Holon edge states in organic conductors (TMTTF)$_2$X in the charge-gap regime

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Using the bosonization technique, which separates charge and spin degrees of freedom, we study a possibility of formation of the holon edge states in a one-dimensional electron system with an energy gap in the charge sector. The results are applied to the quasi-one-dimensional organic conductors (TMTTF)$_2$X. The different roles of the bond and site dimmerizations in this material are discussed. We predict that the holon edge states should appear below the temperature of the recently discovered ferroelectric transition, where the inorganic anions X displace to asymmetric positions.

When the bulk electron states have an energy gap, additional states may exist on the surface with the energies inside the gap. Such surface states were studied for a long time in the cases where the gap has a band-structure origin. More recently, edge states attracted much interest in the cases where the gap originates from a phase transition in the electron system. Examples are midgap states in the high-$T_c$ d-wave cuprate superconductors and chiral states in the p-wave superconductor Sr$_2$RuO$_4$ (see, for example, Ref. [8] and references therein). Edge states in the quasi-one-dimensional (Q1D) organic conductors (TMTSF)$_2$X were studied for the triplet superconducting state and for the magnetic-field-induced spin-density-wave (FISDW) state, which exhibits the quantum Hall effect. In all of these cases, noninteracting electrons were subject to a mean-field potential, so the problem reduced to a single-particle Schrödinger-like equation with a boundary. However, it is known that a one-dimensional (1D) system of interacting electrons can be described in terms of separate charge and spin sectors (see, for example, review [9]). An edge state in such a system with a gap in the spin channel was studied in Ref. [8]. In this Letter, we show that one source of dimerization controls the existence and the localization length the edge states, whereas the other source determines their energy.

In our theoretical model, we neglect interchain coupling and consider just one semi-infinite chain. For simplicity, we will refer to holes as electrons and set $h = 1$. The electron band structure of the chain is described by the Hamiltonian

$$\hat{H} = \frac{t}{2} \sum_{n=1, s} \left[ \hat{\psi}_{n,s} \hat{\psi}_{n+1,s} + \text{H.c.} + \mu_n \hat{\psi}_{n,s} \hat{\psi}_{n,s} \right],$$

$$t_n = t - (-1)^n t/2, \quad \mu_n = \mu - (-1)^n \mu,$$

where the index $n$ labels the TMTTF sites, $s = \uparrow, \downarrow$ is the spin index, and $\hat{\psi}_{n,s}^{(t)}$ are the creation and annihilation operators of electrons. The mean values of the intersite tunneling amplitude and the chemical potential are $t$ and $\mu$, whereas $t$ and $\mu$ are their staggering parts produced by dimerization of the chain bonds and sites, respectively.

The energy dispersion for the Hamiltonian (1) and (2) is sketched in Fig. 1. For a given chemical potential $\mu$, there exist two Fermi points $\pm k_F$. To study low-energy properties of the system, we introduce the operators $\hat{R}$ and $\hat{L}$ describing the right- and left-moving electrons with the momenta close to $+k_F$ and $-k_F$.

![FIG. 1. A sketch of the (TMTTF)$_2$X chain. The vertical rectangles represent the organic molecules TMTTF, and the circles indicate the inorganic anions X. The filled objects (n = 0, 1, ..., ) show the actual chain, whereas the open objects (n = 0, -1, -2, ...) represent an artificial expansion of the system by the mirror reflection around the site n = 0.](image-url)
The wave functions $\psi_n$ expanded from the interval $(0, l)$ to include the site $n$ cause the chain dimerization. The correlation gap at $k = \pm \pi/4d$ is caused by umklapp interaction.

Using Eq. (3), the latter condition gives $\psi_1 = 0$, while keeping only the antisymmetric wave functions $(\hat{R})$, because there is no direct coupling between the intervals $(-l, 0)$ and $(0, l)$ other than through the point $n = 0$, where the wave function vanishes. As Fig. 2 shows, the mirror reflection changes the sign of the bond dimerization parameter $\bar{\epsilon}$, but keeps the same sign for the site dimerization $\bar{\mu}$. Thus, for the expanded problem, Eq. (3) should be replaced by $t_n = t - \text{sgn}(n)(-1)^n \bar{\epsilon}$. In the continuous expanded system, the boundary condition $\psi(0) = 0$ is satisfied by demanding that $\psi(x) = -\psi(-x)$. Using Eq. (3), the latter condition gives

$$R(x) = L(-x).$$

Dimerized chain at half filling. As a warm-up, let us study the edge states for noninteracting electrons at half filling, where $\mu = 0$ and $k_F = \pi/2d$ (see Fig. 2). Although the model (1) and (2) at half filling does not correspond to (TMTTF)$_2$X, it does describe some 1D polymers (12), which have both site and bond dimerization. The nondimerized part of the Hamiltonian (1) is

$$\hat{H}_0 = \sum_s \int_0^l dx v_F \left[ -\hat{R}_s(x) i\partial_x \hat{R}_s(x) + \hat{L}_s(x) i\partial_x \hat{L}_s(x) \right],$$

where $v_F = 2td$ is the Fermi velocity. The dimerized part of the Hamiltonian (1) gives the backscattering term:

$$\hat{H}_{bs} = \sum_s \int_0^l dx \left[ (-\bar{\mu} + i\bar{\tilde{t}}) \hat{R}_{s}^+(x) \hat{L}_s(x) + \text{H.c.} \right].$$

The energies $\varepsilon$ and the wave functions $R(x)$ and $L(x)$ of electron eigenstates can be found from the corresponding Schrödinger equation

$$\left( -i v_F \partial_x - \bar{\mu} + i\bar{\tilde{t}} \right) R(x) = \varepsilon \left( R(x) + L(x) \right).$$

Eq. (6) gives the spectrum $\varepsilon = \sqrt{v_F^2 k^2 + \Delta^2}$ for the bulk states with the energy gap $\Delta = \sqrt{\bar{\mu}^2 + \bar{\tilde{t}}^2}$.

With the boundary condition $\psi(0) = 0$, which translates into $R(0) = L(0)$ using Eq. (3), Eq. (6) also gives a solution localized at the edge (the Shockley state (8)):

$$R_e(x) = L_e(x) = e^{-\kappa x}, \quad \kappa = -\bar{\epsilon}/v_F.$$

Eq. (7) shows that the energy of the edge state is determined by the site dimerization $\bar{\mu}$, whereas its localization length $1/\kappa$ by the bond dimerization $\bar{\tilde{t}}$. The edge state exists only when $\bar{\tilde{t}} < 0$, i.e. when the edge site $n = 1$ is connected to the next site $(n = 2)$ by the long bond. That configuration is opposite to what is drawn in Fig. 2 where the first bond is short.

Using Eq. (6), we get Eq. (8) in the expanded picture:

$$- i\partial_x R(x) - [\bar{\mu} - i\bar{\tilde{t}} \text{sgn}(x)] R(-x) = \varepsilon R(x).$$

The edge state (8) maps onto a state localized around the kink in the imaginary part of the potential in Eq. (6), which is produced by the sign change of the bond dimerization $\bar{\tilde{t}}$ upon mirror reflection around $n = 0$. Such soliton states were studied for polymers in Ref. (12).

Quarter filling. In this case, $k_F = \pi/4d$, as shown in Fig. 2, and there is no single-particle energy gap at the Fermi level. However, a correlation gap (shown as the shaded bar in Fig. 4) may develop at the Fermi level due to interaction between electrons. Thus, we add the Hubbard interaction $U \sum_n \hat{c}_{n\uparrow} \hat{c}_{n\downarrow} \hat{c}_{n\downarrow} \hat{c}_{n\uparrow}$. It can be rewritten in the standard $g$-ology form (7) in terms of the slow fields $\hat{R}$ and $\hat{L}$. Without dimerization, one obtains

$$\hat{H}_{int} = \sum_{s,s'} \int_0^l dx \left\{ 2(g_{11} \delta_{ss'} + g_{1\downarrow} \delta_{ss'}) \hat{R}_{s'}^\dagger \hat{L}_{s'} \hat{R}_{s} \hat{L}_{s} + 2g_2 \hat{R}_{s'}^\dagger \hat{L}_{s'} \hat{R}_{s} \hat{L}_{s} + g_4 [\hat{R}_{s'}^\dagger \hat{R}_{s} \hat{R}_{s} \hat{L}_{s} + (\hat{R} \rightarrow \hat{L})] \right\},$$

where $\bar{s} = \downarrow, \uparrow$ for $s = \downarrow, \uparrow$.

Introducing the densities of spin and charge

$$\hat{\rho}_R = \frac{\hat{R}_{s}^\dagger \hat{R}_{s} + \hat{R}_{s'}^\dagger \hat{R}_{s'}}{\sqrt{2}}, \quad \hat{\sigma}_R = \frac{\hat{R}_{s}^\dagger \hat{R}_{s} - \hat{R}_{s'}^\dagger \hat{R}_{s'}}{\sqrt{2}},$$

the interaction Hamiltonian (8) can be written as
where \( g_5 = g_1 \parallel - 2g_2 \).

**The umklapp term.** Taking into account that dimerization (2), treated as a perturbation, hybridizes the states with the momenta \( k = \pm k_F = \pm \pi/4d \) and \( k = \mp 3\pi/4d \), we make the following replacement in Eq. (3):

\[
e^{\pm ik_F x} \rightarrow e^{\pm i\pi n / 4} - \frac{\hat{p}_x \mp i\hat{d}/\sqrt{2}}{\delta E} e^{\mp i3\pi n / 4},
\]

(14)

where \( \delta E = 2t\sqrt{2} \). Inserting Eqs. (3) and (14) into the Hubbard interaction term, we obtain the umklapp term

\[
\hat{H}_{\text{um}} = \int_0^l dx \left[ (g_3^2 + ig_3^4) \hat{R}_l^\dagger \hat{R}_l \hat{L}_l + \text{H.c.} \right],
\]

(15)

\[
g_3^2 = -\sqrt{2} U \hat{d} d / t, \quad g_3^4 = U \hat{d} d / t.
\]

(16)

The real part \( g_3^2 \) of the umklapp amplitude is proportional to the site dimerization energy \( \bar{\mu} \), which occurs due to the anion displacement, and the imaginary part \( g_3^4 \) is proportional to the bond dimerization \( \bar{t} \).

**Bosonization with a boundary.** As Eq. (4) shows, the problem on the expanded interval \((-l, l)\) can be formulated in terms of the right-moving electrons only. The kinetic energy \( \hat{H}_0 \) becomes

\[
\hat{H}_0 = -v_F \sum_s \int_{-l}^l dx \hat{R}_s^\dagger(x) i \partial_x \hat{R}_s(x),
\]

(17)

where \( v_F = td / \sqrt{2} \) for the quarter filling. Imposing the periodic boundary condition \( \hat{R}(-l) = \hat{R}(l) \) together with Eq. (1) results in the vanishing boundary condition on \( \hat{\psi} \) at the other end of the chain: \( \hat{\psi}(l) = 0 \). Now we can use the standard bosonization technique [2] for \( \hat{R} \). The fermion fields \( \hat{R}_s(x) \) can be represented in terms of the Bose fields \( \hat{\theta}_s(x) \):

\[
\hat{R}_s(x) = \hat{\eta}_s e^{i\hat{\theta}_s(x)} (2\pi\zeta)^{-1 / 2},
\]

(18)

where \( \zeta \) is a short-range cut-off distance of the order of \( d \), and \( \hat{\eta}_s \) are the Majorana fermions: \( \{\hat{\eta}_s, \hat{\eta}_t\} = 0, \hat{\eta}_s^2 = 1 \). The Bose fields obey the commutation relations

\[
[\hat{\theta}_s(x), \hat{\theta}_{s'}(x')] = i\pi \delta_{s s'} \text{sgn}(x - x').
\]

(19)

Using the linear combinations

\[
\hat{\rho}_s = (\hat{\theta}_s + \hat{\eta}_s) / \sqrt{2}, \quad \hat{\sigma}_s = (\hat{\theta}_s - \hat{\eta}_s) / \sqrt{2},
\]

(20)

the charge and spin densities (11), can be expressed in terms of the charge and spin Bose fields (18):

\[
\hat{\rho}_R(x) = \partial_x \hat{\theta}_R(x) / 2\pi, \quad \hat{\sigma}_R(x) = \partial_x \hat{\sigma}_R(x) / 2\pi.
\]

(21)

The Hamiltonian (17) can be rewritten in terms of the densities (21):

\[
\hat{H}_0 = v_F \int_{-l}^l dx \left[ \hat{\rho}_R^2(x) + \hat{\sigma}_R^2(x) \right].
\]

(22)

Substituting Eqs. (1) and (15) into the interaction Hamiltonian (11) and (13) and adding the kinetic energy (22), we get the full Hamiltonian of the system in the bosonized form. It takes the form \( \hat{H}_0 + \hat{H}_\sigma \), where the spin and charge sectors are separated. The charge Hamiltonian is

\[
\hat{H}_\rho = \int_{-l}^l dx \left[ \hat{\rho}_R^2(x) - g_5 \hat{\rho}_R(x) \hat{\rho}_R(-x) + \frac{2g_1}{(2\pi\zeta)^2} e^{-i\sqrt{2} \theta(x) - \hat{\theta}_R(-x)} \right].
\]

(23)

Notice that the imaginary part of the umklapp amplitude in Eq. (23) has a kink, because it is proportional to \( \bar{t} \), which changes sign between \( x < 0 \) and \( x > 0 \). The spin Hamiltonian is

\[
\hat{H}_\sigma = \int_{-l}^l dx \left[ \hat{\sigma}_R^2(x) - g_5 \hat{\sigma}_R(x) \hat{\sigma}_R(-x) + \frac{2g_1}{(2\pi\zeta)^2} e^{-i\sqrt{2} \theta(x) - \hat{\theta}_R(-x)} \right].
\]

(24)

In Eqs. (23) and (24), \( v_{\rho, \sigma} = v_F \pm g_5 / \pi \).

The quadratic parts of the Hamiltonians (23) and (24) can be diagonalized by the Bogoliubov transformations

\[
\hat{\theta}_{\rho, \sigma}(x) = \hat{\theta}_{\rho, \sigma}(x) \cos \phi_{\rho, \sigma} - \hat{\bar{\theta}}_{\rho, \sigma}(-x) \sinh \phi_{\rho, \sigma},
\]

(25)

\[
\hat{\rho}_R(x) = \hat{\bar{\rho}}(x) \cos \phi_{\rho} + \hat{\rho}(-x) \sinh \phi_{\rho},
\]

(26)

\[
\hat{\sigma}_R(x) = \hat{\bar{\sigma}}(x) \cos \phi_{\sigma} + \hat{\sigma}(-x) \sinh \phi_{\sigma},
\]

(27)

where \( \tanh 2\phi_{\rho} = g_5 / \pi v_F \) and \( \tanh 2\phi_{\sigma} = g_5 / \pi v_{\rho, \sigma} \). The charge Hamiltonian becomes

\[
\hat{H}_\rho = \int_{-l}^l dx \left[ \pi v_{\rho} (\partial_x \hat{\theta}_\rho(x) / 2\pi)^2 - \frac{g_5^2 + ig_5^4 \text{sgn}(x)}{(2\pi\zeta)^2} e^{-i\sqrt{2} \theta(x) - \hat{\theta}_R(-x)} \right],
\]

(28)

where \( v_{\rho} = v_F / \cosh 2\phi_{\rho} \) and \( K_{\rho} = e^{2\phi_{\rho}} \). Similarly, for the spin Hamiltonian, we get

\[
\hat{H}_\sigma = \int_{-l}^l dx \left[ \pi v_{\sigma} (\partial_x \hat{\theta}_\sigma(x) / 2\pi)^2 + \frac{2g_1}{(2\pi\zeta)^2} e^{-i\sqrt{2} \theta(x) - \hat{\theta}_R(-x)} \right],
\]

(29)

where \( v_{\sigma} = v_F / \cosh 2\phi_{\sigma} \) and \( K_{\sigma} = e^{2\phi_{\sigma}} \). The umklapp term [the last term in Eq. (23)] is irrelevant when \( K_{\rho} > 1 \). In the opposite case \( K_{\rho} < 1 \), this
term is relevant and leads to opening of an energy gap in the charge sector. At the particular value \( K_\rho = 1/2 \), the charge Hamiltonian \( \hat{H}_\rho \) can be mapped to a model of noninteracting fermions with an energy gap [3]. By introducing the effective fermions (holons)

\[
\tilde{\psi}_\rho(x) = e^{i\theta_\rho(x)}(2\pi\zeta)^{-1/2},
\]

and taking into account the commutation relations [19], the last term in Eq. (28) can be written as

\[
e^{-i(\theta_\rho(x) - \theta_\rho(-x))} \frac{(2\pi\zeta)^2}{(2\pi\zeta)^2} = -i \text{sign}(x) \frac{\tilde{\psi}_\rho^\dagger(x)\tilde{\psi}_\rho(-x)}{2\pi\zeta}.
\]

Then the charge Hamiltonian (28) becomes

\[
\hat{H}_\rho = \int dx \left\{ -\tilde{\psi}_\rho \tilde{\psi}^\dagger_\rho(x) i\partial_x \tilde{\psi}_\rho(x) - [g_3^b - ig_3^a \text{sign}(x)] \tilde{\psi}_\rho^\dagger(x) \tilde{\psi}_\rho(-x)/2\pi \right\}.
\]

The energy spectrum \( \varepsilon_\rho \) of the Hamiltonian (32) can found from the corresponding Schrödinger equation

\[
-i\tilde{\psi}_\rho \partial_x \tilde{\psi}^\dagger_\rho(x) - \frac{g_3^b - ig_3^a \text{sign}(x)}{2\pi\zeta} \tilde{\psi}_\rho(-x) = \varepsilon_\rho \tilde{\psi}_\rho(x).
\]

Eq. (33) is formally equivalent to Eq. (8) with \( g_3^b \) and \( g_3^a \) playing the roles of \( \tilde{\mu} \) and \( \tilde{t} \), respectively. However, as Eq. (10) shows, \( g_3^b \propto \tilde{t} \) and \( g_3^a \propto \tilde{\mu} \), so the roles of \( \tilde{\mu} \) and \( \tilde{t} \) are reversed in Eq. (33) compared with Eq. (8). This is a consequence of the factor \( -i \text{sign}(x) \) in Eq. (21). Eq. (33) gives the spectrum \( \varepsilon_\rho = \sqrt{\tilde{\mu}^2 \tilde{t}^2 + \Delta_\rho^2} \) for the bulk states with the charge gap \( \Delta_\rho = \sqrt{(g_3^b)^2 + (g_3^a)^2}/2\pi\zeta \). It also gives an edge solution localized around \( x = 0 \):

\[
\tilde{\psi}_{\text{pc}}(x) = e^{-\kappa |x|},
\]

\[
\varepsilon_{\text{pc}} = -g_3^b/2\pi\zeta = -\Delta_\rho \tilde{t}/\sqrt{\tilde{t}^2 + 2\tilde{\mu}^2};
\]

\[
\kappa = -g_3^a/2\pi\zeta \tilde{\mu} = (\Delta_\rho/\tilde{\mu}) \tilde{\mu}/\sqrt{\tilde{t}^2 + 2\tilde{\mu}^2}/2.
\]

where we used Eq. (10) assuming \( U > 0 \) for the repulsive Hubbard model. We see that, opposite to the electron edge state [8], the energy (34) of the holon edge state [24] is determined by the bond dimerization \( \tilde{t} \) and its localization length (36) is controlled by the site dimerization \( \tilde{\mu} \). The holon edge state exists only when \( g_3^a < 0 \), i.e. \( \tilde{\mu} > 0 \). Taking into account Eq. (2), we conclude that the holon edge state exists when the chemical potential of the edge site \( n = 1 \) is higher, i.e. when the anion displaces toward the edge site, as shown in Fig. 2. Thus, we predict that the holon edges states should appear in (TMTTF)_2X below the anion transition temperature [1]. Their energies (35) depend on whether the first bond at the edge is short or long.

Similar consideration [8] can be done for the spin Hamiltonian [29]. A gap in the spin sector opens when \( K_\rho < 1 \), i.e. \( g_{11} < 0 \) [7], whereas the required condition for the existence of an edge state is \( g_{11} > 0 \). However, \( g_{11} = g_{11} \) in a physical system because of the spin SU(2) invariance. So, it is not possible to satisfy the conditions for opening of a gap and existence of an edge state simultaneously. Thus, we conclude, contrary to Ref. [8], that spin edge states cannot exist.

In conclusion, we have shown that holon edge states may appear in a 1D model of interacting electrons with an energy gap in the charge sector. The existence of the holon edge state and its localization length are controlled by the real part of the umklapp interaction amplitude, whereas its energy is determined by the imaginary part. In the quasi-one-dimensional organic conductors (TMTTF)_2X, these umklapp amplitudes are proportional to the site and bond dimerizations, correspondingly. The bond dimerization is always present in these materials. However, the site dimerization occurs only below the recently discovered ferroelectric transition, where the inorganic anions X displace to asymmetric positions [11]. We predict that the holon edge states should appear below the anion transition. They could be probed by electron tunneling into the ends of 1D chains or by other types of spectroscopy.

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[1] S. G. Davison and M. Stešlicka, Basic Theory of Surface States (Oxford University Press, Oxford, 1996).
[2] C.-R. Hu, Phys. Rev. Lett. 72, 1526 (1994).
[3] K. Sengupta, H.-J. Kwon, and V. M. Yakovenko, cond-mat/0106198.
[4] TMTSF stands for tetramethyltetraselenafalvalene, X for inorganic anions such as PF_6 and AsF_6, and TMTTF for tetramethyltetrafluafulvalene.
[5] K. Sengupta, I. Žutić, H.-J. Kwon, V. M. Yakovenko, and S. Das Sarma, Phys. Rev. B 63, 144531 (2001).
[6] K. Sengupta, H.-J. Kwon and V. M. Yakovenko, Phys. Rev. Lett. 86, 1094 (2001).
[7] Yu. A. Firsov, V. N. Prigorin, and Chr. Seidel, Physics Reports 126, 245 (1985).
[8] M. Fabrizio and A. O. Gogolin, Phys. Rev. B 51, 17827 (1995).
[9] A. O. Gogolin, Phys. Rev. B 54, 16063 (1996); K. Le Hur, Europhys. Lett. 49, 768 (2000).
[10] T. Ishiguro, K. Yamaji, and G. Saito, Organic Superconductors (Springer, Berlin, 1998).
[11] F. Nad, P. Monceau, C. Carcel, and J. M. Fabre, J. Phys. Cond. Matt. 12, L435 (2000); D. S. Chow et al., Phys. Rev. Lett. 85, 1698 (2000); P. Monceau, F. Ya. Nad, and S. Brazovskii, Phys. Rev. Lett. 86, 4080 (2001).
[12] S. A. Brazovskii, Zh. Eksp. Teor. Fiz. 78, 677 (1980) [Sov. Phys. JETP 51, 342 (1980)]; S. A. Brazovskii, N. N. Kirova, and S. I. Matveenko, Zh. Eksp. Teor. Fiz. 86, 743 (1984) [Sov. Phys. JETP 59, 434 (1984)].
[13] A. Luther and V. J. Emery, Phys. Rev. Lett. 33, 589 (1974).