Re-integerization of fractional charges in the correlated quarter-filled band

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Previous work has demonstrated the existence of soliton defect states with charges $\pm e/2$ in the limits of zero and of infinite on-site Coulomb interactions in the one-dimensional (1D) quarter-filled band. For large but finite on-site Coulomb interaction, the low temperature $2k_F$ bond distortion that occurs within the $4k_F$ bond-distorted phase is accompanied by charge-ordering on the sites. We show that a “re-integerization” of the defect charge occurs in this bond-charge density wave (BCDW) state due to a “binding” of the fractional charges. We indicate briefly possible implications of this result for mechanisms of organic superconductivity.

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One of the most dramatic and exciting predictions of the initial model studies of quasi-1D organic $\pi$-conjugated polymers and charge transfer solids (CTS) was the existence of exotic excitations, including solitons with unusual spin-charge relations $\pm$ and fractional charge $\pm e/2$. For trans-polyacetylene, with a 1/2-filled 1D band, it was shown within the Su-Schrieffer-Heeger (SSH) one-electron model that the neutral solitons have spin 1/2, while charged solitons are spinless $[1,2]$. This result remains unaltered upon inclusion of the Coulomb electron-electron (e-e) interactions $[3,4]$. In the case of the 1D 1/3- and 1/4-filled bands, any non-zero electron-phonon (e-ph)coupling leads to $2k_F$ Peierls transitions corresponding to trimerization and tetramerization of the respective lattices, and defect soliton charges are $\pm 2e/3$, $\pm e/2$, and $\pm e/2$ respectively. Effects of e-e interactions on the soliton charge in non-1/2-filled bands have been investigated only for the 1/4-filled band, primarily for the limiting case of large on-site Hubbard repulsion ($U \rightarrow \infty$) $[5,6]$. For $U \rightarrow \infty$, the 1D 1/4-filled Hubbard band of electrons reduces to a 1/2-filled band of noninteracting spinless fermions $[3,4]$. Hence in the presence of an e-ph coupling, a Peierls transition occurs at twice the fermi wave vector corresponding to the spinless fermions, which is four times the original $k_F$ ($k_F = \pi/4a$, where $a$ is the undistorted lattice constant). Depending on the nature of the phonons, this leads to bond or site dimerization of the lattice. A single doped hole/electron generates two charged soliton defects in the dimerized lattice, which therefore have charge $\pm e/2$ again. Since soliton charges are $e/2$ at both $U = 0$ and $U \rightarrow \infty$, a continuity between these two limits has been claimed $[5]$. In the case where the $4k_F$ metal-insulator transition is due to bond distortion, a $2k_F$ spin-Peierls (SP) dimerization of the dimerization (i.e., tetramerization) occurs at low temperatures for finite $U$ $[7]$. Reference $[6]$, which claimed the persistence of fractional charge in the $2k_F$ phase, did not actually probe the nature of the $2k_F$. We have recently shown that the $2k_F$ SP bond tetramerization is also accompanied by an on-site $2k_F$ CDW $[2]$, and the correct description of this state is a bond-charge density wave (BCDW). Clearly an important theoretical question is whether fractionally charged solitons continue to exist in the BCDW ground state.

This issue is of considerably more than mere theoretical interest in the case of the organic CTS. The original applications of the “large-$U$” 1/4-filled band theory were to 1:2 anionic TCNQ solids $[13]$, where, however, no direct evidence for fractional charge was found, in spite of experimental attempts. More recently, interest has shifted to the nominally 1/4-filled 2:1 cationic CTS, many of which exhibit superconductivity and other novel phases at low temperatures $[4]$. The most strongly 1D systems here, (TMTTF)$_2$X ($X = \text{PF}_6, \text{AsF}_6$ etc.) exhibit a high temperature metal-insulator (presumably 4$k_F$) transition, and a SP transition at $T_{\text{SP}} < 20$ K. Again, no evidence for fractionally charged defect states has emerged. The question that arises then is whether the half-integer charges are unobservable, or the right experiments have not been done yet. This question acquires added importance when the entire family of 2:1 cationic CTS is considered. In our recent theoretical studies, for example, we have shown that the BCDW persists in the interacting 1/4-filled band for all $t_\perp \leq t$, where $t$ and $t_\perp$ are the intra- and interchain one-electron hopping integrals, respectively, and furthermore, in the small $t_\perp$ region the BCDW also coexists with a spin-density wave (SDW), giving a BCSDW $[15,16]$. Experimentally, charge-ordering $[14]$ has been found in the 1D (TMTTF)$_2$X which are SP systems, while the BCSDW has been seen in (TMTSF)$_2$X $[17,18]$ and $\alpha$-(BEDT-TTF)$_2$Mg(SCN)$_4$ $[21]$. Evidence for coexisting SP-like states and charge-ordering is also beginning to emerge in other BEDT-TTF systems $[19,22]$. Based on the persistent BCDW that is obtained theoretically and also observed experimentally, we have suggested that superconductivity in these strongly correlated systems is a consequence of pairing of commensurability defects of...
the BCDW phase \[14\]. If these commensurability defects are fractionally charged then, an obvious question that emerges is whether the the superconducting “pairs” are actually “quadruplets”!

In the present Letter, we show that charge-fractionalization does not occur in the low temperature \(2k_F\) SP phase of the interacting 1D 1/4-filled band: the charge-ordering associated with the SP tetramerization causes a “re-integerization” of the fractionally charged defects that occur within the \(4k_F\) dimerized phase. This re-integerization provides support to the idea that superconductivity in the quasi-2D TMTSF and BEDT-TTF may be due to pairing of integer charged commensurability defects in a background BCDW, although it does not necessarily exclude the “melting” of the BCDW at the superconducting transition.

To establish this result, we will consider the 1D Peierls-extended Hubbard Hamiltonian for the case of bandfilling slightly away from 1/4, and will present both many-body numerical results as well as heuristic physical arguments. No SP transition can occur within the \(4k_F\) CDW \[14\], and therefore the the experimentally observed SP transition in (TMTSF)_2X proves that the \(4k_F\) metal-insulator transition is to a bond-order wave (BOW) that occurs for intersite e-e interaction \(V < V_c \sim 2|t|\) \[14\]. Upon the exclusion of the \(4k_F\) charge-ordering, there are four possible equivalent charge-orderings that can occur for nonzero \(U\) and \(V < V_c\), viz., ...1100..., ...0110..., ...0011..., and ...1001... (here and below a ‘1’ implies charge 0.5 + \(\epsilon\), and a ‘0’ implies 0.5 – \(\epsilon\)). The \(4k_F\) bond dimerization breaks a twofold symmetry and the ground state is a superposition of the type ...1100... + ...0011..., with weak (W) ‘11’ and ‘00’ bonds, and strong (S) ‘10’ and ‘01’ bonds. The \(2k_F\) SP transition breaks yet another twofold symmetry, and the ground state is now either ...1100... or ...0011..., with the ‘11’ (W') and ‘00’ (W) bonds now inequivalent, and the bond distortion pattern W'SW'SW'. Our goal is to calculate defect charges within this W'SW'SW' state.

Since our many-body numerical results are for finite chains, it is useful to establish our methodology by first solving the known case of \(U \to \infty, V = 0\). The spinless fermion Hamiltonian here is written as,

\[
H_{SF} = -t \sum_j (a_j^\dagger a_{j+1} + h.c) \tag{1}
\]

For simplicity, we have not included the SSH e-ph interaction that gives the bond dimerization in the above form. As we show below, calculations of the bond orders, defined as \(\langle B_{j,j+1} \rangle = \langle a_j^\dagger a_{j+1} + h.c \rangle\), and of site charge densities, of an open long finite chain with uniform hopping \(t\) show spontaneous modulations of the bond orders and charge densities, with the same modulation patterns as expected within a fully self-consistent calculation of a periodic electron-phonon coupled ring. The actual lattice dimerization occurs for 0\(^{+}\) electron-phonon coupling in the infinite chain.

Figure 1(a) shows the bond orders of a 64-site open chain of noninteracting spinless fermions with uniform hopping integrals; the spontaneous period-two dimerization of the chain is evident in spite of end effects. In Figure 1(b), we show the result of adding two holes. The two holes produce four defects (regions where consecutive bond orders are equal), each of which then have charge +\(e/2\). Charge density calculations (not shown) give uniform \(\langle n_j \rangle = 0.5\) for the undoped chains, and four defects in the doped chain, with maximum deviations from 0.5 occurring exactly in the regions where consecutive bond orders are equal.

![Figure 1](https://example.com/figure1.png)

**FIG. 1.** The bond-orders of a 64-site uniform open chain of noninteracting spinless fermions with (a) 32 fermions, showing the spontaneous dimerization that occurs for the effective half-filled band; (b) two doped holes (30 fermions), showing the resulting four defects.

Although the above figures reproduce known results, it is useful to give a configuration space interpretation of these results. In Figure 1(a) we show the spontaneously dimerized ground state, with equal \(\langle n_j \rangle = 0.5\) on each site. Here the bonds between the sites within a box are stronger than the bonds between sites that occur in neighboring boxes. Removal of a single electron initially removes two charges 0.5 from each of two adjacent sites connected by a weak bond (see first diagram, Figure 1(b)). The configuration with adjacent defect sites has higher energy than the one in which they are separated (second diagram, Figure 1(b)), each carrying charge e/2. The defects are shown localized to a single site in Fig. 1(b) for simplicity; as seen in the numerical data of Fig. 1(b), each defect actually spreads.
out over several sites.

a) $\begin{array}{cccccccc} 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \end{array}$

b) $\begin{array}{cccccccc} 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \end{array}$

c) $\begin{array}{cccccccc} 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \end{array}$

d) $\begin{array}{cccccccc} 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \end{array}$

e) $\begin{array}{cccccccc} 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \end{array}$

FIG. 2. (a) The undoped $4k_F$ dimerized 1/4-filled band. Boxes represent the “dimers”, i.e., sites coupled by strong bonds. (b) creation of two $e/2$ solitons upon the removal of one electron from the configuration of (a). (c) The BCDW state that describes the interacting 1/4-filled band, below the $2k_F$ SP transition (see text). (d) A doped hole removes a single ‘1’, and soliton charge is now e. (e) Configuration with two doped holes in the $2k_F$ BCDW.

To explore the defect charges for finite $U$ below the $2k_F$ transition, we study the Hamiltonian [16,23]:

$$H = -t_1 \sum_{j,\sigma} B_{2j-1,2j,\sigma} - \sum_{j,\sigma} [t_2 - \alpha \Delta_j] B_{2j,2j+1,\sigma} + \frac{K}{2} \sum_j \Delta_j^2 + U \sum_j n_{j,\uparrow} n_{j,\downarrow} + V \sum_j n_j n_{j+1}.$$  \hspace{1cm} (2)

In the above $B_{i,j,\sigma} = c_{i,\sigma}^\dagger c_{j,\sigma} + h.c.$ is the standard hopping operator for an electron with spin $\sigma$, $n_{j,\sigma} = c_{j,\sigma}^\dagger c_{j,\sigma}$ and $n_j = \sum_\sigma n_{j,\sigma}$ the standard electron-number operators, $\alpha$ and $K$ the electron-phonon coupling and the spring constants, respectively, and $\Delta_j$ is the displacement of each dimer from equilibrium. The intra-dimer hopping $t_1$ is larger than the inter-dimer hopping $t_2$ because of the $4k_F$ bond dimerization which is assumed to have occurred already.

Before showing our numerical data, we present physical arguments based on a configuration space picture that already suggest re-integerization of the fractional charge within the above Hamiltonian. As shown in our previous work (see also below), the ground state of the commensurate interacting 1/4-filled band is the BCDW state shown in Figure 2(c). Here each ‘10’ and ‘01’ within a box are connected by the strong (S) bond, while the “double” and “single” bonds correspond to the W’ and W bonds, respectively. The ...1100... charge-ordering dictates that “doping” now will involve removal of a whole electron from a single site, as shown in the first diagram of Figure 2(d). Simply removing the ‘1’ creates an energetically unfavorable asymmetric situation with three ‘0’s in a row, and energy is gained by the reorganization shown in the second step of Figure 2(d), which reduces the number of weak ‘0-0’ bonds. The difference from the $U \to \infty$ case is then as follows. The defect induced charge deficiency now occupies a single box and no further separation between the charges can occur. Clearly, the soliton charge is then $+e$ and not $+e/2$. Note that the charge reorganization creates phases of inter-dimer bond dimerizations that are different on the left and the right of the soliton defect (this may be seen most easily by numbering the boxes sequentially). Soliton defects with integer charge therefore occur in pairs, where a second hole “heals” the “phase-problem” induced by the first hole, as shown in Figure 2(e). Note that the above physical picture, though qualitative, predicts two important numerically testable details, viz., (i) the intra-dimer bonds become weak near the defect center, with a minimum in the intra-dimer bond order occurring over a single dimer, (ii) the inter-dimer bonds around a defect *increase* in strength, and reach their maximum values on both sides of the weakest intra-dimer bond.

In our numerical investigation we study the bond orders $\sum_\sigma \langle B_{j,j+1,\sigma} \rangle$ and charge density $\sum_\sigma \langle n_{j,\sigma} \rangle$, at and near 1/4-filling. We use the Stochastic Series Expansion (SSE) quantum Monte Carlo (QMC) method [24], which is exact to within statistical error for this 1D system: there is no approximation in the discretization of imaginary time, as in many other QMC methods. As SSE is a finite-temperature QMC method, a sufficiently low temperature must be used to obtain ground-state results. In the results shown below, inverse temperatures $\beta = 4L$ ($L$=chain length) were used, which showed essentially no difference from $\beta = 2L$ computations. Since bond-distortions in open chains decrease with length, unlike in periodic rings, where they increase (convergence to the same finite amplitude for the BOW occurs in the long chain limit) our initial calculations are for relatively short chains with 32 sites. Figure 3(a) shows the bond orders for a 32-site open chain with 16 electrons and $U = 6$, $V = 1$, and hopping integrals $t_1 = 1.4$ and $t_2 = 0.6$ (in units of $t = (t_1 + t_2)/2$). It is seen that the strong intra-dimer bonds have nearly uniform bond-orders, but there occurs a *spontaneous alternation of the inter-dimer bond orders*, giving an overall bond distortion pattern W’SWS. Figure 3(b) shows the charge densities in this undoped 1/4-filled system, and there is clear spontaneous site-CDW with periodicity ...1100... in the center of the chain, with relatively weak chain end effects. These results show that once the $4k_F$ bond dimerization ($t_1 \neq t_2$) is explicitly put in “by hand”, further dimerization of the dimerization is unconditional.

In Figure 3(c) we show the bond orders for the dimer chain “doped” with two holes. There occur now only two defects, centered on the dimer bonds between sites 9 and 10, and sites 23 and 24, respectively. These defects therefore have integer charges. Note that the intradimer bond orders are smallest for the 9–10 and 23–24 bonds, while the interdimer “weak” bonds on both sides of the defect centers reach their strongest values, in complete agreement with Figures 2(d) and (e).

The very large difference between $t_1$ and $t_2$ in Figures 3(a) - (c) was chosen merely to make the results visually most accessible, and is not a required condition for obtaining defects with integer charge. To demonstrate...
FIG. 3. SSE bond orders of 32 site open chains with $U = 6$, $V = 1$. The lines are guides to the eye. (a) Undoped dimerized $1/4$-filled system, $t_1 = 1.4$ and $t_2 = 0.6$. Spontaneous dimerization of the dimer lattice results in the alternation of weaker bond orders. (b) Charge densities of the undoped chain, showing $...1100...$ ordering. (c) Bond orders with two added holes, with the same parameters as in (a). (d) Same as (c), but with weaker intrinsic dimerization, $t_1 = 1.2$ and $t_2 = 0.8$.

In Figure 3(d) we show our results for the same 32-site system with two doped holes, but now for weaker $4k_F$ dimerization $t_1 = 1.2$ and $t_2 = 0.8$. No change in the defect structure is seen with the weaker dimerization.

Finally, it is important to demonstrate that the occurrence of only two defects in Figures 3(c) and (d) is not a consequence of short chain lengths and overlapping defects. We have therefore performed our calculations also for 64 sites, a chain length where $U \rightarrow \infty$ shows clear evidence for four defects (see Figure 4). Based on the similarity between large and moderate $t_1 - t_2$ in Figures 3(c) and (d), we performed our calculations here for only large $t_1 - t_2$, viz., $t_1 = 1.4$, $t_2 = 0.6$. Our SSE results for a 64-site open chain with 30 spinful electrons are shown in Figure 4, where once again only two defects (centered on the dimer bonds between sites 17 and 18, and sites 45 and 46, respectively) are seen. An important feature that is clearer in this longer chain is that the weaker bond orders correctly recover their strong-weak character away from the defect centers.

To conclude, the apparent continuity of fractional charges between the $U = 0$ and $U \rightarrow \infty$ limits in the $1/4$-filled band [25] arises only when the existence of the $2k_F$ BCDW ground state at finite $U$ is ignored. The charge $e/2$ solitons that occur at $U = 0$ are domain walls between four distinct density wave phases, while at $U \rightarrow \infty$ they are domain walls between only two such phases. The $e/2$ charge at $U \rightarrow \infty$ is thus a consequence of site-occupancies of 0.5 electrons alone, and re-integerization of the fractional charge occurs in the $2k_F$ BCDW ground state. The integer charge solitons do not bind in 1D, but it is conceivable that integer charge commensurability defects in the 2D BCDW bind into large bipolarons, thereby giving the superconductivity observed in the 2D CTS. Recent demonstrations of large bipolarons [26] with strongly interacting 2D electrons, and the finite mobility of such intersite bipolarons [26,27] are highly promising results in these context.

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