Co-operative density wave and giant spin gap in the quarter-filled zigzag ladder

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Strong co-operative interactions occur between four different broken symmetries involving charge-ordering and bond distortions in the quarter-filled correlated zigzag electron ladder. The ground state is singlet, with spin gap several times larger than in the spin-Peierls state of the one-dimensional quarter-filled chain with the same parameters. We propose the quarter-filled zigzag electron ladder model for several different organic charge-transfer solids with coupled pairs of quasi-one-dimensional stacks, the spin-gap transition temperatures in which are unusually high.

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A characteristic feature of one-dimensional (1D) metals is the Peierls transition, where electron-phonon (e-ph) interactions lead to the opening of energy gaps in charge and spin degrees of freedom (DOF) and an insulating ground state. In the presence of strong electron-electron (e-e) repulsive interaction, electronic Hamiltonians describing a 1/2-filled band may be reduced to an antiferromagnetic Heisenberg spin Hamiltonian in which the charge DOF are absent. With nonzero spin-phonon coupling a spin gap (SG) appears again in the so-called spin-Peierls (SP) state, in which there occurs lattice dimerization accompanied by the formation of singlet spin-bonded pairs of electrons. This mechanism of SG formation is absent in the two dimensional (2D) 1/2-filled band, where antiferromagnetism rather than the SP state dominates.

Away from 1/2-filling, charge DOF are important over and above the spin DOF, and the SP transition in 1D occurs only after a metal-insulator (M-I) transition freezes the charge DOF within an electronic Hamiltonian. The most studied case is that of the 1/4-filled chain, where the SP transition is accompanied by charge ordering (CO)\textsuperscript{a,b}. Consider the 1D extended Peierls-Hubbard model,

\begin{equation}
H_{1D} = -\sum_j \left[ t - \alpha \Delta_{j,j+1} \right] B_{j,j+1} + \frac{K}{2} \sum_j (\Delta_{j,j+1})^2 + U \sum_j n_j \sigma \rightarrow n_j \sigma + V \sum_j n_j n_{j+1}. \tag{1}
\end{equation}

In the above $B_{ij} = \sum_\sigma (c_{i,\sigma}^\dagger c_{j,\sigma} + c_{j,\sigma}^\dagger c_{i,\sigma})$ with $\sigma$ the electron spin, $\alpha$ and $K$ are the inter-site e-ph coupling and spring constant, respectively, $\Delta_{j,j+1}$ is the Peiers distortion of the $j$th bond, and $n_j = \sum_\sigma c_{j,\sigma}^\dagger c_{j,\sigma}$ is the total number of electrons on site $j$. $U$ and $V$ are on-site and nearest neighbor (n.n) Coulomb interactions. Within this model, for $V < V_c(U)$ the SP bond modulation is accompanied by $2k_F$ CO, with site charge densities going as $0.5 + \epsilon$, $0.5 + \epsilon$, $0.5 - \epsilon$, $0.5 - \epsilon$. We shall refer to this CO pattern as ...1100..., or as a bond-charge density wave (BCDW). For $V > V_c(U)$, the M-I transition is to the CO state ...1010..., and the SP transition involves dimerization of the bond distances between the “occu-

FIG. 1: (a) The 1D ...1100... BCDW SP state. Black (white) circles represent large (small) charges. Bond strengths decrease as solid bond > double dotted > single dotted. (b) 1D 1/4-filled SP state with ...1010.. CO. (c) The 1/4-filled rectangular ladder. (d) BCDW state in the 1/4-filled zigzag ladder. Bonds are alternately strong and weak along the stacks, and have periodicity 4 along the zigzag interstack direction.
teraction between multiple broken symmetries, SGs considerably larger than those found in the 1/4-filled single chain are possible. We then point out that that this state is likely realized in certain organic CTS with coupled chains.

To understand the BCDW and cooperative effects in the 1/4-filled zigzag ladder, we first consider the appropriate one-electron Hamiltonian which includes intersite e-ph interactions.

\[
H_{zz}^{1c} = - \sum_{\langle ij \rangle, \sigma} [t_s - \alpha_s \Delta_{ij}^s] B_{i,j}^s + \frac{K_s}{2} \sum_{i} (\Delta_{ij}^s)^2
\]

\[
- \sum_{\langle ij \rangle, \sigma} [t_d - \alpha_d \Delta_{ij}^d] B_{i,j}^d + \frac{K_d}{2} \sum_{i} (\Delta_{ij}^d)^2
\]  

(2)

In the above, subscripts \(s\) and \(d\) label respectively intrastack and diagonal zigzag interstack hopping integrals and bond distortions (see Fig. 1(d)), and \(\langle \cdot \rangle\) and \(\langle \cdot \rangle\) denote intrastack and interstack n.n. bonds. The broken symmetry of Fig. 1(d) is then simply the 2\(k_F\) Peierls distortion that is expected when the zigzag ladder is considered as a 1D chain with n.n. hopping \(t_d\) and n.n.n. hopping \(t_s\). Unconditional Peierls transition occurs for \(t_d > 0.5858 \ t_s\). We have chosen \(t_d/t_s = 0.7\). Such large \(t_d\) have been estimated for the experimental CTS we are interested in and are due to the close interchain contacts involving sulfur atoms.\(^8\,9\,10\). An interesting aspect of this Peierls distorted state is that the expected period 2 \(2k_F\) Peierls bond and charge distortions along the zigzag interstack direction are accompanied by period 2 distortions of the same quantities along the stacks. This has important ramifications in the presence of e-e interactions, as we show below.

We now ask whether this broken symmetry state persists when Coulomb interactions are added. To the one-electron Hamiltonian of Eq. 2 we add an additional term containing e-e interactions:

\[
H_{zz}^{ee} = U \sum_i n_i^\sigma n_i^{-\sigma} + V_s \sum_{\langle ij \rangle} n_i n_j + V_d \sum_{\langle ij \rangle} n_i n_j
\]  

(3)

\(U, V_s, V_d\) are the on-site, intrastack n.n., and interstack n.n. Coulomb interactions. We have investigated Hamiltonian \(H = H_{zz}^{1c} + H_{zz}^{ee}\) numerically, performing exact diagonalization calculations for 16-site periodic zigzag clusters and Constrained Path Quantum Monte Carlo (CPMC) calculations of long (up to 128 sites) open as well as periodic zigzag ladders. Investigating the complete phase space would require varying three Coulomb interaction parameters, two hopping integrals as well as the different e-ph couplings. We have therefore restricted ourselves to the parameter regime appropriate for organic CTS, viz., \(U > 4t_d, \ t_s > t_d, \ V_d < V_s < U/2\).

In what follows, we have taken \(t_s = 1\). The procedure for the self-consistent exact diagonalization is the same as in Refs.\(^1\,12\) for 1D periodic rings with n.n. hopping. For the range of parameters above the ground state we find is either completely uniform, or is the broken symmetry state of Fig. 1(d). We evaluate self-consistently all \(\langle B_{ij}^s \rangle, \langle B_{ij}^d \rangle\) and \(\langle n_i \rangle\) and define order parameters (i) \(f(B_s)\), the absolute value of the difference between consecutive \(\langle B_{ij}^s \rangle\) along the stacks, divided by the average \(\langle B_{ij}^s \rangle\), (ii) \(f(B_d)\), the difference between the strongest and the weakest \(\langle B_{ij}^d \rangle\) along the zigzag direction, divided by the average \(\langle B_{ij}^d \rangle\), and (iii) \(\Delta_n\), the difference between the charge densities of consecutive sites along the stacks.

Co-operative broken symmetry requires that all three order parameters are simultaneously nonzero.

Fig. 2(a) shows the behavior of the three order parameters for fixed \(U = 6, V_s = 1, V_d = 0.5\), as a function of the dimensionless e-ph coupling \(\lambda_s = \alpha_s^2/K_s t_s\), with the other e-ph coupling \(\lambda_d = \alpha_d^2/K_d t_s\) held at 0. All three order parameters simultaneously become nonzero at \(\lambda_s = \lambda_s^c = 0.045\). \(\lambda_s^c\) should be 0\(^{th}\) in the thermodynamic limit for the transition to be unconditional, suggesting that it should decrease with increasing size of finite clusters; we verified that \(\lambda_s^c\) is indeed smaller in 16 site compared to the 8 site zigzag clusters (for 8 sites, \(\lambda_s^c = 0.245\)). Similar behavior are also seen in Fig. 2(b) as a function now of \(\lambda_d\), for fixed \(\lambda_s = 0.045\). Taken together, Figs. 2(a) and (b) clearly indicate the cooperative nature of the transition to the BCDW state in the 1/4-filled zigzag ladder.

The broken symmetries within the correlated zigzag ladder are far stronger than in 1D. To demonstrate this we compare \(\Delta n\) in the two cases as a function of \(U\) with...
e-ph coupling $\lambda = \alpha^2 / Kt = 1.28$ for 1D and $\lambda_s = 0.125$, $\lambda_d = 0$ for the zigzag ladder. The distortion amplitudes decrease rapidly with $U$ in 1D (see below), which necessitates the larger $\lambda$ in this case. In Fig. 2(c) we have plotted the $\Delta n_1$ normalized by its value for $U = 0$ for both cases. For all nonzero $U$ we have chosen $V = 1$ for the 1D ring and $V_s = 1, V_d = 0.5$ for the zigzag cluster. The distortion in the zigzag ladder is affected very weakly by e-e interactions because of the co-operative nature of the transition here. As pointed out above, the charge and bond periodicities along the stack direction in Fig. 1(d) are $4k_F$, even as these have $2k_F$ periodicities along the zigzag interstack direction. In purely 1D the $4k_F$ distortions get stronger with e-e interactions, while the $2k_F$ distortions get weaker. There is thus a tendency to cancellation of these effects in the zigzag cluster, with the distortion amplitude remaining the same.

As one goal of our work is to apply our theory to organic CTS with molecular sites we have also investigated the effect of Holstein electron-molecular vibration coupling:

$$H_\beta = \beta \sum_i v_i n_i + \frac{K_\beta}{2} \sum_i v_i^2$$

Here $\beta$ is the intrasite e-ph coupling with corresponding spring constant $K_\beta$, and $v_i$ is the amplitude of the internal molecular vibration. In Fig. 2(d) we have plotted the order parameters for $H = H_{zz}^e + H_{ee}^e + H_\beta$ against $\lambda_\beta = \beta^2 / K_{zz}^e$, with fixed $\lambda_s = \lambda_d = 6.045$. All three order parameters again increase with $\lambda_\beta$. Our conclusions regarding cooperative broken symmetries remain the same whether or not the Holstein interaction is included.

We have verified the coexisting broken symmetries for larger lattices by performing CPMC calculations for long zigzag clusters with open boundary condition (OBC). In 1D, the central region of long open chains exhibit spontaneous charge or bond-order distortions, even with uniform hopping integrals and zero e-ph coupling. We have performed CPMC calculations for a 64-site zigzag open ladder with $\lambda_s = \lambda_d = \lambda_\beta = 0$, and for the same $U, V_s, t_s$ and $t_d$ as in Fig. 2(a). With OBC, $f(B_s), f(B_d)$ and $\Delta n$ depend on the locations of the sites being considered, and we have therefore plotted the charge densities ($n_i$) and the bond orders $\langle B_{ij}^s \rangle$ at chain centers in Fig. 3. Simultaneous $4k_F$ dimerizations of charge and bond along the stacks (Figs. 3(a) and (b)) and simultaneous $2k_F$ modulations of these quantities along the diagonal zigzag direction (Figs. 3(c) and (d)) are seen, in complete agreement with the results of Fig. 2.

The SG in the distorted zigzag 1/4-filled ladder is due to the formation of a strong 1-1 local singlet bond in the ...1100... zigzag BCDW. We have calculated the SG in the BCDW state of the zigzag ladder using CPMC. Our calculations are for long periodic zigzag clusters, for the same parameters as in Fig. 3. For comparison, we also evaluate the SGs in the ...1100... BCDW state of a 1D periodic ring (Eq. 1, Fig. 1(a)), with $U = 6, V = 1, \gamma = 1$, using the Stochastic Series Expansion Monte Carlo method. The reason for choosing the ...1100... state is that the SG in the zigzag ladder for one value of $\lambda$ is several times larger in the zigzag electron ladder than in 1D ($\Delta \sigma$; the same large difference between the zigzag bonds as in Fig. 1(d) and along the linear chain as in Fig. 1(a)). We evaluate the singlet-triplet gaps $\Delta \sigma$, using CPMC for periodic zigzag ladders with $N = 32, 64$ and 128 sites, and for periodic 1D rings with $N = 32, 64$ and 96 sites, for several different $\epsilon$. For each $\epsilon$, the $\Delta \sigma$ and $\Delta n$ at $N \to \infty$ are found from extrapolations against $1/N$. In Fig. 4 we have plotted the extrapolated $\Delta \sigma$ against $\Delta n$ for both the 1D system and the zigzag electron ladder. The finite size scaling of $\Delta \sigma$ for the zigzag ladder for one value of $\epsilon$ is shown in the inset. For the same $\Delta n$, $\sigma_\epsilon$ is several times larger in the zigzag electron ladder than in 1D ($\Delta \sigma$ can be plotted also against $|\epsilon|$; the same large difference between the zigzag ladder and 1D is obtained.) The large SG in the zigzag ladder is a direct consequence of the strong local interstack 1-1 singlet bond, which in turn results from stronger distortions than in 1D.

Several recently discovered 1/4-filled band CTS are very likely structurally zigzag ladders. These systems consist of pairs of 1D stacks of organic donor molecules, and the zipper-like shape of these systems is also common in the observed 1/4-filled band CTS.
with strong intrapair interchain couplings, and weak inter-
pair couplings. They undergo M-I transition at \(T_{M-I} > 200\) K, followed by an insulator-insulator (I-I)
transition which is accompanied by the opening of a
SG at lower temperature \(T_{SG}\). The peculiarity of these paired-stack systems is that while
\(T_{SP} \sim 10 - 20\) K in the 1D CTS, \(T_{SG} \sim 70\) K in
(DT-TTF)\(_2\)Au(mnt) and is even higher at 170 K in
(BDTFP)\(_2\)PF\(_6\)(PhCl)\(_2\). The very large \(T_{SG}\), and
therefore the large SG in these systems are highly unus-
ual.

To explain the large SG in these systems, an ef-
cfective two-leg rectangular spin-ladder model has been
proposed. It is known experimentally that each
individual 1/4-filled stack dimerizes below \(T_{M}\). Within
the dimerized rectangular ladder lattice motif, if each
dimer unit along the legs containing one localized spin
is assumed to be equivalent to an effective single site
(see Fig. 6 in Ref. 9), then an 1/2-filled rectangular
spin ladder is obtained. For strong enough interstack
spin coupling, large SG is now obtained. The mapping
from the 1/4-filled dimerized rectangular electron ladder
to the 1/2-filled spin ladder, however, has not been for-
manly proved.

We believe, however, that the zigzag electron ladder is
the more appropriate model for these systems for a num-
ber of reasons. The crystal structures of the materials
(see Fig. 2(a) in Ref. 8 and Fig. 2 in Ref. 10) indicate that
each molecular site is coupled to two molecules on the
partner stack, as would occur in the zigzag ladder.
Quantum chemical calculations of hopping integrals
support this viewpoint. Most importantly, it has been suggested
from EPR linewidth studies that transition to a CO state
might be occurring in (BDTFP)\(_2\)PF\(_6\)(PhCl)\(_2\). This
last result, if correct, will be in agreement with the zigzag
electron ladder model. The key difference between spin-
ladders and 1/4-filled electron-ladders is that CO is ab-
sent in the former, while it is a prerequisite to large SG
in the latter. Experiments have previously demonstrated
CO in 1D, as well as 2D CTS, while very recently, the
occurrence of the ...1100... BCDW has been experimen-
tally confirmed in a CTS. We predict that experimental
investigation of the coupled-stack CTS will find evidence
for CO.

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