Magnetic Field Effect in One-Dimensional Charge Ordering Systems

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We study the effects of an external magnetic field on charge ordering in the one-dimensional extended Hubbard model at quarter filling by the quantum Monte Carlo method. We find that the Zeeman coupling enhances the charge order correlation, which is prominent when the system is located in the critical regime near the charge ordering transition at zero magnetic field. This behavior is interpreted in terms of the crossover to the fully spin-polarized limit where the model is exactly solvable. Furthermore, by incorporating the interchain Coulomb repulsion, we show that the charge-ordering transition temperature is increased by the magnetic field. We also discuss the relevance of our results to magnetoresistance effects observed in molecular conductors.

In strongly correlated electron systems, the application of an external field can lead to nontrivial responses owing to their collective nature. As a typical example, in molecular conductors, nonlinear electron conduction is widely observed in charge ordering (CO) systems under an electric field.\textsuperscript{1,2} On the other hand, the effects of a magnetic field in such CO systems have been less intensively studied, although they have been widely investigated in the case of metallic systems.\textsuperscript{3} Recently, it has been found that several molecular conductors, which are considered as potential CO systems, exhibit relatively large positive magnetoresistance (MR) effects.\textsuperscript{4,5} These phenomena were considered to be induced by the Zeeman effect, as judged from their little dependence on the orientation of the applied magnetic field. This is in sharp contrast to the orbital effect, which generally plays an important role in metallic molecular crystals;\textsuperscript{6} owing to their anisotropic electronic structures, the responses are very sensitive to the orientation.

One such compound is TPP\{Co(Pc)(CN)\}_2,\textsuperscript{6} a highly one-dimensional (1D) system in which uniform columns of Co(Pc)(CN)\textsubscript{2} molecules form a quarter-filled π-electronic band. Its resistivity is semiconducting below about 250 K,\textsuperscript{6} and asymmetric NQR spectra are observed below 5 K, suggesting the existence of CO correlation,\textsuperscript{4} although whether a long-range order exists in the ground state remains elusive. The positive MR is prominent at low temperatures (T) of \(T \lesssim 20\) K.\textsuperscript{4} At \(T = 1.7\) K, for instance, there is no dependence on the direction of the applied magnetic field of \(B < 10\) T, indicating the Zeeman effect as its origin.\textsuperscript{4} Another example is \(\theta-(BEDT-TTF)_2CoZn(SCN)_2\).\textsuperscript{7} This compound is a quasi-two-dimensional material in which short-range CO correlations develop,\textsuperscript{6} the observed positive MR at low \(T\) is interpreted in terms of the spin polarization in localized paramagnetic spins near the CO domain boundaries, namely, the Zeeman effect, which suppresses the electron conduction because of the Pauli exclusion principle.\textsuperscript{5}

In the CO insulating states, the spin degree of freedom typically behaves as localized spin systems, analogous to the case of Mott insulators. This is a common feature of insulating states driven by strong correlation. The remaining magnetic sector, therefore, can respond to a magnetic field through the Zeeman coupling. Theoretically, to describe such CO insulating states in molecular conductors, the extended Hubbard model (EHM), including not only the on-site but also the intersite Coulomb interactions, has been widely used.\textsuperscript{9} However, little is known about the effect of the magnetic field in the EHM even on the simplest lattice structures, which is the subject of this study.

In this work, we numerically investigate the 1D quarter-filled EHM coupled to the magnetic field via the Zeeman term. Although such a model was previously studied from several viewpoints,\textsuperscript{10-13} how CO is affected by the magnetic field has been less discussed. By a quantum Monte Carlo method, we show that the CO correlation is enhanced by the applied magnetic field, and the behavior is continuously connected to the fully spin-polarized limit where exact results are known. We further take into account the interchain Coulomb inter-

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action and show that the CO transition temperature is increased by the magnetic field.

We begin with the EHM for a 1D chain in an applied magnetic field, whose Hamiltonian is given by,

$$\mathcal{H} = -t \sum_{i<\sigma} (c_i^\dagger \sigma_i c_{i+1\sigma} + \text{h.c.}) + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

$$+ V \sum_i n_i n_{i+1} - h \sum_i (n_{i\uparrow} - n_{i\downarrow}),$$

(1)

where \(c_{i\sigma} (c_{i\sigma}^\dagger)\) is an annihilation (creation) operator of an electron with spin \(\sigma\) at site \(i\), and \(n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}\) is the number operator. The on-site and intersite Coulomb interactions are denoted by \(U\) and \(V\), respectively. The last term represents the Zeeman coupling to the magnetic field \(h\) applied in the \(z\) direction. We consider the case of quarter filling, i.e., \(\sum_i n_i / N = 1/2\) with \(N\) being the number of sites.

The properties of this model at \(h = 0\) are well known.\(^9\) For repulsive interactions, the CO insulating phase appears at \(T = 0\) in the region of large \((U/t, V/t)\) beyond a critical line; otherwise, the system is metallic (Tomonaga-Luttinger liquid), and the spin degree of freedom behaves as a 1D \(S = 1/2\) Heisenberg model as a consequence of spin-charge separation.\(^{14}\) The on-site Coulomb repulsion is fixed at \(U/t = 6\) in this paper, where the CO phase transition occurs at a critical point of \(V_c/t_0 \approx 3.5\) for \(h = 0.\(^{15}\)\) At finite \(T\), the long-range order is prevented by thermal fluctuations in 1D systems.

We investigate the 1D model by the quantum Monte Carlo method based on the stochastic series expansion (SSE) with the operator-loop update.\(^{16-18}\) An advantage of this method is that it can incorporate the magnetic field unlike other methods that work on the canonical ensemble with a fixed total magnetization. The calculations fully include thermal and quantum fluctuations in an unbiased manner. We have studied the system consisting of \(N = 64\) sites under the periodic boundary condition and confirmed that finite-size effects are negligible down to \(T/t = 0.02\). We calculate the charge and spin structure factors,

$$C(q) = \frac{1}{N} \sum_{j,k} e^{i q (j-k)} \langle (n_j - 1/2)(n_k - 1/2) \rangle,$$

(2)

$$S(q) = \frac{1}{N} \sum_{j,k} e^{i q (j-k)} \langle (n_{j\uparrow} - n_{j\downarrow})(n_{k\uparrow} - n_{k\downarrow}) \rangle,$$

(3)

respectively.

First, let us discuss how the magnetic field affects the overall features in the charge and spin degrees of freedom. In Fig. 1, we show the charge and spin structure factors at \(V/t = 3\) and \(T/t = 0.05\) for various values of the magnetic field \(h\). In the absence of the magnetic field, the characteristic peaks of the charge and spin structures are located at \(q = \pi\) and \(q = \pi/2\), respectively. The former represents the \(4k_F\) \((k_F:\text{Fermi}\text{\ momentum at } h = 0)\) \(\text{CO}\ correlation\ originating in the intersite interaction } V. \text{ Although the CO does not achieve a long-range order in the ground state for this value of } V/t, the CO correlation is dominant as the system is in the critical regime near \(V_c\). The peak of \(S(q)\) at \(q = \pi/2\) indicates an antiferromagnetic (AF) correlation resulting from a superexchange coupling between every other sites appearing in the fourth-order perturbation from the strong coupling limit under CO. Once the magnetic field is switched on, the CO peak \(C(\pi)\) is notably enhanced; meanwhile, in the spin sector, \(S(\pi/2)\) becomes gradually blurred and two peaks at other momenta develop instead. One is the ferromagnetic component \(S(0)\), as a consequence of the magnetization induced by the applied magnetic field. The other peak develops at \(q = \pi\) along with the enhancement of \(C(\sigma)\); in fact, \(S(\pi)\) approaches \(C(\pi)\) in the fully spin-polarized limit as discussed below. The overall variation driven by the magnetic field is schematically depicted in Fig. 1(c).

The magnetic field dependence of the characteristic peak values is plotted in Fig. 2 for different values of \(V/t\). All the data monotonically vary as \(h/t\) increases. The CO correlation \(C(\pi)\) [Fig. 2(a)] develops together with the ferromagnetic component \(S(0)\) [Fig. 2(b)]. However, a large enhancement in the former is only observed for \(V/t > 2\), which we interpret as follows. The \(h/t = \infty\) limit corresponds to the fully spin-polarized...
state, which is confirmed by $S(0)$ approaching the saturated value for large $h/t$. In this limit, the system can be described by the 1D interacting spinless fermion model:

$$
\mathcal{H}_{\text{SF}} = -t \sum_i (a_i^\dagger a_{i+1} + h.c.) + V \sum_i \tilde{n}_i \tilde{n}_{i+1},
$$

where $a_i (a_i^\dagger)$ annihilates (creates) a spinless fermion at site $i$ and $\tilde{n}_i = a_i^\dagger a_i$ is the number operator. Because of the perfect spin polarization, the system effectively becomes half-filled, and the on-site interaction $U$ can be omitted. The exact solution of this model gives the transition point, $V_c/t = 2$, between the metallic and CO insulating states.\(^{20,21}\) Our result that the CO is enhanced mainly for $V/t > 2$ is consistent with this critical value of $V_c/t$, since the system with $V/t < V_c/t$ remains metallic even in the spin-polarized limit.

The crossover to the fully spin-polarized limit is also confirmed in the behavior of other peak values. The AF correlation $S(\pi/2)$, which is characteristic of the EHM at $h = 0$, is gradually depressed by the magnetic field, as shown in Fig. 2(d). This indicates that the virtual superexchange processes become forbidden in the spin-polarized limit. Furthermore, $C(q)$ and $S(q)$ defined in Eqs. (2) and (3) are identical to each other in this limit except for $q = 0$ [for $q = \pi$, see Figs. 2(a) and 2(c)]. This accounts for the above-mentioned development of $S(\pi)$ in Fig. 1(b).

The $h/t$-dependences of the double occupancy and kinetic energy are shown in Fig. 3. When the spins become polarized by increasing $h/t$, the double occupancy is suppressed owing to the Pauli exclusion principle. In addition, the effective filling is increased from a quarter to a half. As a result, the kinetic-energy gain is also suppressed [Fig. 3(b)]. These results indicate that the electrons approaching the spin-polarized limit possess a more localized character than those of the EHM even at the same value of $V/t$; the magnetic field effectively enhances the effect of $U/t$. This is the reason why CO is stabilized by $h$.

Another feature in Fig. 2(a) is that the relative enhancement in $C(\pi)$ is prominent at intermediate $V/t$. This can be clearly observed from the enhancement ratio, as shown in Fig. 4. Here, the ratio of $C(\pi)$ for $h > 0$ to that at $h = 0$ is plotted as functions of $V/t$. We find that the peaks are located at $V/t = 3 - 4$, which is in the vicinity of the critical point $V_c/t \approx 3.5$ at $h/t = 0$. Furthermore, the value of $V/t$ at which the ratio is maximum becomes smaller when the magnetic field is increased. This indicates that the CO region in the phase diagram expands to a smaller $U$-$V$ region.

The enhancement of CO by the magnetic field is not directly anticipated from the studies for $h = 0$. For instance, the bosonization studies for $h = 0$ have clarified that the low-energy properties of the EHM are described by the phase Hamiltonian with spin-charge separation, and the CO instability originates in the higher-order Umklapp scattering in the charge part.\(^{14}\) However, our observation that the magnetic field enhances CO implies the strong interplay between the spin and charge degrees of freedom under a magnetic field.\(^{22}\)

Next, we consider the effect of the magnetic field on the finite-$T$ CO phase transition by including the interchain coupling term to the model in Eq. (1). We treat the interchain Coulomb repulsion between neighboring chains $V_\perp$ within the mean-field approximation, as in our previous works.\(^{23-25}\) The resulting additional term to Eq. (1) is

$$
\mathcal{H}^{\text{MF}} = zV_\perp n_{\text{CO}} \sum_i (-1)^i n_i + \frac{1}{2} zNV_\perp n_{\text{CO}}^2,
$$

where $n_{\text{CO}}$ is the CO order parameter with twofold periodicity determined self-consistently and $z$ is the number of nearest-neighbor chains, which we take as 2 in this

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**Fig. 2.** (Color online) Charge structure factor at $q = \pi$ (a) and spin structure factors at $q = 0$ (b), $q = \pi$ (c), and $q = \pi/2$ (d) as functions of the magnetic field $h/t$ for $U/t = 6$ and $T/t = 0.05 (N = 64)$. 

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work. This interchain term gives rise to the finite-T CO phase transition.

The results show that the transition temperature $T_{CO}$ is increased by applying the magnetic field, as expected from the results that we have observed for the 1D model. The $T$ dependence of the CO order parameter $n_{CO}$ is plotted in Fig. 5. For $V/t = 2.5$ and $V_{\perp}/t = 0.5$, $T_{CO}/t$ is increased monotonically from $\sim 0.3$ at $h/t = 0$ to $\sim 0.4$ at $h/t = 0.4$, where the system nearly reaches the spin-polarized regime. We note that $n_{CO}$ slightly decreases at low $T$ for $h/t \lesssim 0.1$, which was ascribed to the development of the $2k_F$-AF correlations caused by the superexchange interaction between the charge-rich sites in the case of $h = 0$. On the other hand, in higher magnetic fields, the dominant magnetic correlation becomes ferromagnetic; $S(0)$ develops and thereby $S(\pi/2)$ is suppressed at low $T$, as shown in Fig. 6. Consequently, CO becomes further stabilized for $h/t \gtrsim 0.15$ with the decrease in $T/t$.

Now, let us discuss our results in comparison with experiments. Our finding that the magnetic field stabilizes CO is consistent with the positive MR effect observed in quasi-1D molecular conductors such as TPP[Co(Pc)(CN)$_2$]$_2$. In the 1D systems, the Umklapp scattering is responsible for increasing the resistivity as well as stabilizing CO at $h = 0$. Thus, the positive MR can be interpreted as a consequence of the enhancement of such Umklapp processes under a magnetic field, which is detected as the stabilized CO in our calculations. On the other hand, the same explanation is not directly applicable to the MR effect observed in $\theta$-(BEDT-TTF)$_2$CoZn(SCN)$_2$. Even though
it is also positive. The \( \theta \text{-BEDT-TTF)}_2X \) family has a two-dimensional (2D) band structure, and furthermore, the CO phenomena in these compounds are considered to involve additional ingredients such as geometrical frustration and coupling to the lattice degree of freedom.\(^9,26,27\) Such situations are beyond our simple 1D model. Indeed, recent measurements on related 2D compounds, where the CO transition is more clearly seen than in the above-mentioned materials, indicate that the MR ranges from positive to negative near \( T_{\text{CO}} \) depending on the compound.\(^28\) Although it may be difficult to discuss such experiments, we expect that CO is a key ingredient for the MR effects.

Finally, we discuss our results in relation to the giant negative MR effect observed in TPP[Fe(Pc)(CN)]\(_2\). This material is an analog of the Pc-based compound mentioned above; by substituting Co with Fe, the MR changes from positive to negative (and large),\(^29\) and its origin has been discussed theoretically.\(^30,31\) In this compound, localized magnetic moments from \( d \) electrons of Fe atoms in the center of each molecule have strong Ising anisotropy, and an AF correlation between them is observed.\(^32\) As a result, \( \pi \) electrons on the Pc unit, which form the 1D conduction band, are subjected to the effective staggered magnetic field from the \( d \) electrons through \( \pi-d \) coupling. In a previous work,\(^33\) the authors found that the CO correlation is also monotonically enhanced by the staggered magnetic field. Hence, a uniform magnetic field brings about two opposite effects on CO in the actual material. Namely, although it enhances the CO correlation in \( \pi \) electrons, as shown in the current study, it will disturb the AF correlation between the \( d \) spins and suppress the effect that enhances CO through the \( \pi-d \) coupling. It might depend on the parameters, such as the \( \pi-d \) coupling and \( g \)-factors for the \( \pi \) and \( d \) electrons, whether CO is eventually enhanced or depressed by the applied magnetic field. The experiments showing the negative MR suggest that the negative effect through the \( \pi-d \) coupling is larger in TPP[Fe(Pc)(CN)]\(_2\). Although the competition was studied in terms of the charge gap, it will be helpful to perform comprehensive studies including finite-\( T \) effects on the MR phenomena. This is left for a future study.

In summary, we have investigated the effects of the applied magnetic field on the one-dimensional extended Hubbard model at quarter filling by the quantum Monte Carlo method. The charge-order correlation is monotonically enhanced by the magnetic field. The behavior is understood on the basis of a crossover to the fully spin-polarized limit. The enhancement of charge order is prominent near the phase boundary between the paramagnetic metal and the charge-ordered insulator in the absence of the magnetic field. We have shown that the magnetic field increases the transition temperature to the charge-ordered state within an interchain mean-field approach.

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