Novel Charge Order and Superconductivity in Two-Dimensional Frustrated Lattice at Quarter Filling

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Motivated by the various physical properties observed in $\theta$-(BEDT-TTF)$_2$X, we study the ground state of extended Hubbard model on two-dimensional anisotropic triangular lattice at 1/4-filling with variational Monte Carlo method. It is shown that the nearest-neighbor Coulomb interaction enhances the charge fluctuation and it induces the anomalous state such as charge-ordered metallic state and the triplet next-nearest-neighbor $f$-wave superconductivity. We discuss the relation to the real materials and propose the unified view of the family of $\theta$-(BEDT-TTF)$_2$X.

KEYWORDS: charge order, charge fluctuation, superconductivity, organic conductor, $\theta$-(BEDT-TTF)$_2$X, variational Monte Carlo method

Charge order (CO) is one of the important phenomena in strongly correlated electron systems as well as superconductivity and magnetism. In a charge-ordered system, the cooperation or competition between charge and spin degrees of freedom cause the various interesting properties as seen in manganese oxides,\textsuperscript{1,2} vanadium oxides,\textsuperscript{3} high-$T_c$ cuprates\textsuperscript{4} and organic conductors.\textsuperscript{5,6} Above all, the family of organic conductors $\theta$-(BEDT-TTF)$_2$X (we denote $\theta$-(ET)$_2$X in the following) is known to exhibit some anomalous COs\textsuperscript{7,8} and it is suggested that the superconductivity is induced by charge fluctuation in the vicinity of the CO state.\textsuperscript{9}

$\theta$-(ET)$_2$X consists of alternating stack of $X^-$ (closed shell) and ET$^{1/2+}$ (3/4-filled) layers and the latter contribute electrical conductivity. ET layer can be regarded as two-dimensional anisotropic triangular lattice with 3/4-filled band. In a system away from half-filling, the charge degrees of freedom become important as well as the spin degrees of freedom. In addition, we have to take into account the long-range Coulomb interaction because the screening effect is rather weak in this system. To treat this problem, an extended Hubbard model which includes the nearest-neighbor Coulomb interaction $V_{ij}$ have been studied extensively. The mean-field study by Seo\textsuperscript{10} successfully reproduces the horizontal stripe CO (insulator) in $X$=RbZn(SCN)$_4$ confirmed by some experiments and supports the validity of the model. On the other hand, recent X-ray diffraction experiments have shown the existence of non-stripe type CO in some materials. In $X$=RbZn(SCN)$_4$, short-range CO with wave vector $q = (1/3, k, 1/4)$ is observed in a high temperature metallic region.\textsuperscript{8} In $X$=CsCo(SCN)$_4$, the coexistence of different COs, $q_1 = (2/3, k, 1/3)$ and $q_2 = (0, k, 1/2)$, is suggested.\textsuperscript{7} These non-stripe type COs are not long-range order and only seen in a metallic region. It is considered that the large value of nearest-neighbor Coulomb interaction $V_{ij}$ and the geometrical frustration cause the charge fluctuation and the anomalous COs. Theoretically, several mean-field studies\textsuperscript{11,12} for the extended Hubbard model suggest the existence of non-stripe CO with “3-fold” periodicity in the relevant parameter spaces for real materials.

As for the superconductivity in $X$=I$_3$, its detailed property is still uncertain. Some theoretical studies discuss the charge fluctuation mechanism caused by the nearest-neighbor Coulomb interaction $V$. In a square lattice, the large value of $V$ enhances the charge fluctuation at $(\pi, \pi)$ and it leads to the checkerboard-type CO\textsuperscript{13,14} and the $d_{xy}$-wave superconductivity.\textsuperscript{15,16} On the other hand, in a triangular lattice, the RPA study shows that $V$ enhances the charge fluctuation at $(2\pi/3, 2\pi/3)$ and the triplet next-nearest-neighbor $f$-wave superconductivity is induced.\textsuperscript{17} This result is quite interesting since the triplet superconductivity is hard to be realized compared with the singlet one in general. However, the above studies are limited to the mean-field level. Therefore, we need more accurate calculations which can treat the charge fluctuation more correctly.

With these facts in mind, we study the following extended Hubbard model in a two-dimensional anisotropic triangular lattice as the relevant model of $\theta$-(ET)$_2$X,

$$H = \sum_{\langle i,j \rangle} \left( t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \text{h.c.} \right) + U \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{\langle i,j \rangle} V_{ij} n_{i\uparrow} n_{j\uparrow},$$

where $\langle i,j \rangle$ denotes the summation over the nearest-neighbor sites. As shown in Fig. 1(a), the values of $t_{ij}$ and $V_{ij}$ depend on their directions: $t_p$ and $V_p$ for the di-
Fig. 2. Three different CO patterns studied in this paper. (a) Vertical stripe and (b) diagonal stripe state. Circles with up or down arrow denote charge-rich sites and open circles denote charge-poor sites. (c) The 3-fold state where black (gray) circles represent charge-rich A (charge-poor B and C) sublattices.

tagonal direction and \( t_c \) and \( V_c \) for the vertical direction, respectively. This lattice structure is topologically equivalent to a frustrated square lattice as shown in Fig. 1(b). We set \( U/t_p = 10 \) and \( t_c/t_p = 0 \) as the relevant values for \( X=\text{CsCo(SCN)}_4 \) and vary the values of \( V_p \) and \( V_c \). To investigate the ground state of this Hamiltonian, we use variational Monte Carlo (VMC) method. We introduce the following Jastrow-type trial wave function,

\[
|\Psi\rangle = P_V P_W P_G |\Phi\rangle,
\]

where

\[
P_G = g \sum_i n_i \bar{n}_i,
\]

\[
P_W = w \sum_i n_i \bar{n}_i,
\]

\[
P_V = v \sum_i n_i \bar{n}_i.
\]

\( P_G \) is a Gutzwiller projection operator which reduces the probability of double occupancy of electrons at the same site. \( P_W \) and \( P_V \) are nearest-neighbor projection operators which control the weight of the electron configuration at the nearest-neighbor sites. Summations over \( (p) \) and \( (c) \) correspond to the diagonal and vertical directions, respectively. The parameters \( g, w, \) and \( v \) are variational parameters with \( 0 \leq g, w, v \leq 1 \). If we set \( g = w = v = 1 \), \( |\Psi\rangle \) is reduced to \( |\Phi\rangle \) which is constructed from a mean-field solution of a certain Hamiltonian such as paramagnetic metal, CO and superconductivity.

For the trial wave function of CO, we consider three different patterns as shown in Fig. 2. We call them (a) vertical stripe, (b) diagonal stripe and (c) 3-fold state, respectively. When \( V_p \gg V_c \), the vertical stripe is expected because this pattern fully avoids the energy loss of \( V_p \). For the same reason, the diagonal stripe is expected when \( V_p \ll V_c \). On the other hand, when \( V_p \simeq V_c \), the possibility of non-stripe type CO exists since the stripe CO does not avoid both \( V_p \) and \( V_c \) simultaneously. Although we can consider other various types of non-stripe COs with long periodicity, we study the so-called “3-fold” state proposed by Mori and discussed in a mean-field study as the first step. The 3-fold state consists of charge-rich A sublattice and charge-poor B and C sublattices, as shown in Fig. 2(c). This state is always metallic because the charge gap opens away from the Fermi energy. It is due to the fact that the 3-fold state is incommensurate for the triangular lattice with 1/4-filled band.

For the trial wave function of superconductivity, we adopt the BCS-type wave function. The wave function with fixed electron numbers is used for calculational convenience. The explicit form is given previously.

Figure 3 shows the phase diagram in \( V_p - V_c \) plane obtained in the present VMC calculations. The vertical stripe is stable in the lower right-hand region \( (V_p \gg V_c) \) and the diagonal stripe is stable in the upper left-hand region \( (V_p \ll V_c) \), as expected. This result is consistent with the exact diagonalization study. In the upper right-hand region, where the nearest-neighbor interactions are competing and large, the 3-fold metallic state is stable. This state is always metallic as mentioned before and have no spin order due to the geometrical frustration. In the center of the phase diagram, on the other hand, the stripes and the 3-fold state have almost comparable condensation energies as shown in Fig. 4. Interestingly, all of them are not insulating because they have semi-metallic Fermi surface with hole pockets and electron pockets as shown in Fig. 5. These “charge-ordered metal” states are intermediate ones caused by the frustration of nearest-neighbor Coulomb interaction.

Let us here compare our results with experiments. In \( X=\text{CsCo(SCN)}_4 \), the coexistence of different short-range
The RPA study shows the same result. If the interaction is nearly isotropic, pairing becomes possible on the nnn sites like the 3-fold is introduced, electrons avoid each other and nearest-neighbor pairing is suppressed. As a result, most stable pairing becomes possible on the nnn sites like the 3-fold state (Fig 2(c)). If the interaction is nearly isotropic, namely $V_p \approx V_c$, the 3-fold type charge fluctuation at $q = (2\pi/3, 2\pi/3)$ is enhanced and nnn pairing is favored. The RPA study shows the same result. This “charge-fluctuation-induced” superconductivity is a novel one in contrast to the “spin-fluctuation-induced” $d_{x^2-y^2}$-wave superconductivity in high-$T_c$ cuprates.

In the previous paper, we discussed the possibility of the nnn $f$-wave superconductivity in two-dimensional isotropic triangular lattice with electron density $n = 2/3$, having the superconductivity of Na$_{0.35}$CoO$_2$·1.3H$_2$O in mind. In that case, the 3-fold type CO is commensurate to the triangular lattice and greatly favored. Then the nnn $f$-wave has no chance to be stabilized since the condensation energy of the 3-fold state is much larger. The 1/N expansion study by Motrunich and Lee also shows that the obtained $T_c$ is too small, although the most favored pairing is the nnn $f$-wave. In contrast, the stability of the 3-fold state at $n = 1/2$ (1/4-filling) studied in this paper is much weaker than the case of $n = 2/3$ because of the incommensurability. We can say that the stable 3-fold state is “melted” by the electron doping. In this condition, the nnn $f$-wave has comparable condensation energy and becomes the candidate of the ground state. It is possible that the superconductivity observed in $X=I_3$ has nnn $f$-wave symmetry in the present mechanism. Although we set $t_c/t_p = 0$ in our calculation, the value of $t_c/t_p$ in $X=I_3$ is estimated to be $1.5$, $t_c/t_p$ dependence of the stability of the nnn $f$-wave superconductivity is an interesting future problem.

Finally, we discuss an unified view of the family of $\theta$-(ET)$_2$X. When we replace the anion molecule X, the symmetry of the system is kept unchanged and the change of the nearest-neighbor Coulomb interaction will be small. However, the hopping integrals change drastically and in particular the ratio $t_c/t_p$ varies approximately from $-0.5$ to $1.5$. We consider that the value of $t_c/t_p$ plays important roles and causes various physical properties. In the present paper, we study the case of $t_c/t_p = 0$ and show the possibility of the coexistence of the stripes and the 3-fold state suggested in $X=CsCo(SCN)_4$. For the case of $t_c/t_p = -0.5$, we obtain the result (not shown here) that the stripe COs are greatly favored and their region in the $V_p - V_c$ diagram are enlarged compared with the case of $t_c/t_p = 0$. Moreover, the region where the stripes and the 3-fold state are competing disappears. Combining with the mean-field study which includes the effect of lattice distortion, we can explain the metal-
insulator transition with structural change observed in X=RbM'(SCN)$_4$[M'=Co,Zn] and X=TlCo(SCN)$_4$. For the case of $t_c/t_p = 0.5$, on the other hand, the stripes and the 3-fold state are suppressed and the paramagnetic metal state becomes dominant in the $V_p \simeq V_c$ region. Thus the value of $t_c/t_p$ is crucial for the stability of CO and it will correspond to the horizontal axis of the experimental phase diagram of $\theta$-(ET)$_2$X proposed by Mori et al.\textsuperscript{5}

In summary, we have studied the extended Hubbard model on the two-dimensional anisotropic triangular lattice at 1/4-filling with variational Monte Carlo method. We have shown that for $t_c/t_p = 0$, the stripes and the 3-fold state are energetically competing with each other indicating the coexistence of different CO in $\theta$-(ET)$_2$CsCo(SCN)$_4$. We also have shown that the 3-fold type charge fluctuation enhances the next-nearest-neighbor $f$-wave superconductivity and that it can be applicable to the superconductivity in $\theta$-(ET)$_2$I$_3$. The most important parameter is the value of $t_c/t_p$, which leads to a unified view of the family of $\theta$-(ET)$_2$X.

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