Charge order and superconductivity in a two-dimensional triangular lattice at $n = 2/3$

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To investigate the possibility of charge order and superconductivity in a doped two-dimensional triangular lattice, we study the extended Hubbard model with variational Monte Carlo method. At $n = 2/3$, a commensurate filling for a triangular lattice, it is shown that the nearest-neighbor Coulomb interaction $V$ induces honeycomb-type charge order and antiferromagnetic spin order at $U \gtrsim 10t$. We also discuss the possibility of superconductivity induced by charge fluctuation and the relation to the superconductivity in Na$_{0.35}$CoO$_2$·1.3H$_2$O and $\theta$-type organic conductors.

KEYWORDS: charge order, charge fluctuation, superconductivity, Na$_{0.35}$CoO$_2$·1.3H$_2$O, $\theta$-type organic conductor, variational Monte Carlo method

Since the discovery of high-$T_c$ cuprates, it has been clarified that superconductivity and magnetism are closely connected with each other in strongly correlated electron systems. Hubbard model and $t$-$J$ model in a two-dimensional square lattice have successfully described the relation between them and showed that antiferromagnetic spin fluctuation induces $d_{x^2−y^2}$-wave superconductivity in doped Mott insulators.

In a frustrated system like a two-dimensional triangular lattice, on the other hand, the relation between superconductivity and magnetism have not been clarified yet. Generally, frustration suppresses long-range magnetic orders and induces large fluctuation. Anderson first proposed a resonating valence bond (RVB) state for the ground state of an antiferromagnetic two-dimensional triangular lattice, as a notion substituted for the Fermi liquid. Since then, study of frustrated spin systems has been greatly improved and various interesting phenomena have been clarified. However, when some carriers are doped into the frustrated lattices, the character of electron systems has not been clarified extensively. Actually, materials considered as doped frustrated systems like $\theta$-type organic conductors$^2$ and Na$_x$CoO$_2$·$y$H$_2$O$^3,4$ show various magnetic and charge orders, as well as unconventional superconductivity.

In a system away from half filling, carriers obtain a large mobility and the charge fluctuation is enhanced by strong electron correlation. Then, the charge degrees of freedom become important as well as the spin degrees of freedom. To deal with the charge fluctuation correctly, we have to take into account the long-range Coulomb interaction which is not contained in the Hubbard model or $t$-$J$ model. An extended Hubbard model with on-site Coulomb interaction $U$ and nearest-neighbor one $V$ is an appropriate model to treat this problem. The competition between $U$ and $V$ is considered to induce various states. For example, in a two-dimensional square lattice with quarter-filled band, previous theoretical studies show that a checkerboard-type charge order (CO) becomes stable at large $V$ region$^5$ and $d_{x^2−y^2}$-wave superconductivity is stabilized at intermediate $V$ region$^6,7$

In this letter, we study an extended Hubbard model in a two-dimensional triangular lattice with variational Monte Carlo method having the Na$_x$CoO$_2$ system in mind. Although the multi-orbital effect may be important for superconductivity,$^8,9$ we focus on the single-band model$^{10–15}$ with charge fluctuation.$^{16–18}$

We show that the competition between $U$ and $V$ induces the two types of CO states and discuss the possibility of superconductivity induced by charge fluctuation.

We introduce the following extended Hubbard model in a two-dimensional triangular lattice,

$$H = \sum_{k\sigma} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_{\langle i,j \rangle} n_i n_j, \quad (1)$$

where $\langle i,j \rangle$ denotes the summation over the nearest-neighbor sites. The bare energy dispersion is given by

$$\epsilon_k = -2t(\cos k_x + 2 \cos \frac{1}{2} k_x \cos \sqrt{3} k_y). \quad (2)$$

In this non-bipartite lattice, there is no electron-hole symmetry and the sign of $t$ is crucial. The sign of $t$ should be determined so as to reproduces the shape of the Fermi surface obtained from experiments or band calculations for each material under consideration. For the superconducting material Na$_{0.35}$CoO$_2$·1.3H$_2$O, the choice of $t < 0$ and $n = 4/3$ reproduces the large Fermi surface around $\Gamma$ point calculated by the LDA calculation$^{19}$ or observed by ARPES experiments.$^{20,21}$ In the following, we use $t > 0$ and $n = 2/3$ by using the electron-hole transformation as shown in Fig. 1. To study the ground state, we use

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Fig. 1. First Brillouin zone and Fermi surface used in this paper.
BIP

PM

AFI

AF

BP

PCO

Fig. 2. Three different charge and spin ordered states in a two-dimensional triangular lattice for \( n = 2/3 \). (a) Paramagnetic CO where solid (open) circles represent preferred B and C (avoided A) sublattices. (b) Bipolaronic state where electrons prefer A sublattice in spite of double occupancy. (c) AF - Antiferromagnetic state with honeycomb-type charge order. (d) The folded first Brillouin zone for a honeycomb-type charge order. Dashed line represents the original first Brillouin zone.

The competition between commensurate charge-ordered states. The competition between several honeycomb-type states as shown in Fig. 2 are its explicit form is discussed shortly.

In a two-dimensional triangular lattice at \( n = 2/3 \), several honeycomb-type states as shown in Fig. 2 are commensurate charge-ordered states. In the following, we denote the three different states as paramagnetic charge order (PCO), bipolaronic charge order (BP), and antiferromagnetic charge order (AF) as shown in Fig. 2(a)-(c). Trial wave functions corresponding to these states are obtained from the solution of the mean-field Hamiltonian

\[
H_\sigma = \sum_{k \sigma} \varepsilon_k c_{k \sigma}^\dagger c_{k \sigma} + 2\Delta_c \sum_i \cos(Q \cdot \mathbf{r}_i)n_i - 2\Delta_s \sum_i \cos(\mathbf{Q} \cdot \mathbf{r}_i + \sigma \frac{2\pi}{3}) n_{i\sigma},
\]  

(6)

where \( \Delta_c \) is an order parameter of charge order, \( \Delta_s \) is an order parameter of spin order and \( \mathbf{Q} = (\frac{2\pi}{3}, 0) \) is an ordering wave vector. PCO is a state in which electrons prefer B and C sublattices and avoid A sublattice, and there is no spin order. Thus we can choose \( \Delta_c > 0, \Delta_s = 0 \). BP is a bipolaronic state in which electrons prefer A sublattice and avoid B and C sublattices with double occupancy, i.e., \( \Delta_c < 0, \Delta_s = 0 \). Finally, AF is a state that charge order and antiferromagnetic spin order coexist\(^{24} \) \( (\Delta_c > 0, \Delta_s > 0) \). If we set \( \Delta_c = \Delta_s = 0 \), the state reduces to paramagnetic metal (PM).

For the trial wave function of superconductivity, we employ the BCS type wave function,

\[
|\Phi\rangle = \prod_k \left( u_k + v_k c_{k \uparrow}^\dagger c_{k \downarrow}^\dagger \right) |0\rangle.
\]  

(7)

The form of this wave function is not convenient for the VMF method because the number of electrons are not fixed. To obtain the wave function with a fixed number of electrons, we extract the term involving \( N_e \) electrons as,

\[
|\Phi\rangle \propto \left( \sum_{i,j} a_{ij} c_{i \uparrow}^\dagger c_{j \downarrow}^\dagger \right)^{N_e/2} |0\rangle
\]  

(8)

where

\[
a_{ij} = \frac{1}{\sqrt{N_e}} \sum_k \frac{v_k}{u_k} \frac{e^{ik(\mathbf{r}_i - \mathbf{r}_j)}}{\xi_k + \sqrt{\xi_k^2 + |\Delta_k|^2}}.
\]  

(9)

The matrix element \( a_{ij} \) reflects the symmetry of Cooper pairs: for singlet pairing, \( a_{ji} = a_{ij} \) and for triplet, \( a_{ji} = -a_{ij} \). The possible paring symmetry of \( \Delta_k \), the gap function of superconductivity, is determined by group

Fig. 3. Phase diagram in a \( U - V \) plane for \( n = 128/192 = 2/3 \). Solid lines represent the first-order transition boundaries. The boundary between BPI and AFI is well fitted by the dotted line of \( V = U/3 \).
theory. The six candidates are $s, d, i$ (singlet) and $p, f$, next-nearest-neighbor $f$ (triplet) symmetries.

We determine the phase diagram in a $U - V$ plane by optimizing the ground state energies of trial wave functions. Figure 3 shows the phase diagram in a $U - V$ plane. For large value of $V$, BPI (“T” denotes insulator) state is stable because the effect of $V$ overcomes $U$ and the electrons concentrate in one of the three sublattices in spite of double occupancies. At $U \gtrsim 10t$, there appears an AFI region between paramagnetic metal (PM) and BPI regions. For small $U$, the state changes as PM $\rightarrow$ BPI as $V$ increases. For large $U$, however, electrons try to order without loss of on-site potential energy. Then the state changes as PM $\rightarrow$ AFM $\rightarrow$ BPI. Since the energy loss in the Coulomb interactions in BPI and AFI are $U/3$ and $V$ per site, the critical value of $V \simeq U/3$ can be easily expected. On the other hand, we find that the PCO region does not exist in this phase diagram because the calculated total energy of PCO is always higher than AFI. That is to say, the order parameters of charge order and spin order grow simultaneously.

Interestingly, we find that all three phase transitions (PM $\rightarrow$ BPI, PM $\rightarrow$ AFI and AFI $\rightarrow$ BPI) are first order. At $V = V_c$, the critical value of $V$, the order parameter has a jump and the variational energies of the states cross. Reflecting the first order character, the physical quantities like magnetization or charge density change discontinuously. In order to understand the reason of this first order transition, we show the change of the band structure in Fig. 4. When $\Delta_c = 0$, the system is a paramagnetic metal (PM, Fig. 4(a)) state. As $\Delta_c$ grows, two degenerate bands along A-B line (see Fig. 2(d)) begin to split. When $|\Delta_c| < t/3$, the system shows a metallic behavior because there is an overlap between the upper band and lower band. We call this state as “charge ordered metal (COM, Fig. 4(b))”. If $|\Delta_c| > t/3$, the overlap disappears and we call this state as “charge ordered insulator (COI, Fig. 4(c))”. PM $\rightarrow$ BPI transiton in Fig. 3 is, that is to say, “PM to COI” type first-order transition. COM state is not realized in this condition. This result is interpreted as follows. Since $n = 2/3$ is a commensurate filling for a two-dimensional triangular lattice, the honeycomb-type charge orders like BPI or AFI are greatly favored. We consider that the optimal carrier doping removes the frustration and reduces the charge fluctuation. COM is an intermediate state with weak stability and thus it is suppressed in this condition. Therefore, if we slightly break the commensurability, for example, by the introduction of a lattice anisotropy or doping, the fluctuation is enhanced again and COM state can appear with second-order transition. Indeed, the study of the extended Hubbard model in a two-dimensional anisotropic triangular lattice by Seo shows the existence of COM state in some parameter region.

Finally, let us discuss the possibility of superconductivity in the present case. Our calculation shows that there is no region where a superconductivity becomes stable. This result is reasonable at least for $V = 0$ because the nesting of Fermi surface is absent. Furthermore, the van Hove singularity which is advantageous to superconductivity is away from the Fermi surface. The third-order perturbation calculation and the one-loop renormalization-group calculation for the Hubbard model show the same results. Then the problem is whether the introduction of $V$ induces a superconductivity or not. Qualitatively speaking, possible candidate is next-nearest-neighbor (nnn) $f$-wave pairing. When $V$ is large, electrons avoid each other and nnn pairing is considered to be favored in the real-space representation. Schematic explanation is shown in Fig. 5. Indeed, we find that nnn $f$-wave pairing has a lower energy than the paramagnetic metal state at large value of $V$. However, its condensation energy is quite small compared with those of charge ordered states (BPI and AFI). Motrunich and Lee also showed that the obtained $T_c$ is much
smaller than the realistic value, although the most stable pairing is nnn f-wave near the charge order instability. We speculate that the reason why the superconductivity is not stabilized is the same as the case of COM. Thus, the appropriate breaking of the commensurability will induce the large fluctuation and then the charge order and superconductivity can compete each other.

In the following, we propose two ways to break the commensurability and induce the superconductivity. One is to change the electron density away from the commensurate filling. The RPA study of the extended Hubbard model in a two-dimensional triangular lattice at \( n = 0.8 \) and 1.2 by Tanaka et al.\(^{18} \) shows that nnn f-wave superconductivity is realized near the CDW instability. In this condition, CDW state is incommensurate and its stability is not so strong. Therefore, the charge fluctuation is enhanced near this instability and nnn f-wave superconductivity appears. Since the electron filling of Na\(_{0.35}\)CoO\(_2\) · 1.3H\(_2\)O has not been determined precisely because of the existence of H\(_2\)O\(^+\) ion, the above mechanism might be applicable to this material.

Another way is to introduce some anisotropy. Superconductivity in \( \theta \)-type organic conductors are located next to the charge order state and its origin is considered to be the charge fluctuation. They have quasi-two-dimensional anisotropic triangular lattice with \( n = 1.5 \) filling. For the square lattice, this filling is commensurate and leads to the checkerboard-type charge order. In real materials, however, the anisotropies of hopping or off-site Coulomb interaction break this commensurability and induces various states like several charge orders (three kind of stripe states\(^{26} \) and 3-fold state\(^{30} \)) and, probably, unconventional superconductivity. We can relate this mechanism to the one discussed so far. The study of an anisotropic triangular lattice will interpolate the square- and isotropic triangular lattice and give the consensus about the charge fluctuation. It is left for the future problem.

In summary, we have studied the extended Hubbard model in a two-dimensional triangular lattice and find the two types of charge order states (BPI and AFI) in a\( U - V \) phase diagram. These states are so stable at \( n = 2/3 \) that the superconductivity induced by charge fluctuation has no chance to appear. However, the appropriate breaking of the commensurability can induce the charge fluctuation and the possibility of the superconductivity is expected to arise. We expect that this mechanism is applicable to \( \theta \)-type organic superconductors or Na\(_{0.35}\)CoO\(_2\) · 1.3H\(_2\)O.

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