Pairing competition in a quasi-one-dimensional model of organic superconductors

(TMTSF)$_2$X in magnetic field

Hirohito AIZAWA$^1$, Kazuhiko KUROKI$^1$, and Yukio TANAKA$^2$

$^1$Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182-8585, Japan
$^2$Department of Applied Physics, Nagoya University, Nagoya 464-8603, Japan

We microscopically study the effect of the magnetic field (Zeeman splitting) on the superconducting state in a model for quasi-one-dimensional organic superconductors (TMTSF)$_2$X. We investigate the competition between spin singlet and spin triplet pairings and the Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state by random phase approximation. While we studied the competition by comparison with the eigenvalue of the gap equation at a fixed temperature in our previous study (Phys. Rev. Lett. 102 (2009) 016403), here we obtain both the $T_c$ for each pairing state and a phase diagram in the $T$(temperature)-$h$(field)-$V$ (strength of the charge fluctuation) space. The phase diagram shows that consecutive transitions from singlet pairing to the FFLO state and further to $S_z = 1$ triplet pairing can occur upon increasing the magnetic field when $2k_F$ charge fluctuations coexist with $2k_F$ spin fluctuations. In the FFLO state, the singlet $d$-wave and $S_z = 0$ triplet $f$-wave components are strongly mixed especially when the charge fluctuations are strong.

KEYWORDS: organic conductor, quasi-one-dimensional system, (TMTSF)$_2$X, superconductivity, spin triplet pairing, FFLO state, Zeeman effect

1. Introduction

The superconducting state of quasi-one-dimensional (Q1D) organic conductors (TMTSF)$_2$X (TMTSF=tetramethyl-tetraselenafulvalene, $X=PF_6$, ClO$_4$ etc.) has been an issue of great interest. From the discovery of the first organic superconductor (TMTSF)$_2$PF$_6$, various studies have been performed both experimentally and theoretically.$^{1-13}$ Previous studies for the NMR relaxation rate $1/T_1$,$^{14,15}$ and the impurity effect$^{16-21}$ have strongly suggested the possibility of anisotropic superconductivity where the nodes of the superconducting gap intersect the Fermi surface, although a thermal conductivity measurement has suggested the absence of nodes on the Fermi surface in (TMTSF)$_2$ClO$_4$. $^{22}$

Further experiments concerning the pairing symmetry have suggested the possibility that the pairing state in (TMTSF)$_2$X may be even more fascinating. The NMR Knight measurements for (TMTSF)$_2$PF$_6$ and (TMTSF)$_2$ClO$_4$ have shown that the Knight shift is unchanged across the superconducting critical temperature $T_c$. $^{23-25}$ The upper critical field $H_c2$ for (TMTSF)$_2$PF$_6$ and (TMTSF)$_2$ClO$_4$ has been observed to exceed the Pauli paramagnetic limit $H_P$. $^{26-28}$ These experiments suggest the possibility of spin triplet pairing and/or the Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state,$^{29,30}$ in which the Cooper pairs formed as $(k + Q_c \uparrow, -k + Q_c \downarrow)$ have a finite center of mass momentum $Q_c$.

Very recent experiments show more interesting results. The NMR experiment for (TMTSF)$_2$ClO$_4$ shows that the Knight shift changes across $T_c$ when the magnetic field is small, but it is unchanged when a high magnetic field is applied.$^{31}$ The $H_c2$ measurements for (TMTSF)$_2$ClO$_4$ show the possibility of two or three different pairing states. In the intermediate field regime, superconductivity is easily destroyed by tilting the magnetic field (between $H_P$ and about 4T) from the conductive $a$-$b$ plane, while in the high field regime, superconductivity is sensitive to the broadening of the impurity scattering potential of the nonmagnetic impurity, namely, if the broadening of the impurity potential is large, the upturn curve of the critical temperature vanishes.$^{32,33}$ These experiments suggest that spin singlet pairing occurs in the field regime lower than the Pauli limit, but spin triplet pairing and/or the FFLO state occurs in the higher field regime.

Theoretically, various studies on the pairing state in (TMTSF)$_2$X have elucidated not only the unconventional pairing state with a nodal gap function$^{34-38}$ but also the possibility of the spin triplet pairing$^{39-54}$ and/or the FFLO state.$^{54-59}$ In particular, we have previously shown that the spin triplet “$f$-wave” pairing can compete with the spin singlet “$d$-wave” pairing in Q1D systems$^{60}$ when $2k_F$ spin fluctuations coexist with $2k_F$ charge fluctuations since the Fermi surface is disconnected in the $b$-direction.$^{39-41}$ In fact, the coexistence of $2k_F$ charge density wave and $2k_F$ spin density wave in the insulating phase has been observed by the diffuse X-ray scattering experiments in (TMTSF)$_2$PF$_6$.$^{61,62}$ A similar conclusion concerning the pairing state competition has been reached using the renormalization group technique.$^{42,43}$ As a method for identifying spin-triplet $f$-wave pairing, tunneling spectroscopy$^{63,64}$ via the mid gap Andreev resonant state$^{65,66}$ and Josephson effect$^{67}$ have been proposed. In particular, the experiment of the proximity effect in the junctions with a diffusive normal metal is promising since an anomalous proximity effect with a zero-energy peak in the density of states, specific to spin-triplet superconductor junctions, has been predicted.$^{68-73}$
There have also been various studies for the pairing state in the magnetic field. The possibility of the FFLO state in finite magnetic field in a Q1D model for (TMTSF)$_2$X has been suggested in several studies.\textsuperscript{55–59} The possibility of field-induced spin triplet pairing has also been discussed by a phenomenological theory and a renormalization technique.\textsuperscript{44–52} Recently, we have microscopically studied the magnetic field effect on the pairing state in Q1D systems. We found that the $S_z = 1$ triplet pairing mediated by $2k_F$ spin+$2k_F$ charge fluctuations is strongly enhanced by the magnetic field and showed the temperature-magnetic field phase diagram indicating the competition between the singlet and triplet pairings.\textsuperscript{53} We further found that the spin singlet, triplet, and FFLO states are closely competing, and the $S_z = 0$ triplet component is strongly mixed with the singlet component in the FFLO state. There, the pairing state competition has been studied by comparing the eigenvalue of the linearized gap equation in the space of $V_\sigma$ (strength of the charge fluctuation) and $h_z$ (magnetic field).\textsuperscript{54}

The FFLO state has recently been studied actively not only in Q1D but also in general systems.\textsuperscript{74,75} Previous theoretical studies have revealed various properties of the FFLO superconductivity from the viewpoint of (i) the orbital effect,\textsuperscript{76–87} (ii) the impurity effect,\textsuperscript{88–92} and (iii) the anisotropy of the system.\textsuperscript{93–101} One of the interesting aspects of the FFLO state is parity mixing, i.e., even and odd parity pairings can be mixed to stabilize the FFLO state, which has been shown in phenomenological theories.\textsuperscript{102,103} Recent microscopic studies have also shown that the $S_z = 0$ triplet pairing is mixed with singlet pairing in the FFLO state of the Hubbard model on the two-leg ladder-type lattice,\textsuperscript{104} the square lattice,\textsuperscript{105,106} and the Q1D extended Hubbard model.\textsuperscript{54} Yanase has pointed out that the parity mixing stabilizes the FFLO state, even in the vicinity of the quantum critical point, where the quasi-particle lifetime decreases owing to the scattering caused by spin fluctuations.\textsuperscript{105} In addition to these works, superconducting properties of the FFLO state have been studied theoretically.\textsuperscript{107–109}

Recent experiments strongly show the possibility of the FFLO state with an anisotropic gap function in CeCoIn$_5$.\textsuperscript{110–130} Other candidate materials exhibiting the FFLO state are quasi-two-dimensional (Q2D) organic materials, such as $\lambda$-(BETS)$_2$X (BETS=bis(ethylenedithio)tetrathiafulvalene, $X=$GaCl$_4$,\textsuperscript{131} and FeCl$_4$\textsuperscript{132–134}) and $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ (BEDT-TTF=bis(ethylenedithio)tetrathiafulvalene),\textsuperscript{135–137} and also a Q1D one (TMTSF)$_2$ClO$_4$.\textsuperscript{31–33} These materials have stimulated extensive studies in this field. The FFLO state attracts us not only in the field of superconductivity or superfluidity in condensed matter but also in the quantum chromodynamics\textsuperscript{74} and the ultracold fermionic atom gas.\textsuperscript{138,139}

Given the above background, in this study, we investigate the pairing competition between the spin singlet and spin triplet pairings, and the FFLO state of the superconductivity mediated by spin and charge fluctuations in a Q1D extended Hubbard model for (TMTSF)$_2$X by random phase approximation (RPA).\textsuperscript{140–144} While the competition was studied only by comparison with the eigenvalue of the gap equation at a fixed temperature as indicated in ref. 54, here we calculate the superconducting temperature $T_c$ for each pairing state. This enables us to obtain a phase diagram in the $T$ (temperature)- $h_z$ (field)- $V_\sigma$ (strength of the charge fluctuation) space, where we find that (i) consecutive transitions from singlet pairing to the FFLO state and further to $S_z = 1$ triplet pairing can occur upon increasing the magnetic field in the vicinity of the SDW+CDW phase, and (ii) the enhancement of the charge fluctuations leads to a significant increase in parity mixing in the FFLO state, where the $S_z = 0$ triplet/singlet component ratio in the gap function can be close to unity.

### 2. Formulation

The extended Hubbard model for (TMTSF)$_2$X [Fig. 1(a)] that takes into account the Zeeman effect is given as

\begin{equation}
H = \sum_{i,j,\sigma,\sigma'} t_{ij\sigma} c_{i\sigma}^\dagger c_{j\sigma'} + \frac{U}{2} \sum_i n_{i\uparrow} n_{i\downarrow} \nonumber \\
+ \sum_{i,j,\sigma,\sigma'} V_{ij} n_{i\sigma} n_{j\sigma'}.
\end{equation}

Here, $t_{ij\sigma} = t_{ij} + h_z \text{sgn}(\sigma) \delta_{ij}$, where the hopping parameters $t_{ij}$ considered are the intrachain ($a$-axis direction in (TMTSF)$_2$X) nearest-neighbor $t_x$ and the interchain ($b$-axis direction) nearest-neighbor $t_y$, $t_z = 1.0$ being taken as the energy unit. $U$ is the on-site interaction, and $V_{ij}$ are the off-site interactions: $V_x$, $V_{z_2}$, and $V_{z_3}$ are the nearest-, next-nearest, and 3rd-nearest-neighbor interactions within the chains, and $V_y$ is the interchain interaction. Note that we ignore the orbital effect, assuming that the magnetic field is applied parallel to the conductive $x$-$y$ plane, assuming a sufficiently large Maki parameter. (Since we neglect the orbital effect, the direction of the magnetic field within the $x$-$y$ plane is irrelevant within our approach.)

The bare susceptibilities, consisting of bubble-type and ladder-type diagrams, are written as

\begin{equation}
\chi_0^{\sigma\sigma'}(k) = -\frac{1}{N} \sum_q \frac{f(\xi_\sigma(k+q)) - f(\xi_\sigma(q))}{\xi_\sigma(k+q) - \xi_\sigma(q)},
\end{equation}

\begin{equation}
\chi_0^+-\chi_0^-(k) = -\frac{1}{N} \sum_q \frac{f(\xi_\sigma(k+q)) - f(\xi_\sigma(q))}{\xi_\sigma(k+q) - \xi_\sigma(q)},
\end{equation}

where $\xi_\sigma(k)$ is the band dispersion that takes into account the Zeeman effect measured from the chemical potential $\mu$ and $f(\xi)$ is the Fermi distribution function.

Within RPA that takes into account the magnetic field parallel to the spin quantization axis $\hat{z}^{53,54}$ the longitudinal spin and charge susceptibilities are given by

\begin{equation}
\chi_{sp}^{zz} = \frac{1}{2} (\lambda_{1\uparrow\downarrow} + \lambda_{1\downarrow\uparrow} - \lambda_{1\uparrow\uparrow} - \lambda_{1\downarrow\downarrow}),
\end{equation}

\begin{equation}
\chi_{ch} = \frac{1}{2} (\lambda_{1\uparrow\downarrow} + \lambda_{1\downarrow\uparrow} + \lambda_{1\uparrow\uparrow} + \lambda_{1\downarrow\downarrow}),
\end{equation}

where $\lambda_{1\uparrow\downarrow}$ and $\lambda_{1\downarrow\uparrow}$ are the nearest-neighbor interactions within the chains, and $\lambda_{1\uparrow\uparrow}$ and $\lambda_{1\downarrow\downarrow}$ are the next-nearest-neighbor interactions within the chains.
The transverse spin susceptibility is given by

\[ \chi_{\sigma\sigma}(k) = \frac{1}{N} \sum_q [V_{\text{sub}}^{\sigma\sigma}(k - q) + V_{\text{lad}}^{\sigma\sigma}(k + q)] \]

where \( q = q_\pm = q \pm Q_c \), and \( \lambda_{Q_c}^{\sigma\sigma} \) is the eigenvalue of this linearized gap equation. The center of mass momentum \( Q_c \), which gives the maximum value of \( \lambda_{Q_c}^{\sigma\sigma} \), lies in the \( x \)-direction, while \( \lambda_{Q_c}^{\sigma\sigma} \) takes its maximum at \( Q_c = (0, 0) \) because the electrons with the same spin can be paired as \((k \sigma, -k \sigma)\) for all \( k \).

In our calculation, the spin singlet and triplet components of the gap function in the opposite spin pairing channel as

\[ \varphi_{SS}(k) = \frac{\varphi^{1\uparrow}(k) - \varphi^{1\downarrow}(k)}{2}, \]
\[ \varphi_{ST}(k) = \frac{\varphi^{1\uparrow}(k) + \varphi^{1\downarrow}(k)}{2}. \]

The pairing interactions from the bubble and ladder diagrams are given by

\[
\begin{align*}
V_{\text{sub}}^{\sigma\sigma}(k) &= U + V(k) + \frac{U^2}{2} \chi_{\text{sp}}^{\sigma\sigma}(k) \\
&\quad - \frac{U + 2V(k)}{2} \chi_{ch}(k), \\
V_{\text{lad}}^{\sigma\sigma}(k) &= U^2 \chi_{\text{sp}}^{\sigma\sigma}(k), \\
V_{\text{sub}}^{\sigma\sigma}(k) &= V(k) - 2[U + V(k)] V(k) \chi_{\sigma\sigma}(k) \\
&\quad - V(k)^2 \chi_{\sigma\sigma}(k) - [U + V(k)]^2 \chi_{\sigma\sigma}(k), \\
V_{\text{lad}}^{\sigma\sigma}(k) &= 0.
\end{align*}
\]

The linearized gap equation for Cooper pairs with the total momentum \( 2Q_c \) (\( Q_c \) represents the center of mass momentum) is given by

\[ \lambda_{Q_c}^{\sigma\sigma}(k) = \frac{1}{N} \sum_q [V_{\text{sub}}^{\sigma\sigma}(k - q) + V_{\text{lad}}^{\sigma\sigma}(k + q)] \]

where \( q = q_\pm = q \pm Q_c \), and \( \lambda_{Q_c}^{\sigma\sigma} \) is the eigenvalue of this linearized gap equation. The center of mass momentum \( Q_c \), which gives the maximum value of \( \lambda_{Q_c}^{\sigma\sigma} \), lies in the \( x \)-direction, while \( \lambda_{Q_c}^{\sigma\sigma} \) takes its maximum at \( Q_c = (0, 0) \) because the electrons with the same spin can be paired as \((k \sigma, -k \sigma)\) for all \( k \).

We define the singlet and triplet components of the gap function in the opposite spin pairing channel as

\[ \varphi_{SS}(k) = \frac{\varphi^{1\uparrow}(k) - \varphi^{1\downarrow}(k)}{2}, \]
\[ \varphi_{ST}(k) = \frac{\varphi^{1\uparrow}(k) + \varphi^{1\downarrow}(k)}{2}. \]

In our calculation, the spin singlet and triplet components of the gap function in the FFLO state are essentially the d-wave and f-wave, respectively, as schematically shown in Fig. 1(b): thus, we write the singlet \((S_z = 0)\) component of the FFLO gap \( \varphi_{SS}(\varphi_{ST}) \) in eq. (15) as \( \varphi_{SSd}(\varphi_{STf}) \), where \( SSd(\text{STf}) \) stands for spin singlet d-wave (spin triplet f-wave) with \( S_z = 0 \) pairing. The eigenvalue of each pairing state is determined as follows. \( \lambda_{Q_c}^{\sigma\sigma} \) with \( Q_c = (0, 0) \) gives the eigenvalue of the singlet d-wave pairing \( \lambda_{Q_c}^{\sigma\sigma} \) with \( Q_c = (0, 0) \) gives the eigenvalue for the spin triplet d-wave pairing \( S_{z+} = +1 \) \((S_{z-} = -1) \) states of the FFLO state, and \( \lambda_{Q_c}^{\sigma\sigma} \) gives the eigenvalue for the spin triplet d-wave pairing with \( S_{z_+} = +1 \) \((S_{z-} = -1) \) states of the FFLO state. The above-mentioned results of the determination of the eigenvalues are listed in Table I.

| Table I. Results of the determination of the eigenvalue of the linearized gap equation \( \lambda_{Q_c}^{\sigma\sigma} \). |
|---|
| Center of mass momentum and paired spins | Pairing symmetry or SC state |
| \( Q_c = 0, \sigma \neq \sigma' \) | singlet d-wave (\( \lambda_{SSd} \)) for \( \varphi_{STf}(k) = 0 \) |
| \( Q_c = 0, \sigma \neq \sigma' \) | \( S_z = 0 \) triplet f-wave (\( \lambda_{STf} \)) for \( \varphi_{SSd}(k) = 0 \) |
| \( Q_c = 0, \sigma = \sigma' \) | \( S_z = \pm 1 \) triplet f-wave (\( \lambda_{STf} \)) |
| \( Q_c \neq 0, \sigma \neq \sigma' \) | FFLO state (\( \lambda_{FFLO} \)) |
| \( Q_c \neq 0, \sigma = \sigma' \) | not dominant state |

Although RPA is quantitatively insufficient for discussing the absolute value of \( T_c \), we expect this approach to be valid for studying the competition between different pairing symmetries. In this paper, we fix the hopping parameters as \( t_x = 1.0 \) and \( t_y = 0.2 \), and the electron-electron interactions as \( U = 1.7, V_x = 0.9, V_{x2} = 0.45 \), and \( V_{x3} = 0.1 \), and vary \( V_y \). Since the dimerization of
TMTSF molecules is very small in (TMTSF)$_2$X compounds, we ignore the dimerization and fix the band filling as $n = 1.5$ (3/4 filling), where $n$ = number of electrons/number of sites. 1024×128 k-point meshes are taken, where we take a large number of $k_x$ meshes since the center of mass momentum $Q_c$, which gives the maximum value of the FFLO state, lies in the $x$-direction.

3. Results

3.1 Center of mass momentum and the gap function

In this section, we study the nature of the FFLO state in our model. Let us first study the center of mass momentum at which the FFLO state is most stabilized. The optimum $Q_c$ that most stabilizes the FFLO state can be determined as $Q_c$ at which the eigenvalue of the gap equation is maximized. In the following results, we set the interchain off-site interaction as $V_y = 0.35$. $\lambda^{ss}_{Q_c}$ with $Q_c = (Q_{cx}, Q_{cy})$ are given in units of $\pi/512$ for the $x$-direction and $\pi/64$ for the $y$-direction. Figure 2 shows the eigenvalue of the linearized gap equation in the opposite-spin pairing channel $\lambda^{ss}_{Q_c}$ as a function of the $x$-component of the center of mass momentum $Q_{cx}$ for various $Q_{cy}$. When the magnetic field is small ($h_z = 0.01$), the pairing state with $Q_c = (0, 0)$ dominates over other finite momentum states, as seen in Fig. 2(a). For a larger magnetic field ($h_z = 0.03$), a finite momentum pairing state with $Q_{cx} = 3$ and $Q_{cy} = 0$ dominates over other states in the opposite-spin pairing channel, as shown in Fig. 2(b). When the magnetic field is increased up to $h_z = 0.06$, a finite momentum pairing state with $Q_{cx} = 7$ and $Q_{cy} = 0$ is the most dominant, but the eigenvalue $\lambda^{ss}_{Q_c}$ itself decreases, as shown in Fig. 2(c). Further studying other $h_z$ cases, we find that the most dominant center of mass momentum lies in the $x$-direction, and the magnitude of the center of mass momentum increases with increasing magnetic field.

The direction of the center of mass momentum vector $Q_c$ can be understood from the Fermi surface split by the Zeeman effect shown in Fig. 3. The electron pair part, i.e., the particle-particle susceptibility, in the linearized gap equation is rewritten as

$$f(\xi_\sigma(q + Q_c)) - f(\xi_\sigma(-q + Q_c))$$

$$= \frac{1}{\beta} \sum_{\epsilon_n} G_\sigma(q + Q_c, i\epsilon_n) G_{\sigma'}(-q + Q_c, -i\epsilon_n),$$

(16)

where $\xi_\sigma(\epsilon + k + Q_c)$ is the same as $\xi_\sigma(k - Q_c)$ since $\xi_\sigma(k) = \xi_\sigma(-k)$ is satisfied. If the $\sigma$ spin electron energy at the wave vector $q + Q_c$ and the $\sigma'$ spin electron energy at the wave vector $-q + Q_c$ are close to the Fermi energy, the denominator is small and eq. (16) can take a large value. For a quasi-one-dimensional system, the number of wave vectors $q$ that satisfies such a condition becomes the largest when the vector $Q_c$ is in the $k_x$ direction.

Next, we study the gap functions normalized by the maximum value of the singlet component gap function in the FFLO state. We set the parameters as $h_z = 0.03$, $V_y = 0.35$, and $T = 0.012$, where the FFLO state which has the finite center of mass momentum as $(Q_{cx}, Q_{cy}) = (3, 0)$ is the most dominant, as described later. Note that the $S_z = \pm 1$ triplet pairings always have the maximum value of the eigenvalue $\lambda^{ss}_{Q_c}$ at $Q_c = (0, 0)$, as mentioned previously. As shown in Figs. 4(a) and 4(b), the singlet component of the gap function in the FFLO state is the $d$-wave and the $S_z = 0$ triplet component is the $f$-wave. The maximum value of the $S_z = 0$ triplet gap component in the FFLO state almost reaches unity. Thus, the singlet $d$-wave component and the $S_z = 0$ triplet $f$-wave component strongly mix in this FFLO state. The gap function in the $S_z = \pm 1$ triplet pairings has the $f$-wave form shown in Figs. 4(c) and 4(d).
neighboring repulsive interaction, favors the triplet \( f \)wave pairing in the Q1D extended Hubbard model at quarter filling.\(^{39-43}\) The reason why the spin triplet \( f \)wave pairing can compete with the spin singlet \( d \)wave pairing in the Q1D extended Hubbard model is (i) the contribution of the \( 2k_F \) charge fluctuations in the pairing interaction enhances the spin triplet \( f \)wave pairing and suppresses the spin singlet \( d \)wave pairing, and (ii) \( f \) and \( d \)wave pairings have the same number of gap nodes intersecting the Fermi surface due to the disconnectivity of the Fermi surface (quasi-one-dimensionality). The above mechanism is valid even in the presence of the magnetic field, but more importantly, the spin triplet \( f \)wave-pairing mediated by the \( 2k_F \) spin + \( 2k_F \) charge fluctuations can be enhanced by applying the magnetic field since the bubble-type diagram enhanced by the field contributes to the pairing interaction without being paired with the bubble-type diagram, which is suppressed by the field.\(^{53}\)

Actually, our previous work shows a clear correlation between the \( S_z = 0 \) triplet ratio in the FFLO state and the ratio of the eigenvalue between the \( S_z = 0 \) triplet and singlet pairings obtained by the formulation of separating the singlet and \( S_z = 0 \) triplet channels.\(^{34}\) From the above, we can understand not only the appearance of the \( d \)wave \(( f \)wave\) gap in the singlet \(( S_z = 0 \) triplet\) component of the opposite-spin pairing channel and the \( f \)wave gap in the parallel-spin pairing channel, but also the large parity mixing of the singlet and \( S_z = 0 \) triplet components in the FFLO state.

Figure 5 shows the parity mixing \( \varphi_{ST}/\varphi_{S\bar{S}d} \) in the opposite-spin pairing channel as a function of the \( x \)component of the center of mass momentum \( Q_{cx} \) for several \( Q_{cy} \). Note that we need to bear the \( Q_c \) dependence of the eigenvalue \( \lambda_{Q_c}^2 \), as shown in Fig. 2, in order to see the \( Q_c \) dependence of the parity mixing rate because the most dominant pairing state in the opposite-spin pairing state is determined by the value of \( \lambda_{Q_c}^2 \). For instance, we have seen in Fig. 2(a) that the singlet \( d \)wave pairing, i.e., the opposite-spin pairing state with \( (Q_{cx}, Q_{cy}) = (0, 0) \), is the most dominant in the small magnetic field regime. In Fig. 5(a), the parity mixing rate for \( h_z = 0.01 \varphi_{ST}/\varphi_{S\bar{S}d} \) is zero at \( (Q_{cx}, Q_{cy}) = (0, 0) \). Therefore, no \( S_z = 0 \) triplet \( f \)wave component is present in this pairing state, and the opposite-spin pairing channel is a purely spin singlet \( d \)wave. For \( h_z = 0.03 \), we have seen in Fig. 2(b) that the FFLO state with \( Q_{cx} = 3 \) and \( Q_{cy} = 0 \) is dominant. As shown in Fig. 5(b), the parity mixing rate for \( Q_{cx} = 3 \) and \( Q_{cy} = 0 \) takes a large value \( \varphi_{ST}/\varphi_{S\bar{S}d} \approx 0.8 \). For \( h_z = 0.06 \), where the FFLO state with \( Q_{cx} = 7 \) and \( Q_{cy} = 0 \) is dominant (Fig. 2(c)), the parity mixing rate increases, i.e., \( \varphi_{ST}/\varphi_{S\bar{S}d} \approx 1.0 \), as shown in Fig. 5(c), which means that the singlet \( d \)wave component and the \( S_z = 0 \) triplet \( f \)wave component are strongly mixed in this FFLO state (provided this state is actually realized). The strong parity mixing in the FFLO state can be understood as a consequence of the breaking of the spacial inversion symmetry in the superconducting state. Previous theoretical studies have shown that the parity mixing with the singlet and triplet pairings stabilizes the FFLO state more when only the singlet

The appearance of the \( d \)wave gap in the singlet component and the \( f \)wave gap in the \( S_z = 0 \) triplet component in the FFLO state is understood as follows. In zero field, the singlet \( d \)wave pairing mediated by the \( 2k_F \) spin fluctuations is favored in the Q1D Hubbard model, namely, the large pairing interaction due to the \( 2k_F \) spin fluctuations stabilizes the spin singlet \( d \)wave pairing.\(^{34-37,39}\) Moreover, the coexistence of \( 2k_F \) charge fluctuations, which is induced by the second-nearest-
Fig. 5. (Color online) $Q_{cx}$-dependence of the parity mixing in the opposite-spin pairing channel, $\phi_{STf}/\phi_{SSd}$, for (a) $h_z = 0.01$, (b) $h_z = 0.03$, and (c) $h_z = 0.06$ at $V_y = 0.35$.

Fig. 6. (Color online) Eigenvalue of the linearized gap equation, $\lambda^{\sigma \bar{\sigma}}_{Q_c}$, plotted as a function of the temperature $T$ for (a) $h_z = 0.01$, (b) $h_z = 0.03$, and (c) $h_z = 0.06$ with $V_y = 0.35$. Note that SSd and ST$_{f\pm 1}$ have $Q_c = 0$, and the FFLO state has a finite $Q_c$ that maximizes the eigenvalue of the opposite-spin channel in Fig. 2.

component is considered.

3.2 Temperature dependence

Next, we investigate the temperature dependence of the eigenvalue, $\lambda^{\sigma \bar{\sigma}}_{Q_c}$, in both the opposite- and parallel-spin pairing states. We have confirmed that the center of mass momentum that most stabilizes the FFLO state is unchanged upon lowering the temperature for a fixed magnetic field. For $h_z = 0.01$, the eigenvalue $\lambda_{SSd} = \lambda^{\sigma \bar{\sigma}}_{Q_c = 0}$ of the spin singlet $d$-wave pairing reaches unity, as shown in Fig. 6(a). In this small magnetic field regime, the FFLO state is absent, as shown in Fig. 2(a). For $h_z = 0.03$, the singlet $d$-wave pairing is suppressed and the eigenvalue $\lambda_{FFLO} = \lambda^{\sigma \bar{\sigma}}_{Q_c = 0}$ of the FFLO state with $Q_{cx} = 3$ and $Q_{cy} = 0$ reaches unity as seen in Fig. 6(b). For $h_z = 0.06$, the FFLO state with $Q_{cx} = 7$ and $Q_{cy} = 0$ does not develop much upon lowering the temperature, while the eigenvalue $\lambda_{ST_{f\pm 1}} = \lambda^{\sigma \bar{\sigma}}_{Q_c = 0}$ for the $S_z = 1$ triplet $f$-wave state reaches unity, as shown in Fig. 6(c). The eigenvalue of the singlet $d$-wave and
$S_z = -1$ triplet $f$-wave pairings remains small even in the low temperature regime.

### 3.3 Calculated phase diagram

We now obtain a phase diagram in the temperature $T$ versus the magnetic field $h_z$ for several values of interchain off-site interaction $V_y$ (which controls the strength of the charge fluctuations). Figure 7(a) shows a plot of the critical temperature $T_c$ against the magnetic field $h_z$ for $V_y = 0.35$, where the $2k_F$ charge fluctuations are slightly weaker than the $2k_F$ spin fluctuations. The critical temperature in zero field is $T_c \simeq 0.012$ and the estimated value of Pauli's paramagnetic field is $h_z^P \simeq 0.03$. We see that a consecutive transition from singlet pairing to the FFLO state and further to $S_z = 1$ triplet pairing occurs upon increasing the magnetic field.

This consecutive pairing transition can be understood as follows. It is known that the FFLO state can be stabilized by the quasi-one-dimensionality, namely, the nesting of the Fermi surface. Thus, the quasi-one-dimensionality of the present model is one of the origins of the transition from the $d$-wave to the FFLO state. The origin of the pairing transition from the FFLO state to the $S_z = 1$ triplet pairing is understood by our previous study, where we have shown that the triplet pairing due to the coexisting $2k_F$ spin and $2k_F$ charge fluctuations is strongly enhanced by the direct contribution of the unpaired bubble diagram enhanced by the field.

Here, we emphasize that we ignore the orbital pair breaking effect in this study because our aim in this work is to study the competition between the singlet, FFLO, and triplet pairings in the case when the magnetic field is applied in the conductive plane, i.e., the $a$-$b$ plane of (TMTSF)$_2$X. For discussing the above pairing competition, the Zeeman splitting effect is essential for the FFLO state; thus, we ignore the orbital pair breaking effect at the beginning. Although this effect is small in applying the magnetic field parallel to the conductive plane, the orbital pair breaking effect is present in actual materials. Furthermore, previous studies have shown that the orbital pair breaking effect is important in discussing the FFLO superconductivity.

As shown in Fig. 7(a), there seems to be a reentrance from the superconducting state to another superconducting state intervened by the normal state. However, it is much more reasonable to consider that this reentrance does not actually occur owing the presence of the orbital pair breaking effect. If this effect is taken into account, not only the FFLO state but also the singlet and triplet pairing states should strongly be suppressed upon increasing the magnetic field. Figure 7(b) shows a schematic figure of the effect of the orbital pair breaking, where the $T_c$ obtained (without the orbital effect) in Fig. 7(a) (thin curve) is suppressed down to the thick curve. The thick curve in Fig. 7(b) is reminiscent of the experimental $T$-$H$ phase diagram in the $T$-$h_z$ space, where black solid arrows schematically represent the orbital pair breaking effect.

![Fig. 7. (Color online) (a) Calculated phase diagram in $h_z$-$T$ space for $V_y = 0.35$, where the green dashed line indicates the $T_c$ for the spin singlet $d$-wave, the red solid line represents that for the FFLO state, and the blue dotted line indicates that for the $S_z = 1$ spin triplet $f$-wave. The spin singlet $d$-wave is omitted as SSD and the $S_z = 1$ spin triplet $f$-wave is ST$f^{+1}$. The same notation is used in Figs. 8 and 9. (b) Schematic figure of the orbital pair breaking effect on the superconducting phase diagram in $T$-$h_z$ space, where black solid arrows schematically represent the orbital pair breaking effect.](image)

Next, we study the effect of the interchain interaction $V_y$ on the phase diagram in the temperature $T$ versus the magnetic field $h_z$ space. Figure 8(a) shows the critical temperature $T_c$ at each magnetic field $h_z$ for $V_y = 0.38$. The magnetic field at which the transition from the FFLO state to the $S_z = 1$ triplet $f$-wave pairing occurs is smaller than that in the $V_y = 0.35$ case. The critical temperature $T_c$ for $V_y = 0.32$ is shown in Fig. 8(b), which shows that the magnetic field at which the FFLO state gives way to the $S_z = 1$ triplet $f$-wave pairing is larger than those in the previous phase diagrams shown in Figs. 7(a) and 8(a). The difference between the two phase diagrams is due to the fact that the $2k_F$ charge fluctuations enhance the triplet $f$-wave pairing; thus, the FFLO state appears only in a small parameter regime in between the $d$- and $f$-wave pairings.

Summarizing the above-mentioned features, we show the phase diagram in $T$-$V_y$-$h_z$ space in Fig. 9. When $V_y$ is small and thus the $2k_F$ spin fluctuations are dominant over the $2k_F$ charge fluctuations, $T_c$ decreases and the transition from the spin singlet $d$-wave to the FFLO state occurs upon increasing $h_z$. In this FFLO state, the
strong parity mixing with the spin singlet $d$-wave component and the $S_z = 0$ spin triplet $f$-wave component occurs. In the large $V_y$ regime, the $2k_F$ charge fluctuations compete with the $2k_F$ spin fluctuations, and the consecutive pairing state transition from the spin singlet $d$-wave to the FFLO state and further to the $S_z = 1$ spin triplet $f$-wave upon increasing the $h_z$ at the critical temperature $T_c$ occurs. The $T_c$ enhancement of the $S_z = 1$ spin triplet $f$-wave pairing in the large $h_z$ regime can be understood by our previous work.\(^{53}\)

4. Conclusion

We have studied the competition between spin singlet, triplet, and FFLO superconductivities in a model for (TMTSF)$_2$X by applying the RPA method and solving the linearized gap equation within the weak coupling theory. We find the following:

(i) consecutive pairing transitions from singlet pairing to the FFLO state and further to $S_z = 1$ triplet pairing can occur upon increasing the magnetic field in the vicinity of the SDW+CDW coexisting phase.

(ii) in the FFLO state, the $S_z = 0$ spin triplet pairing component is mixed with the spin singlet pairing component, thus resulting in a large parity mixing.

Recent experiments for (TMTSF)$_2$ClO$_4$ suggest differences in superconducting properties in the low and high field regimes. The Knight shift study shows the presence of low field and high field pairing states, where the former is the spin singlet pairing and the latter is the FFLO state or the spin triplet pairing.\(^{31}\) The upper critical field studies have shown that only the clean sample, or more strictly, samples where the broadening of the nonmagnetic impurity is small, exhibits an upturn of the critical temperature curve in the high field parallel to the $a$ axis regime above $4T$; thus, the high field superconducting state is sensitive to the impurity content or the anisotropy of the impurity scattering potential.\(^{33}\) Between $4T$ and the Pauli limit around $2.5T$, there seems to be a different high field pairing state, in which superconductivity is stable against the impurities, but it is very sensitive to the tilt of the magnetic field out of the $a$-$b$ plane. The bottom line of these experiments is that there may be three kinds of pairing states, i.e., one low field state and two high field states. The correspondence between these experimental observations and the present study is not clear at the present stage, but the appearance of the three kinds of pairing states is indeed intriguing. It would be interesting to further investigate experimentally the possibility and nature of two kinds of high field pairing states.

One point that should be mentioned for (TMTSF)$_2$ClO$_4$ in particular is the presence of the anion ordering with the modulation wave vector $Q_{AO} = (0, \pi/b)$, which takes place near $T_{AO} \approx 24K$ when slowly cooled. Recent studies show that the anion ordering potential $(V_{AO})$ is around $0.02t_x$.\(^{145,146}\) The anion ordering leads to a folding of the Brillouin zone in the $k_y$-direction ($b$-direction), and in that case, the $d$-wave (and also $f$-wave in the same sense) gap can become nodeless because the folded Fermi surface becomes disconnected near the nodes of the gap, as has been suggested by Shimahara.\(^{147}\) This effect is neglected in our present study, and its effect on the pairing symmetry competition is an interesting future problem.

Another point to be mentioned is that in the present study, we do not take account of the retardation effect. By taking account of this effect, i.e., the frequency de-
dependence of the gap function, we can discuss the odd-frequency pairing state.148–150 It has been shown that odd-frequency pairing can be realized in a certain quasi-one-dimensional lattice.151 In particular, in the presence of non-uniformity, the odd-frequency pairing amplitude is ubiquitously generated.152–157 It is a future interesting problem to study the possible existence of odd-frequency pairing in quasi-one-dimensional organic superconductors.

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