Ground-state properties of the two-band model for halogen-bridged metal complexes

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Based on a symmetry argument, we systematically reveal Hartree-Fock broken-symmetry solutions of the one-dimensional two-band extended Peierls-Hubbard model. Performing numerical investigations as well, the possibility of novel density-wave states appearing is argued.

Keywords: Electron-density calculations, Magnetic phase transitions

I. INTRODUCTION

One-dimensional two-band models with competing electron-electron (el-el) and electron-phonon (el-ph) interactions have been attracting considerable interest. Such models cover quasi-one-dimensional materials such as halogen-bridged transition-metal (MX) linear-chain complexes and charge-transfer (CT) salts with mixed-stacks of alternating donor and acceptor molecules.

One of the most interesting consequences of intrinsic multiband effects and the competition between el-el and el-ph interactions may be the variety of ground states [3][4]. Mixed-stack CT compounds [3][4] such as TTF-chloranil and TTeC2TTF-TCNQ may be described by a half-filled two-band model with site-off-diagonal el-ph coupling. They are dimerized into bond-order-wave (BOW) states at low temperatures, which is recognized as a charge-transfer-induced spin-Peierls transition. Ground states of MX compounds, which may be described by a 3/4-filled two-band model with site-diagonal el-ph coupling, strongly depend on the constituent metal and halogen ions. The conventional Pt compounds have the ground state with a charge density wave (CDW) on the metal sites induced by a dimerization of the halogen-ion sublattice, whereas recently synthesized Ni compounds [9][10] show a regular-chain structure with a spin density wave (SDW) on the metal sites. Although the interchain hydrogen-bond networks are not negligible here, yet the competition between the CDW and SDW states may more or less be recognized as a crossover between the Peierls and Mott insulators. Thus one-dimensional el-ph systems show rich phase diagrams and may possess further ground states unrevealed.

II. MODEL HAMILTONIAN

We study the one-dimensional two-band extended Peierls-Hubbard model:

\[
\mathcal{H} = \sum_{n=1}^{L} \sum_{s=\pm} \left[ \varepsilon_M - \beta(u_n - u_{n-1}) \right] a_{1:n,s}^\dagger a_{1:n,s} + \sum_{s=\pm} \varepsilon_X a_{2:n,s}^\dagger a_{2:n,s}
\]

\[
- \sum_{n=1}^{L} \sum_{s=\pm} \left[ (t - \alpha u_n) a_{1:n,s}^\dagger a_{2:n,s} + (t + \alpha u_{n-1}) a_{1:n,s} a_{2:n-1,s} + \text{H.c.} \right] \\
+ \sum_{n=1}^{L} U_M a_{1:n,+}^\dagger a_{1:n,+} a_{1:n,-}^\dagger a_{1:n,-} \\
+ \sum_{n=1}^{L} U_X a_{2:n,+}^\dagger a_{2:n,+} a_{2:n,-}^\dagger a_{2:n,-} \\
+ \sum_{n=1}^{L} \sum_{s,s' = \pm} \left[ a_{1:n,s}^\dagger a_{1:n,s} a_{2:n,s'}^\dagger a_{2:n,s'} + \frac{K}{2} \sum_{n=1}^{L} u_n^2 \right].
\] (2.1)

Here we assume the Hamiltonian to describe MX chains. Now the notation of the Hamiltonian (2.1) is recognized as follows: \(a_{1:n,s}^\dagger\) and \(a_{2:n,s}^\dagger\) are the creation operators of an electron with spin \(s\) in the metal \(d_z\) and halogen \(p_z\) orbitals at the unit cell \(n\), respectively, \(u_n\) the chain-direction displacement from the uniform lattice spacing of the halogen atom at the unit cell \(n\), and \(L\) the number of unit cells; \(\varepsilon_M\) and \(\varepsilon_X\) are the energies of the metal \(d_z\) and halogen \(p_z\) orbitals on isolated atoms, respectively, \(t\) the transfer energy of hopping between these levels, \(U_M\), \(U_X\), and \(V\) the el-el interactions on the metal atoms, on the halogen atoms, and between the neighboring metal and halogen atoms, respectively; \(\alpha\), \(\beta\), and \(K\) denote the site-off-diagonal and site-diagonal el-ph coupling constants and the elastic constant, respectively. We note that the model is rather general and may essentially be applied to various materials. For example, replacing the \(d_z\) and \(p_z\) orbitals by \(p\) orbitals of donor and acceptor molecules, we can immediately switch our argument to organic mixed-stack CT compounds. We compactly rewrite Hamiltonian (2.1) as

\[
\mathcal{H} = \sum_{i,j,k,q,s,s'} \langle i : k + q, s | t | j : k', s' \rangle a_{i,k+q,s}^\dagger a_{j,k',s'} + \frac{1}{2} \sum_{i,j,m,n,k',q,s,s',t,t'} \langle i : k + q, s ; m : k', t | j : k, s' ; n : k' + q, t' \rangle \\
\times a_{i,k+q,s}^\dagger a_{m,k',s}^\dagger a_{n,k'+q,t'} a_{j,k',s'} + \frac{K}{2} \sum_k u_k^2.
\] (2.2)
where
\[
\langle i : k + q, s | tl : k, s' \rangle = \langle i : k + q | tl : k \rangle \delta_{ss'},
\]
\[
\langle i : k + q, s; m : k', t | lj : k, s'; n : k' + q, t' \rangle = \langle i : k + q; m : k' | lv : j ; k; n : k' + q \rangle \delta_{ss'} \delta_{tt'}, \tag{2.3}
\]
are specified as
\[
\begin{align*}
(1 : k + q | tl : 1 : k) &= \tilde{\varepsilon}_M \delta_{q0} - \frac{2i \beta}{\sqrt{L}} u_e^* \sin \left( \frac{q}{2} \right), \\
(2 : k + q | tl : 2 : k) &= \tilde{\varepsilon}_X \delta_{q0}, \\
(1 : k + q | tl : 2 : k) &= \frac{2i \alpha}{\sqrt{L}} u_e^* \sin \left( \frac{k + q}{2} \right) - \frac{2t}{L} \delta_{q0} \cos \left( \frac{k}{2} \right), \\
(1 : k + q, 1 : k' | v : 1 : k; 1 : k' + q) &= \frac{U_M}{L}, \\
(2 : k + q, 2 : k' | v : 2 : k; 2 : k' + q) &= \frac{U_X}{L}, \\
(1 : k + q, 2 : k' | v : 1 : k; 2 : k' + q) &= \frac{V_1}{L} \cos \left( \frac{q}{2} \right). \tag{2.4}
\end{align*}
\]
with the renormalized on-site affinities \( \tilde{\varepsilon}_M = \varepsilon_M - U_M/2 \) and \( \tilde{\varepsilon}_X = \varepsilon_X - U_X/2 \).

The symmetry group of the system is generally represented as \( G = P \times S \times T \), where \( P = L_1 \wedge C_2 \) is the space group of a linear chain with the one-dimensional translation group \( L_1 \) whose basis vector is the unit-cell translation, \( S \) the group of spin-rotation, and \( T \) the group of time reversal. Group actions on the creation operators are readily found in Ref. \[1\]. Let \( G \) denote the irreducible representations of \( G \) over the real number field, where their representation space is spanned by the Hermitian operators \( \{a_{1 \times k, s}^\dagger a_{j \times k', s'}\} \). There is a one-to-one correspondence \[2\] between \( G \) and broken-symmetry phases with a definite ordering vector. Any representation \( G \) is obtained as a Kronecker product of the irreducible representations of \( P, S, \) and \( T \) over the real number field: \( G = \hat{P} \otimes \hat{S} \otimes \hat{T} \). \( \hat{P} \) is characterized by an ordering vector \( q \) in the Brillouin zone and an irreducible representation of its little group \( \hat{P}(q) \), and is therefore labeled \( \hat{q}\hat{P}(q) \). The relevant representations of \( S \) are \( \hat{S}^0(u(e, \theta)) = 1 \) and \( \hat{S}^1(u(e, \theta)) = O(u(e, \theta)) \), whereas ones of \( T \) are \( \hat{T}^0(t) = 1 \) \( \hat{T}^1(t) = -1 \), where \( u(e, \theta) = \sigma^0 \cos(\theta/2) - (\sigma \cdot e) \sin(\theta/2) \) represents the spin rotation of angle \( \theta \) around an axis \( e \) and \( O(u(e, \theta)) \) is the 3 \( \times \) 3 orthogonal matrix satisfying \( u(e, \theta) \sigma^\lambda u^\dagger(e, \theta) = \sum_{x=x,y,z} [O(u(e, \theta))]_{\lambda \mu} \sigma_{\nu} \) \((\lambda = x, y, z)\), with the 2 \( \times \) 2 unit matrix \( \sigma^0 = (\sigma^x, \sigma^y, \sigma^z) \). The representations \( \hat{P} \otimes \hat{S}^0 \otimes \hat{T}^0, \hat{P} \otimes \hat{S}^0 \otimes \hat{T}^1, \hat{P} \otimes \hat{S}^1 \otimes \hat{T}^0, \) and \( \hat{P} \otimes \hat{S}^1 \otimes \hat{T}^1 \) correspond to charge-density-wave (CDW), spin-density-wave (SDW), charge-current-wave (CCW), and spin-current-wave (SCW) states, respectively. We leave out current-wave states in our argument, because here in one dimension all of them but one-way uniform-current states break the charge- or spin-conservation law. We consider two ordering vectors \( q = 0 \) and \( q = \pi \), which are labeled \( \Gamma \) and \( X \), respectively. Thus we treat the instabilities characterized as \( \Gamma \hat{P}(\Gamma) \otimes \hat{S}^0 \otimes \hat{T}^0, \hat{X} \hat{P}(X) \otimes \hat{S}^0 \otimes \hat{T}^0, \) \( \Gamma \hat{P}(\Gamma) \otimes \hat{S}^1 \otimes \hat{T}^1, \) and \( \hat{X} \hat{P}(X) \otimes \hat{S}^1 \otimes \hat{T}^1 \). Here \( \hat{P}(\Gamma) \) and \( \hat{P}(X) \) are either \( A \) (\( C_2 \)-symmetric) or \( B \) (\( C_2 \)-antisymmetric) representation of \( C_2 \) because \( \hat{P}(\Gamma) = \hat{P}(X) = C_2 \) in the present system.

### III. Broken Symmetry Solutions

In the HF approximation, the Hamiltonian (2.2) is replaced by
\[
\mathcal{H}_{HF} = \sum_{i,j} \sum_{k,s,s'} \sum_{\lambda=0,\pi} \left[ \chi_{ij}^\lambda(\Gamma; k) a_{i \times k, s}^\dagger a_{j \times k, s'} \right] \sigma_{ss'}^\lambda + x_{ij}^\lambda(X; k) a_{i \times k+\pi, s}^\dagger a_{j \times k, s'} \sigma_{ss'}^\lambda, \tag{3.1}
\]
with
\[
x_{ij}^\lambda(\Gamma; k) = \langle i : k | tl : j : k \rangle + \sum_{m,n} \sum_{k'} \rho_{nm}^\lambda(\Gamma; k') \times \left[ \langle i : k : m : k' | v : j : k \rangle \right],
\]
\[
x_{ij}^\lambda(X; k) = \langle i : k + \pi | tl : j : k \rangle + \sum_{m,n} \sum_{k'} (-1)^{\delta_{nm}} \times \rho_{nm}^\lambda(\Gamma; k') \times \left[ \langle i : k + \pi : m : k' | v : j : k \rangle \right].
\]
Here we have introduced the density matrices
\[
\rho_{ij}^\lambda(\Gamma; k) = \frac{1}{2} \sum_{s,s'} \langle a_{i \times k, s}^\dagger a_{j \times k, s'} \rangle_{HF} \sigma_{ss'}^\lambda, \tag{3.3}
\]
\[
\rho_{ij}^\lambda(X; k) = \frac{1}{2} \sum_{s,s'} \langle a_{i \times k+\pi, s}^\dagger a_{j \times k, s'} \rangle_{HF} \sigma_{ss'}^\lambda,
\]
where \( \langle \cdots \rangle_{HF} \) denotes the quantum average in a HF eigenstate. \( \mathcal{H}_{HF} \) can be decomposed into spatial-symmetry-definite components [13]. Once a broken-symmetry Hamiltonian is given, its invariance group is defined. Keeping in mind that the density matrices characteristic of the given Hamiltonian should also be invariant for its invariance group, we can completely determine qualitative properties of the solution [13].

We are interested in the local charge density on the site \( i \) at the \( n \)th unit cell, \( \rho_{i,n}^\lambda \equiv \sum_{s} \langle a_{i \times n, s}^\dagger a_{i \times n, s} \rangle_{HF} \), the local spin density on the site \( i \) at the \( n \)th unit cell, \( s_{i,n}^\lambda \equiv \frac{1}{2} \sum_{s,s'} \langle a_{i \times n, s}^\dagger a_{i \times n, s'} \rangle_{HF} \sigma_{ss'}^\lambda \), the complex bond order between the site \( i \) at the \( n \)th unit cell and the site
IV. NUMERICAL CALCULATION AND DISCUSSION

We show in Fig. 3 phase diagrams at 3/4 band filling, where \( q = \pi \) states are predominantly stabilized. With the increase of \( \varepsilon_0 \), density waves on the halogen sites are generally reduced and single-band models come to be justified. The phase boundary between M-SDW and X-SDW is roughly given by \( U_X - U_M = 1.8\sigma_0 \), where \( \varepsilon_0 \equiv \varepsilon_M - \varepsilon_X \). In order to realize X-SDW ground states, a small enough \( \varepsilon_0 \) and a large enough \( U_X \) are necessary. We show in Fig. 3 phase diagrams at half band filling, where \( q = 0 \) states are relatively stabilized. The off-site el-ph coupling \( a \) stabilizes BOW, whereas the off-site Coulomb interaction \( V \) is unfavorable to that.

Let us observe the doping dependence of the states. In Fig. 3 we plot macroscopic order parameters, \( O_{M-CDW} = \frac{1}{T} \sum_i (t_{1;i,n,2n-1} - t_{1;n,2n}), \) \( O_{X-SDW} = \frac{1}{T} \sum_i (s_{1;i,n}^z - s_{2;i,n}^z), \) \( O_{BOW} = \frac{1}{T} \sum_i (p_{1;n,2n-1} - p_{1;n,2n}), \) \( O_{SBOW} = \frac{1}{T} \sum_i (t_{1;i,n,2n-1} - t_{1;n,2n}), \) \( O_{FM}^M = \frac{1}{T} \sum_i s_{1;i,n}^z \), and \( O_{FM}^X = \frac{1}{T} \sum_i s_{2;i,n}^z \) as functions of band filling, where the parametrization is as follows: \( U_D/t = 4.0, U_X/t = 2.0 \) for M-CDW, \( U_D/t = 8.0, U_X/t = 3.0 \) for M-SDW, and \( U_D/t = 3.0, U_X/t = 8.0 \) for X-SDW with common values \( \varepsilon_0/t = 1.0, V/t = 1.0, \) \( \alpha/(Kt)^{1/2} = 0.1, \) and \( \beta/(Kt)^{1/2} = 0.1 \). The Coulomb interaction \( V/t = 4.0 \) for BOW, \( U_D/t = 10.0, U_X/t = 9.0, V/t = 2.0 \) for SBOW, and \( U_D/t = 8.0, U_X/t = 3.0, V/t = 1.0 \) for FM with common values \( \varepsilon_0/t = 1.0, \alpha/(Kt)^{1/2} = 0.8, \) and \( \beta/(Kt)^{1/2} = 0.1 \). Now we explicitly find that X-phases are most stabilized at 3/4 band filling, while \( \Gamma \) ones arround half band filling. Although SBOW does not appear in the ground-state phase diagrams shown here, it seems to exist in the vicinity of half band filling with very strong on-site Coulomb repulsions. Even if the solutions are scarcely stabilized into a ground state, they can still be relevant in the ground-state correlations. We note, for example, that low-lying solitonic excitations in a SDW ground state induce SBOW domains around their centers [34]. We note in addition that \( O_{FM}^M \) and \( O_{FM}^X \) have opposite signs, which means spins on the metal and halogen sites are antiparallel to each other (Fig. 3).

We finally stress the wide applicability of the present approach. Our approach never fails to reveal all the possible broken-symmetry phases. We hope that the present argument will motivate further chemical, as well as theoretical, explorations in low-dimensional el-ph systems.
Fig. 1
$\varepsilon_M = 0.0, \varepsilon_X = -1.0, V = 1.0, \alpha = 0.1, \beta = 1.0.$

![Graph](image_url)
Fig. 2(b) $\epsilon_M = 0.0, \epsilon_X = -2.0, V = 1.0, \alpha = 0.1, \beta = 1.0, 3/4$-filling
Fig. 3(a) $\epsilon_m = 0.0$, $\epsilon_x = -1.0$, $V = 1.0$, $\alpha = 0.5$, $\beta = 0.1$, 2/4-filling
Fig. 3(b) $\varepsilon_{\mu} = 0.0$, $\varepsilon_{\chi} = -1.0$, $V = 2.0$, $\alpha = 0.5$, $\beta = 0.1$. 2/4-filling
Fig. 4