_L \rangle + \langle n_1 \rangle n_L - \langle n_1 \rangle \langle n_L \rangle \quad (2)$$

for the bond, where $\langle n_1 \rangle$ and $\langle n_N \rangle$ are the mean fields at sites $i=1$ and L . The Hamiltonian of the bond

$$\begin{aligned}
 H_{1L} = & -t_2 \sum_{\sigma} (c_{1,\sigma}^{\dagger} c_{L,\sigma} + \text{H.c.}) + V(n_1 \langle n_L \rangle \\
 & + \langle n_1 \rangle n_L - \langle n_1 \rangle \langle n_L \rangle),
 \end{aligned} \quad (3)$$

is then added to the Hamiltonian of the cluster Eq. (1). The total Hamiltonian is diagonalized numerically by the Lanczos technique on small clusters, and the mean fields are evaluated as the expectation values of n_1 and n_L for the ground state. The iterations are made to achieve self-consistency in the values of the mean fields $\langle n_1 \rangle$ and $\langle n_L \rangle$. Converged solutions are obtained after 30–70 iterations depending on various conditions including the initial values of $\langle n_1 \rangle$ and $\langle n_L \rangle$. We need to try a number of the initial values in order to confirm that the iteration converges to the unique lowest-energy solution. In some cases, we find two (or pos-

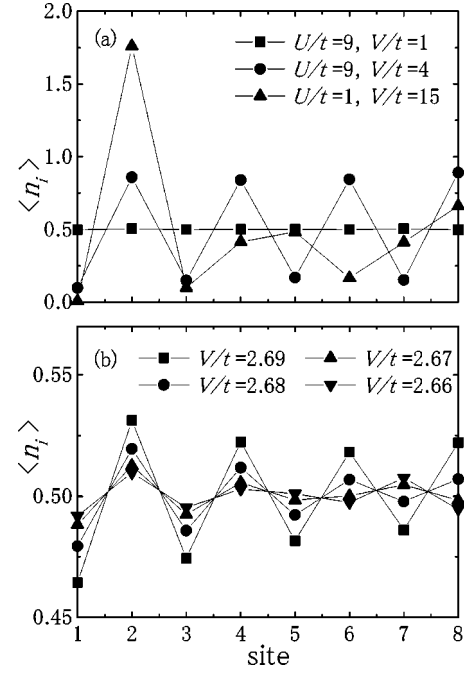


FIG. 2. Converged charge-density distributions for the models without dimerization ($t_1 = t_2 = t$). The cluster of length $L=8$ is used. In (a), three typical solutions are shown: type I (squares), type II (circles), and type III (triangles), which are discussed in the main text. In (b), oscillations of the charge density near the critical point at $U/t=9$ are shown.

sibly more) different solutions, of which we choose the lowest-energy one; we should note that the level crossing in the lowest-energy states sometimes occurs in small-size systems [which is apparent, e.g., in Fig. 3(a) given below].

In Fig. 2(a), we show the converged charge distributions for three typical cases: type I is for the paramagnetic metallic state where a uniform charge distribution is seen, type II is for the CO state where the oscillation of twofold periodicity is clearly seen, and type III is for the parameter region corresponding to phase separation.^{9,11} In Fig. 2(b), we show how the CO oscillation ceases near the critical point with decreasing V ; we find that the $4k_F$ oscillation becomes ill defined between the interaction strength $V/t=2.67$ and 2.68 , at which we decide the critical interaction strength V_c is located. These are the cases without dimerization but the situation is similar even when the dimerization is introduced. We should note that, in some cases, a $2k_F$ oscillation (corresponding to the effect of Friedel impurity scattering) is superimposed on the $4k_F$ CO oscillation, which is, however, rather small except in the region of phase separation.

III. RESULTS AND DISCUSSION

The obtained CO phase boundary of the model is shown in Fig. 3. In case where there is no dimerization ($t_1 = t_2 = t$), we can compare our results with those of the previous studies,^{7,9} where the charge gap and Luttinger-liquid parameter K_ρ were evaluated in small-size systems and the metal-

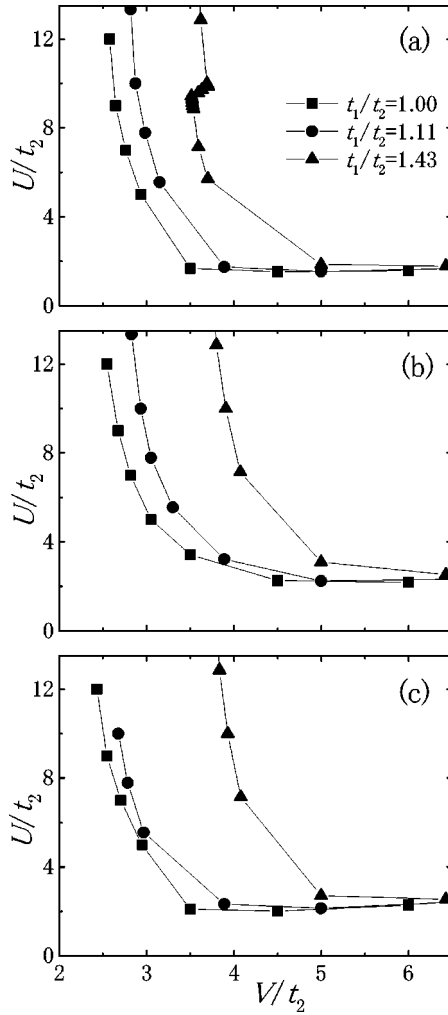


FIG. 3. Dimerization t_1/t_2 dependence of the CO phase boundary. Results are shown for $t_1/t_2=1$ (squares), $t_1/t_2=1.11$ (circles), and $t_1/t_2=1.43$ (triangles). Clusters of the size (a) $L=8$, (b) $L=12$, and (c) $L=16$ are used. The upper-right side of the boundary is the CO phase, and the lower-left side of the boundary is either paramagnetic metallic phase ($t_1=t_2$) or Mott insulating phase ($t_1 > t_2$).

insulator phase boundary (which coincides with the CO phase boundary when $t_1=t_2$) was determined. We find that our results are in good agreement with the previous results. Exact solutions are available for two limiting cases:⁷ $V_c/t = 2$ at $U \rightarrow \infty$ and $U_c/t = 4$ at $V \rightarrow \infty$, which are also consistent with our results. We note that a rather inhomogeneous charge distribution is obtained in the parameter region $V \gg U$ as seen in Fig. 2(a); in this region, the model is reported to have exotic phases where the superconducting pairing fluctuations are dominant or the phase separation occurs.^{9,11}

The cluster-size L dependence of the critical interaction strength V_c for $t_1=t_2$ is shown in Fig. 4. An oscillatory behavior corresponding to the so-called shell effect for periodic boundary condition is found between $L=8m$ (open shell) and $L=8m-4$ (closed shell) where $m=1, 2, \dots$. We find that the values of V_c thus calculated for $L=8, 12$, and 16 appear to be extrapolated well to the value at $1/L \rightarrow 0$ which is estimated from the density-matrix renormalization-

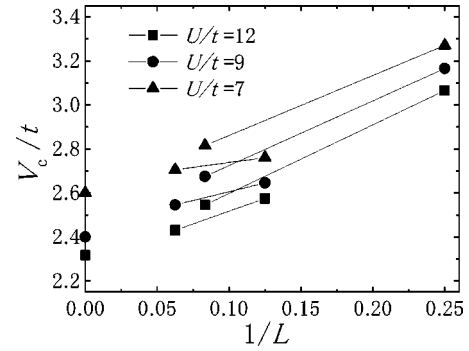


FIG. 4. Cluster-size L dependence of the critical interaction strength V_c . Results are shown at $U/t=7, 9$, and 12 for the model without dimerization ($t_1=t_2=t$). The values of V_c at $1/L \rightarrow 0$ determined from the calculation of the charge gap by the density-matrix renormalization-group method are also shown for comparison.

group (DMRG) calculation of the charge gap Δ_c : The results of Δ_c at $1/L \rightarrow 0$ for several values of V are fitted to the exponential dependence¹⁹ $\Delta_c/t = \alpha \exp[-\beta t/(V-V_c)]$ (obtained from weak-coupling theory near the critical point), from which we determine the value of V_c (in the accuracy of $\pm 0.05t$). The details of our DMRG calculation is given in Ref. 20 We expect from these results that the value of V_c at $t_1 > t_2$ also should not have too strong size dependence when $1/L \rightarrow 0$.

In case where the dimerization is present ($t_1 > t_2$), we first note that the charge gap opens²⁰ except for the noninteracting case ($U=0$); an infinitesimal U value is enough to make the Umklapp process relevant in the renormalization, leading to the opening of the charge gap. When U and V becomes large, we find that the quantum phase transition from this Mott insulating state to a CO state occurs. We can detect this transition by observing the appearance of oscillations in the calculated charge distribution. Note that the mean-field bond is assumed to have the hopping parameter t_2 which is smaller than t_1 , i.e., the bond is chosen so as to connect two “dimers” (where the dimer is a pair of sites with the larger hopping parameter). This is because, in the strong dimerization limit, only a single electron is present in a dimer, and thus V should not work in a dimer.

In Fig. 3, we find that the CO phase boundary exhibits remarkably strong dimerization dependence; i.e., the dimerization suppresses the stability of the CO phase. General features are the following: (i) with increasing dimerization, the boundary in the large U region shifts to the left, i.e., V_c/t_2 becomes large, and (ii) the boundary in the large V region shows a small upward shift with increasing dimerization. These features can be understood as follows: We first note that, in the limit of strong dimerization $t_1 \gg t_2$, the critical V value is determined as $V_c = 4t_1$ when $U \rightarrow \infty$. This is because in this limit the charge (which is either on the left or on the right site of a dimer) may be expressed as the pseudospin and the system becomes equivalent to the 1D quantum Ising model,²² the critical point of which is determined by the competition between the quantum fluctuation t_1 of an electron in a dimer and the interaction V between the two dimers

leading to CO. We therefore have $V_c/(4t_2)=t_1/t_2 \rightarrow \infty$ when $t_1/t_2 \rightarrow \infty$, which explains the behavior (i). When $V \rightarrow \infty$ and U is finite, we find from an estimation of kinetic energy of the lowest-energy charge excitation that the critical U value is given as $U_c=2(t_1+t_2)$, irrespective of the strength of dimerization. Thus we have $U_c/t_2=2(t_1/t_2+1)$, which gives a contribution to the behavior (ii). A clear upward shift of the phase boundary is, however, not seen in Fig. 3, which is partly because sufficiently large values of V and t_1/t_2 are not used and partly because the finite-size effect becomes apparent here.

Besides the limiting cases discussed above, we can compare our results with the results of the mean-field calculation.¹³ Our results shown in Fig. 3 are for two dimerization strengths, $t_2/t_1=0.9$ and 0.7 , which correspond to the realistic values for $(\text{TMTSF})_2\text{ClO}_4$ and $(\text{TMTTF})_2\text{PF}_6$, respectively. We then point out that the critical interaction strength obtained here is much larger than that of the mean-field calculation: e.g., we obtain $V_c/t_2 \approx 3$ at $U/t_2=5$ and $t_2/t_1=0.9$, while the mean-field calculation¹³ gives $V_c/t_2 \approx 0.65$. This is also the case without dimerization ($t_1=t_2=t$): e.g., we obtain $V_c/t=2.9$ at $U/t=5$, while the mean-field calculation¹³ gives $V_c/t=0.4$. These discrepancies stem from the strong quantum fluctuations of the present model.

Finally, let us consider experimental implication of our results. A recent careful estimation²⁰ of the values of the parameter V for real materials has given $V=0.21$ eV (or $V/t_2=0.8$) for $(\text{TMTSF})_2\text{ClO}_4$ and $V=0.18$ eV (or $V/t_2=2.0$) for $(\text{TMTTF})_2\text{PF}_6$. Also the values $U/t_2=5.6$ for $(\text{TMTSF})_2\text{ClO}_4$ and $U/t_2=10$ for $(\text{TMTTF})_2\text{PF}_6$ have been reported.^{20,21} These values of the parameters in the (U, V) plane (see Fig. 3) are thus located in the Mott-insulating uniform phase, far apart from the CO phase boundary. We therefore conclude that the strength of the nearest-neighbor Coulomb repulsion for these two materials is too small for the corresponding 1D extended Hubbard model with dimerization to be in the region of CO. Since there is no CO at $T=0$ K, it seems quite unlikely that the present model at $T>0$ can have the CO even on the implicit assumption of the

presence of weak 3D coupling. Then, to explain the CO observed in $(\text{TMTTF})_2\text{PF}_6$, it seems necessary to take into account any additional degrees of freedom in our 1D model; a comparatively large value of T_{CO} may suggest that there exists a rather strong interchain coupling via the long-range Coulomb interaction, which works to stabilize the CO phase. We may say that, while the electron conduction of $(\text{TMTTF})_2\text{PF}_6$ at $T>T_{\text{CO}}$ is of the 1D nature,^{1,2} the observed CO is due to the presence of the 2D–3D Coulombic coupling between the chains. Coupling to the anionic potential may also play an important role in the stabilization of CO as has recently been suggested in Ref. 23. Whether these effects may be renormalized into the parameter values of our 1D model is a highly nontrivial problem; the issue is thus left for future work.

IV. CONCLUSION

We have studied the CO in the 1D extended Hubbard model at quarter filling by introducing the dimerization in the hopping parameters as well as the nearest-neighbor Coulomb repulsion. We have used the cluster mean-field approximation to take into account the effect of quantum fluctuations, and have determined the CO phase boundary and its dimerization dependence of the model in the (U, V) plane at $T=0$ K. We have thus found that the realistic parameter values for $(\text{TMTTF})_2\text{PF}_6$ and $(\text{TMTSF})_2\text{ClO}_4$ are well outside the region of CO. We have argued that the present 1D model does not provide a sufficient framework for describing the CO observed in $(\text{TMTTF})_2\text{PF}_6$.

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