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Fractionally charged excitations in the charge density wave state of a quarter-filled t-J chain with quantum phonons

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Abstract. Elementary excitations of the $4k_F$ charge density wave state of a quarter-filled strongly correlated electronic one-dimensional chain are investigated in the presence of dispersionless quantum optical phonons using Density Matrix Renormalization Group techniques. Such excitations are shown to be topological solitons carrying charge $e/2$ and spin zero. Relevance to the $4k_F$ charge density wave instability in $(DI-DCNQI)_2Ag$ or recently discovered in $(TMTTF)_2X$ ($X = PF_6$, AsF_6) is discussed.

PACS. 75.10.-b General theory and models of magnetic ordering – 75.50.Ee antiferromagnetics – 71.27.+a Strongly correlated electron systems; heavy fermions – 75.40.Mg Numerical simulation studies

Rapid Note

1 Introduction

It is well know that one-dimensional (1D) Su-Shrieffer-Heeger (SSH) [1] or Hubbard-SSH models exhibit exotic elementary excitations including neutral soliton with spin $\frac{1}{2}$, charged soliton with spin zero ($\frac{1}{2}$-filled band) [2] as well as fractionally charged soliton ($\frac{1}{3}$- and $\frac{1}{4}$-filled band) [3,4]. In these models, the phonons couple to the electrons *via* inter-site interactions which lead to an insulating Bond Order Wave ground state (GS). In fact, such solitonic excitations are also generic in commensurate site-centered Charge Density Wave (CDW) states and, hence, should also exist (in the vicinity of commensurate fillings) in the case of strong short range electronic repulsion leading to commensurate $4k_F$ charge instability. In addition to strong electron-electron correlation, local on-site electron-phonon (e-ph) coupling (to be compared with the inter-site vibration in the SSH model) is of particular relevance in systems where the "site" represents a complex structure with internal degrees of freedom. Molecular crystals such as the quasi-1D charge transfer salts [5] present this type of characteristic. Interplay between electron-electron and e-ph interactions provides a very rich physics. For example, several systems have been recently observed to present transitions towards charge ordered phases where the molecules of the conducting stack support unequal electron densities, and in some cases associated relaxation of their internal geometry. This is for instance the case for the most strongly 1D system of the Bechgaard-Fabre salts family, namely $(TMTTF)_2PF_6$ and $(TMTTF)_2AsF_6$; below the Mott localization temperature T_ρ evidences for an additional transition towards a $4k_F$ (site-centered) CDW state have been recently provided by dielectric response measurements [6], NMR [7] and anomalous temperature dependence of the X-ray Bragg peaks [8]. Similar transitions have been seen in $(BEDT-TTF)_2X$ [9] as well as in $(DI-DCNQI)_2Ag$ [10] which exhibits below 220 K a $4k_F$ CDW associated with geometry modulations of the $DI-DCNQI$ molecules.

A pictorial description of a solitonic state can be simply given assuming *e.g.* a quarter-filled strongly correlated chain, in a $4k_F$ CDW state, provided a doubling of the unit cell. In that case, the GS charge modulation can be parametrized as $\langle n_i \rangle = \frac{1}{2} + A_{4k_F}\cos(4k_F r_i + \phi)$ where $k_F = \pi/4$, A_{4k_F} is the magnitude and ϕ the phase of the charge oscillation. Hence, due to the equivalence between the even and odd sites, the GS is two fold degenerate ($\phi = 0$ and $\phi = \pi$). A solitonic excitation can be described as a state which interpolates between the two different GS patterns with a slowly monotonically varying phase $\phi(r_i)$ from let's say 0 at $r_i \to -\infty$ to π when $r_i \to +\infty$. Simple counting arguments show, in fact, that such an excitation carries a charge $Q = \pm\frac{e}{2}$ and, therefore, can be generated by doping the commensurate CDW GS.

In this paper, we investigate the role of quantum local phononic (optical) modes on the formation and on the stability of the solitonic excitations occurring in an insulating $4k_F$ CDW phase of a quarter-filled strongly correlated electronic chain. This issue is of particular interest since a coupling to local phonons might affect the physics of the solitons (such as its width, its interaction, etc...). Numerical results will be obtained by the Density Matrix Renormalization Group (DMRG) method applied to open or cyclic chain segments carrying no, a single or two solitonic excitations.

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2 Model

The following analysis is based on the 1D t-J-V-Holstein model at quarter filling. This model describing strongly correlated electrons coupled to dispersionless phonons can be written as $H = H_{\rm e} + H_{\rm e-ph}$ with

$$H_{\rm e} = t\sum_{i,\sigma}\left(c^{\dagger}_{i+1,\sigma}c_{i,\sigma} + \text{h.c.}\right) + J\sum_{i}\mathbf{S}_i\cdot\mathbf{S}_{i+1} + V\sum_{i}n_i n_{i+1}$$
$$H_{\rm e-ph} = g\sum_{i}n_i\left(b^{\dagger}_i + b_i\right) + \omega\sum_{i}\left(b^{\dagger}_i b_i + 1/2\right) \qquad (1)$$

where $c^{\dagger}_{i,\sigma}$, $c_{i,\sigma}$ are projected creation and annihilation operators of electrons of spin σ at sites i (doubly occupied sites are projected out, the strong correlation limit is therefore assumed), n_i is the electron number and $\mathbf{S}_i$ is the spin operator at site i. $b^{\dagger}_i$ and b_i are the local phonons creation and annihilation operators. The energy scale is fixed by $t = 1$. Note that the phononic part can be re-written as $\omega\left[\left(b^{\dagger}_i + n_i\frac{g}{\omega}\right)\left(b_i + n_i\frac{g}{\omega}\right)\right] + \text{const.}$ showing that the coupling of the on-site vibrations to the electrons induces displacements of the oscillator proportional to the site charge. In fact, this term mimics the relaxation of the internal geometry of a site as a function of its ionicity.

Before proceeding further, it is interesting to examine the adiabatic limit. Absorbing the e-ph coupling g in the definition of the (classical) on-site displacement $g(b^{\dagger}_i + b_i) \to \delta_i$, the phononic part takes the form of a classical elastic energy $\frac{1}{2}K\sum_i \delta_i^2$. The magnitude of the e-ph coupling is then given by a single parameter, the inverse lattice stiffness $K^{-1} = 2g^2/\omega$. Hence, the adiabatic limit is reached assuming the following limits; $\omega \to 0$, $g \to 0$ and $K^{-1} \to$ const. The phase diagram of this model has been investigated recently by Riera and Poilblanc [12]. It is well know that a quarter-filled infinite-U (*i.e.* $J = 0$) model exhibits a $4k_{\rm F}$ CDW (Mott-Hubbard like) instability only when the nearest neighbor (NN) repulsion V exceeds 2 [11]. This instability is in fact enhanced by the lattice coupling and the $4k_{\rm F}$ CDW phase becomes stable even when $V < 2$ (and J finite) for K^{-1} exceeding a V-dependent critical value [12]. The numerical study of the model with quantum phonons using the infinite system DMRG method [13] requires an approximate (but reliable) treatment of the phonon degrees of freedom [14–16]. Indeed, an infinite number of phononic quantum states lives on each site. In order to render the calculations feasible, the basis set has been truncated on each site to the two lowest vibronic states. This choice is physically reasonable as long as the frequency ω is not too small since only the lowest vibronic states are expected to be involved [16]. In all cases, we kept $m = 216$ states per renormalized block. We have chosen parameters like $V = 1$ and $J = 0.3$ which are generic for strongly correlated 1D materials. For such parameters, the adiabatic GS is a $4k_{\rm F}$ CDW for $K^{-1} > K^{-1}_{\rm crit} \sim 1.1$. GS and solitonic states of the system have been investigated as a function of ω and K^{-1}.

In order to determine the phase diagram at quarter-filling, we have computed the charge gap $\Delta_\rho = E_0(2N, N+1) + E_0(2N, N-1) - 2E_0(2N, N)$ (where $E_0(N_{\rm s}, N_{\rm e})$ is the GS energy of $N_{\rm e}$ electrons on $N_{\rm s}$ sites).

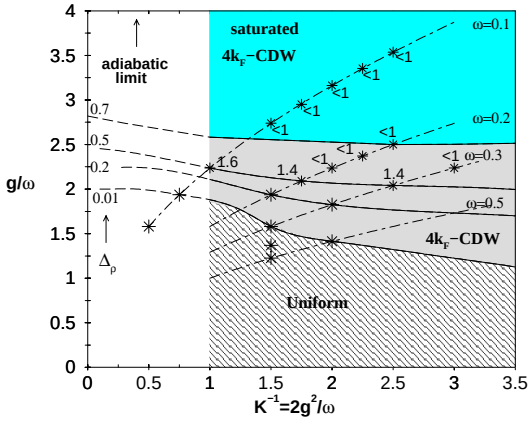

Fig. 1. Schematic phase diagram of a 1/4-filled t-J chain for $J/t = 0.3$ and $V/t = 1$ as a function of $K^{-1} = 2g^2/\omega$ and g/ω. The two shaded regions correspond to insulating $4k_{\rm F}$ CDW phases, the dark-shaded one corresponding to the saturated $4k_{\rm F}$ CDW phase : $A_{4k_{\rm F}} \simeq 1/2$. The slanted region corresponds to the Luttinger liquid uniform phase. The solid lines, extrapolated by dashed lines correspond to iso-gaps curves, the dot-dashed lines correspond to iso-frequencies curves. The numbers correspond to the width, ξ, of the solitons at the reported points.

For that purpose, we have used open boundary conditions (OBC), systems up to 50 sites and extrapolated the results to the thermodynamic limit. Note that OBC are used in gap calculations because the DMRG method performs better in this case than with periodic boundary conditions (PBC). In addition, we have also calculated the charge correlation function $c_n(j) = \langle(n_i - \langle n\rangle)(n_{i+j} - \langle n\rangle)\rangle$ where $\langle n\rangle = N_{\rm e}/N_{\rm s}$.

3 Results and discussion

Figure 1 shows the schematic phase diagram as a function of g/ω and K^{-1} exhibiting a $4k_{\rm F}$ CDW insulating phase and a uniform metallic phase with usual Luttinger liquid characteristics (in particular the power law decrease of the charge and spin correlation functions). It has been argued that, although phononic quantum fluctuations are present, such state still belongs to the Luttinger Liquid universality class [14,16]. The insulating $4k_{\rm F}$ CDW phase was characterized both by a finite charge gap and long range staggered charge correlations associated to the finite order parameter $(-1)^j c_n(j)$. Special care is needed for $\omega \to 0$ since, in this case, the truncation of the phonon basis is no more adequate and more phonon states are expected to be excited. Indeed, $K^{-1}_{\rm crit} \simeq 1.1$ obtained in the adiabatic approximation [12] does not seem to appear as an asymptotic limit for the metal-insulator boundary when $\omega \to 0$ and $g/\omega \to +\infty$. Within our treatment, $K^{-1}_{\rm crit}$ tends towards zero, which seems inconsistent with the finite value $K^{-1}_{\rm crit} \simeq 1.1$ obtained in the adiabatic approximation [12] for the same J and V values. Therefore, we shall restrict in the following analysis to $\omega > 0.1$ where we expect our results to be fully reliable.

Let us now discuss the effect of the frequency ω at fixed K^{-1}: for values of K^{-1} such as the adiabatic GS is in

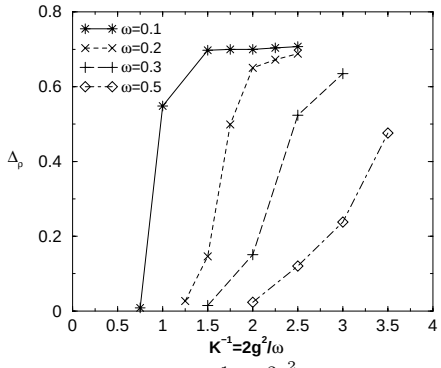

Fig. 2. Charge gap *versus* $K^{-1} = \frac{2g^2}{\omega}$ for different frequencies (as indicated on the plot).

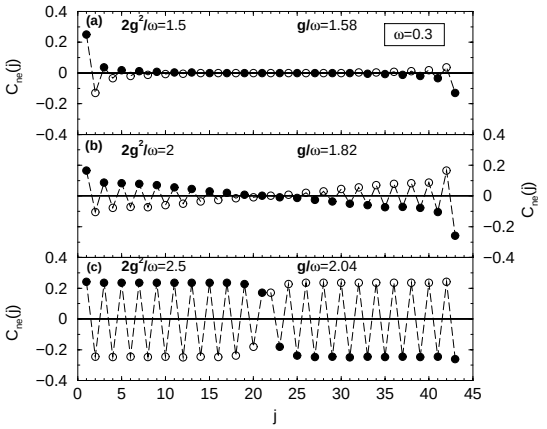

Fig. 3. Charge correlation function of an odd chain $N_s = 43$, $N_e = 22$ for several couplings g. For convenience data of the same (opposite) sign as $(-1)^j$ are shown as full (open) symbols. For clarity, the soliton has been shifted to the center of the chain.

the insulating phase, we found that, by increasing ω, the system becomes metallic. As one can expect, increasing phonon quantum fluctuations suppress long-range CDW order. The opening of the charge gap characteristic of the metal-insulator transition is fully consistent with the formation of the CDW as shown in Figure 2 and in Figure 1 where the iso-gap curves are reported. At intermediate frequencies (let's say $\omega \geq 0.3$), we observe a smooth opening of the gap with a saturation for large value of K^{-1}, whereas for decreasing frequencies the transition seems to become more abrupt. This behavior is in agreement with the first order character of the metal-insulator transitions in the adiabatic limit, as seen in reference [12]. In contrast, our calculation at finite phonon frequency is consistent with a second order phase transition and a Kosterlitz-Thouless exponential gap opening ($\Delta_\rho \sim \mathrm{e}^{-\alpha/(K^{-1}-K_c^{-1})}$). A very accurate determination of the phase transition characteristics would however be difficult. Indeed, as in the $\omega \to 0$ limit, high excited vibronic states should be populated at the transition and therefore the necessary truncation of the phononic basis prevents a precise description of it. In fact systematic bias toward the insulating phase can be expected.

By doping (*e.g.* in electrons) the chain away from the commensurate density of $\langle n \rangle = 1/2$ one can introduce charged soliton-antisoliton pairs. Note that solitons naturally appear in pairs since they are intrinsic topological excitations. However, in a finite chain, it is possible to enforce the existence of a single soliton in the GS by assuming an odd number of sites. For this purpose, we shall deal with odd-length chain with $N_s = 2N + 1$ sites and $N_e = N + 1$ electrons (typically we choose $N = 2p + 1$) and PBC. Chains with size up to 43 sites have been considered. On the other hand, even-length periodic chains with $N_s = 2N$ sites (typically choosing $N = 2p + 1$) doped with 1 extra electron ($N_e = N + 1$) of size up to 42 sites have been considered to study the behavior of a soliton-antisoliton pair. The charge-charge correlation in an odd-length chain carrying a single soliton is shown in Figures 3a–c for different values of the parameter g/ω and fixed frequency $\omega = 0.3$. For increasing e-ph coupling (or equivalently in this case for increasing K^{-1}), the system evolves from a delocalized state with no soliton (*cf.* Fig. 3a) to a state with a soliton confined on a small number of sites. (*cf.* Fig. 3c). Figure 3b shows the intermediate regime where a soliton exists and spreads over a large number of sites (in fact over all the 43 sites of the largest chain considered in this work). In fact, a solitonic excitation becomes stable and acquires a width and an amplitude at the phase transition point where the CDW order parameter starts to grow. This width decreases and the amplitude increases as K^{-1} increases up to saturation (one inter-site distance for the width and 1/2 for the amplitude). It is remarkable to note that the on-site displacements strictly follow the on-site charges, irrespectively to the relative location to the soliton. Similarly, the excited phonon state remains weakly populated even at the soliton location, validating the pertinence of the basis set truncation as long as one is not at the phase transition. In order to estimate the width of the soliton, one can fit the staggered charge correlation function with a usual solitonic function $A \tanh(\frac{x-x_0}{\xi})$ where A is the long-range CDW amplitude, ξ is the width of soliton (reported in Fig. 1) and x_0 is the location of the center of the soliton. When the gap is saturated the soliton is totally confined to, let say, a single site. On the contrary, in the uniform phase, strictly speaking $A \simeq 0$ and the charge correlation function decays as a power law. In that case, the extra $Q = +\frac{e}{2}$ charge is totally spread over the full chain. Around the (infinite size) phase transition line between the uniform and CDW phases, the soliton will appear spread out over the entire finite system whenever its size (in the infinite system limit) becomes larger than the actual system size.

In the CDW phase, the DMRG procedure introduces (despite of the PBC) a small translation symmetry breaking (contained in the initial state) which leads to a localization of the soliton around some arbitrary location x_0 along the chain. This indicates that, in real materials, this type of excitation could very easily get pinned by impurities or defects. However we still expect the soliton to be *mobile* in a perfectly pure system.

So far, we have imposed the presence of a single soliton in the GS by a geometrical mean. However, in order to fully prove the stability of such excitations one should also

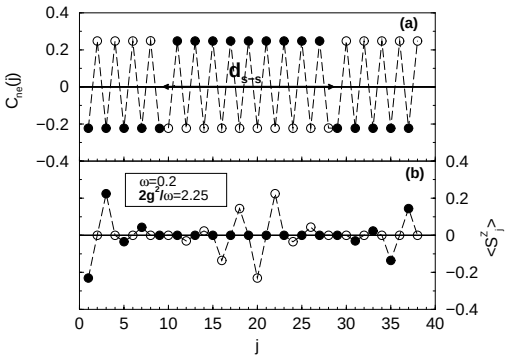

Fig. 4. Charge correlation function (a) and local spin component $\langle S_i^Z \rangle$ (b) for an even chain with $N_s = 38$, $N_e = 20$, frequency $\omega = 0.2$ and $2g^2/\omega = 2.25$. For convenience, the two sets of data corresponding to the two sublattices ("even" and "odd" sites) are shown separately as full and open symbols.

consider a situation where at least two of them can scatter with each other. For this purpose, a full extra charge $Q = +e$ has been added to a cyclic ring with an even number of site on top of the CDW GS. The charge correlation function shown in Figure 4a indicates that a soliton and an antisoliton well separated from each other appear. For a fixed system size and different runs, we have found that the location of the soliton-antisoliton "center of mass" is arbitrary, but the calculated mean distance $d_{s-\bar{s}}$ between the two solitons stays the same. For increasing system size N_s, the distance $d_{s-\bar{s}}$ increases exactly like $d_{s-\bar{s}} = \frac{N_s}{2}$. This demonstrates that independent solitons and anti-solitons are stable in the CDW phase and do not bind into charge e quasiparticles. Note that the solitonic charge $Q = +\frac{e}{2}$ can be directly "measured" by integrating the excess charge over the soliton width. It is also interesting to notice that previous studies on spin $\frac{1}{2}$ solitons in spin-Peierls chains with dynamical phonons [17] have demonstrated that soliton-antisoliton bound states cannot exist unless a two-dimensional coupling is considered. Quite generally reference [4] predicts solitons to have either spin zero or spin-1/2. In fact, the on-site average spin plotted in Figure 4b shows that, in the present case, each soliton carries no spin.

4 Conclusion

We finish this paper by a brief discussion on the possible relevance to experimental systems. It is clear that with on-site CDW associated with differential geometry relaxation of the DI−DCNQI molecules, the $(DI-DCNQI)_2Ag$ compound is the perfect candidate for the present study. Note that under 5.5 K [18] this compound undergoes a second phase transition towards an $4k_F$ CDW, $2k_F$ SDW mixed state. As already mentioned by different authors [16,19], on-site $4k_F$ CDW have the property to allow simultaneous $2k_F$ SDW. Although the metal-insulator instability in $(TMTTF)_2X$ (X = PF_6, AsF_6, etc...) is believed to be of the Mott-Hubbard type, the recent experiments [6–8] revealing, at lower temperatures, a $4k_F$ charge modulation on the (TMTTF) molecules suggest that relaxation of the molecules (together with the coupling to the anions) might play a dominant role. Therefore, fractionally charged excitations should appear (although a dimerization exists along the molecular stacks) and might be revealed in *e.g.* optical experiments. Note that it has also been theoretically suggested that the low temperature spin-Peierls phase would exhibit, in addition to the lattice tetramerization, a site-centered $2k_F$ CDW state [19]. Recent calculations [20] suggest that, in the case of a coexisting $2k_F$ CDW order, two charge $\frac{e}{2}$ solitons would bind. It would therefore be of particular interest to see how molecular relaxation and bond charge density wave resulting from the SP transition would interact and in particular whether the later could coexist with on-site $4k_F$ CDW or whether the lattice dimerization would bind two $e/2$ solitons in order to restore an integer charge defect.

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