Charge versus Fermion Fractionalization in the Quarter-Filled Hubbard-Peierls Model

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We investigate the soliton excitations in the quarter-filled Hubbard-Peierls model in both the large- and small-U limits. For a strictly one-dimensional system at zero temperature, we find that the solitons in both limits are in one-to-one correspondence. In the presence of weak three-dimensional coupling, the large-U system differs qualitatively from the small-U system in that the spin associated with the solitons ceases to be a sharp quantum observable. We suggest a natural explanation of both the magnetic and the dielectric response measured in $(NPM)_x(Phen)_{1-x}TCNQ$ [(N-methylphenazinium)$_x$(phenazine)$_{1-x}$(tetracyanoquinodimethanide)] and $Qn(TCNQ)_2$ (quinolinium ditetracyanoquinodimethanide).

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It is now well established that a topological defect or kink may carry fractional or even irrational charge measured in units of the charge possessed by elementary excitations of the unperturbed medium[1-4]; moreover it has been demonstrated that this fractional charge is a sharp quantum observable.[5-7] The original work of Jackiw and Rebbi[1] suggested a further special possibility: If there exists a charge-conjugation symmetry in the presence of the soliton, then the kink should have two degenerate charge-conjugate states with fermion number $F=\pm\frac{1}{2}$. However, there is not yet an undisputed example of this situation in a realistic model. Indeed, it has been speculated that no real system could have such properties as long as charge-conjugation symmetry continues to hold in the presence of the kink.[8]

Relevant to this debate is the suggestion[9] that the elementary degrees of freedom of a quarter-filled Peierls-Hubbard system in the infinite-coupling limit ($U=\infty$) behave like spinless fermions of a half-filled band in the zero-coupling limit ($U=0$), and that therefore there are two charge-conjugate kink states with charge $Q=\pm\frac{1}{2}e$. Moreover, this large-U Peierls-Hubbard model is believed to be realized in certain charge-transfer salts[10] such as $(NMP)_x(Phen)_{1-x}TCNQ$ [(N-methylphenazinium)$_x$(phenazine)$_{1-x}$tetracyanoquinodimethanide)] and $Qn(TCNQ)_2$ (quinolinium ditetracyanoquinodimethanide).

At $U=\infty$, the ground state is 2^M-fold degenerate where M is the number of electrons, since different spin configurations all share the same energy. It is therefore necessary to study the limit as $U\rightarrow\infty$ in order to make contact with realistic systems. We have studied the system over the range from $U=0$ to $U\rightarrow\infty$. In this paper we summarize the results which will be reported in detail in a forthcoming publication.[11] In the $U\rightarrow\infty$ limit, the effective Hamiltonian which governs the spin excitations is that of a spin-$\frac{1}{2}$ antiferromagnetic spin chain. On the basis of this effective Hamiltonian, we argue that the ground state has a spontaneously broken translational symmetry which consists of a lattice dimerization driven by a half-filled band of spinless fermions, *and* a further much weaker dimerization of the dimers, driven by a spin-Peierls instability. The ground state thus has the same symmetry as for $U=0$. Moreover, we find that the solitons of this $U\rightarrow\infty$ double dimerized system have the same quantum numbers as those of the $U=0$ system though their profiles and relative creation energies are quite different. For all U we find three types of solitons: a spin-$\frac{1}{2}$, neutral, amplitude soliton $S_0^{1/2}$, a spinless phase soliton with $Q=\pm\frac{1}{2}e$, $S_{1/2}^0$, and a spin-$\frac{1}{2}$, $Q=\pm\frac{1}{2}e$, mixed phase and amplitude soliton, $S_{1/2}^{1/2}$. The neutral soliton is self-conjugate, but the degenerate charged-soliton doublets are not. For U large and $T\neq0$, the spin-Peierls instability is very weak, and is likely to be suppressed in many experimentally relevant cases. Thus, we conclude this paper by analyzing the model in the absence of this distortion and its relation to experiments.

The Peierls-Hubbard model is defined by the Hamiltonian

$$H=-\sum_{n=1}^{N}\sum_{s=\pm\frac{1}{2}}[t_0-\alpha(u_n-u_{n+1})](c_{n,s}^\dagger c_{n+1,s}+\mathrm{H.c.})+\frac{K}{2}\sum_{n=1}^{N}(u_n-u_{n+1})^2+U\sum_{n=1}^{N}c_{n,\frac{1}{2}}^\dagger c_{n,\frac{1}{2}}c_{n,-\frac{1}{2}}^\dagger c_{n,-\frac{1}{2}}, \quad (1)$$

where $c_{n,s}^\dagger$ creates an electron of spin s on the latice site n, and u_n denotes the displacement of the nth lattice site. We treat u_n as a classical field. t_0, α, K, and U are coupling constants and N is the number of lattice sites.

At $U=0$, this model is identical to the Su-Schrieffer-Heeger (SSH) model,[4] except that the electron band is only quarter-filled, i.e., $k_F=\pi/4a$, where a is the lattice constant. According to Peierls's theorem, the ground state is a charge-density-wave (CDW) state with period $2k_F$. In contrast to the half-filled SSH model, both the amplitude *and* the phase of the CDW condensate play a dynamical role in this system.[12] For instance, we can define the dimensionless order parameter by

$$\Delta_1(n)=(\sqrt{2}\alpha/t_0)u_n\cos(\pi n/2),\quad \Delta_2(n)=(\sqrt{2}\alpha/t_0)u_n\sin(\pi n/2),$$

or by

$$\Delta(n)e^{i\theta(n)}=\Delta_2(n)+i\Delta_1(n). \tag{2}$$

The various kinds of soliton excitations can be studied by consideration of the continuum limit of the $U=0$ discrete model (1):

$$\frac{H}{t_0}=\sum_s\int dx\,\psi_s^\dagger(x)[i\sigma_z\sqrt{2}a\,\partial_x+\Delta(x)\sigma_x\exp(i\sigma_z\theta(x))]\psi_s(x)+\int\frac{dx}{a}\left[\frac{\Delta^2(x)}{4\lambda}-A\Delta^4(x)\cos4\theta(x)\right], \tag{3}$$

where

$$\psi(x)=\begin{bmatrix}\psi_L(x)\\ \psi_R(x)\end{bmatrix}$$

represents the electronic states near k_F and $-k_F$, respectively, and $\lambda=\alpha^2/Kt_0$ is the dimensionless coupling constant. The last term arises from the *umklapp process* and is the source of the nontrivial phase dependence of the effective potential.[12,13] In the small-Δ limit, $A=(1/2\pi)\ln\Delta_0$.[13] For uniform order parameter, one finds $\Delta=\Delta_0=2\sqrt{2}Wa\exp(-\pi/2\sqrt{2}\lambda)$, where W is the momentum cutoff in the continuum model.

There are four degenerate ground states $A,B,C,$ and D with $\Delta(x)=\Delta_0$ and $\theta(x)=0$, $\pi/2$, π, and $3\pi/2$, respectively. The various solitons are domain walls between degenerate phases, and are partially characterized by the change in the phase $\Delta\theta$ of the order parameter. For instance, the phase boundary between A and B phases is a $\Delta\theta=\pi/2$ soliton, while that between A and C phases is a $\Delta\theta=\pi$ soliton. We have studied the nature of these solitons both by numerically solving the discrete model to find the lattice configuration which minimizes the soliton creation energy and by approximate solution of the continuum model (see also Zhang, Kivelson, and Goldhaber[11] and Hubbard and Ohfuti and Ono[14]). The results can be summarized as follows. (1) There is one localized state associated with the $\pi/2$ soliton. If the state is unoccupied, the soliton has charge $Q=\frac{1}{2}|e|$ and spin 0, and is a pure phase soliton with $\Delta(x)\approx\Delta_0$ and $\theta(x)\approx\tan^{-1}\exp(x/l)$, where $l=a/\Delta_0^2(2A)^{1/2}$. Its creation energy is $E_s/t_0=(2A)^{1/2}\Delta_0^2+o(\Delta_0^3)$. If the state is singly occupied, the soliton has spin $-\frac{1}{2}$ and charge $Q=-\frac{1}{2}|e|$. It has mixed phase and amplitude character with

$$\Delta(x)\approx\Delta_0\tanh(x/\xi_0),\quad \theta(x)\approx\tan^{-1}\exp(x/l),$$

and creation energy $E_s/t_0=2\Delta_0/\pi+(2A)^{1/2}\,\Delta_0^2+o(\Delta_0^3)$, where $\xi_0=a/\Delta_0$ is the correlation length. If the state is doubly occupied, the soliton has creation energy of order Δ_0, and hence it is unstable with respect to formation of a topologically equivalent multiplet of three $\Delta\theta=-\pi/2$ pure phase antisolitons. (2) There is also one localized state associated with the $\Delta\theta=\pi$ soliton. The soliton is only stable if it is singly occupied, in which case it has $Q=0$ and spin $\frac{1}{2}$. This soliton is a pure amplitude soliton, and is precisely analogous to the neutral soliton in polyacetylene. An exact solution of the continuum model for this case gives $\Delta(x)=\Delta_0\tanh(x/\xi_0)$, $\theta(x)=0$ for its profile and $E_s/t_0=2\Delta_0/\pi$ for its creation energy.

Having identified the stable soliton excitations at $U=0$, we now proceed to study the limit $U\to\infty$ in (1). Rice and Mele[9] noticed that at $U=\infty$, the electrons can only singly occupy the sites, and two electrons cannot cross each other. It follows that the spin configuration is a constant of motion and the Hilbert space splits into 2^M disjoint subspaces, each with a definite spin configuration. Within each subspace, the electrons behave effectively like noninteracting fermions. In this case, the band of spinless fermions is half-filled, i.e., $k_F=\pi/2a$. The lattice will dimerize and open a gap in the electronic spectrum about the Fermi level. The ground state corresponds to a completely filled valence band, which can be represented equivalently as a state in which all the Wannier states $|R_n\rangle$ are occupied,[7] where $|R_n\rangle$ is exponentially localized about the center of the strong bond at position R_n. The ground state of a definite spin ordering can be represented by

$$|\Omega,\sigma_1,\ldots,\sigma_M\rangle=c\sum_{n_1<\ldots<n_M}F_{n_1\ldots n_M}^{R_1\ldots R_M}c_{n_1,\sigma_1}^\dagger\cdots c_{n_M,\sigma_M}^\dagger|0\rangle, \tag{4}$$

where $c_{n_j,\sigma_j}^\dagger$ creates the jth electron from the left at site n_j with spin σ_j. F is the determinant of the matrix W_{ij}, where $W_{ij}=\langle n_i|R_{m_j}\rangle$ is the Wannier function and c is a normalization constant.

At finite U, the effective Hamiltonian mixes the different spin configurations, since two electrons can occupy the same site as a virtual state. By straightforward degenerate perturbation theory we obtain the matrix elements of the effective Hamiltonian H_{eff} between the degenerate ground states (5). The resulting effective Hamiltonian can be cast into the form of a one-dimensional spin-$\frac{1}{2}$ Heisenberg chain,

$$H_{\text{eff}} = \sum_{i=1}^{M} J_i (\mathbf{S}_i \cdot \mathbf{S}_{i+1} - 1), \tag{5}$$

where

$$J_i = \frac{c^2}{U} \sum_{n_1 < \ldots < n_M} t_{n_i} t_{n_{i+1}} \delta_{1+n_i, n_{i+1}} F^{R_1 \ldots R_M}_{n_1 \ldots n_M} F^{R_1 \ldots R_i R_{i+1} \ldots R_M}_{n_1 \ldots n_i - 1 n_i \ldots n_M} + \frac{c^2}{U} \sum_{n_1 < \ldots < n_M} t^2_{n_i} \delta_{1+n_i, n_{i+1}} (F^{R_1 \ldots R_M}_{n_i \ldots n_M})^2. \tag{6}$$

In the case where the lattice is perfectly dimerized, J_i is actually independent of i. However, as we shall argue later, the lattice is not simply dimerized, but is doubly dimerized because of the spin-Peierls transition.[15]

It is a bit difficult to study this transition in general since J_i is rather complicated because the nth spin can only be loosely associated with the nth strong bond R_n. However, the model is quantitatively unchanged if we study it in the extremely dimerized limit where the nth spin *is* localized on the nth strong bond. Thus, we consider the limit in which the hopping matrix elements between the strong bonds t_s are much larger than that between the weak bonds t_w, so that we can treat t_w as a perturbation. To the zeroth order in t_w, electrons can only hop between the sites connected by the strong bonds. To second order in t_w, the ground-state spin degeneracy is removed by the hopping between the weak bonds. The resulting effective Hamiltonian is of the same form as Eq. (5), but with

$$J_i = \frac{2t_s^2}{U} t^2_{w,i} \left[\frac{1}{(U-\epsilon_+)(t_s+\epsilon_+)} + \frac{1}{(U-\epsilon_-)(t_s+\epsilon_-)} \right], \tag{7}$$

where $\epsilon_\pm = \frac{1}{2}[U \pm (U^2+16t_s^2)^{1/2}]$ and $t_{w,i}$ is the weak bond between the ith and the $(i+1)$th strong bond.

Because of the spin-Peierls transition, the weak bonds also dimerize in the ground state to form alternating weak and very weak bonds [Fig. 1(a)]. The various defects can be analyzed in the same way as before; in particular, we identify the three stable solitons as the $Q = \frac{1}{2}|e|$, $S=0$ soliton [Fig. 1(b)], the $Q = -\frac{1}{2}|e|$, $S=\frac{1}{2}$ soliton [Fig. 1(c)], and the $Q=0$, $S=\frac{1}{2}$ soliton [Fig. 1(d)].

Therefore, in the extremely dimerized limit, for any U the soliton quantum numbers are in one-to-one correspondence with those of the $U=0$ limit. There is no phase transition at $T=0$ and finite U. However, at large U, the spin-Peierls ordering becomes very weak. Even a small three-dimensional coupling is enough to destroy the spin-Peierls ordering. Moreover, since the characteristic energy of spin excitations is so small, even within a strictly one-dimensional model there is a large range where the temperature T is large compared to the creation energy of the neutral soliton, and hence the spin-density $4k_F$ ordering is completely destroyed, yet T is still small compared to any of the charged-soliton creation energies. Thus, it is interesting to consider the excitations of the large-U system in the absence of a $4k_F$ (double-dimerized) distortion. In this case the ground state is twofold degenerate, and there is only one type of soliton. Simple counting arguments suggest that this soliton has $Q = \pm\frac{1}{2}|e|$ and spin $\pm\frac{1}{4}$. Thus, one might conclude that there is actually half of an electron associated with the soliton!

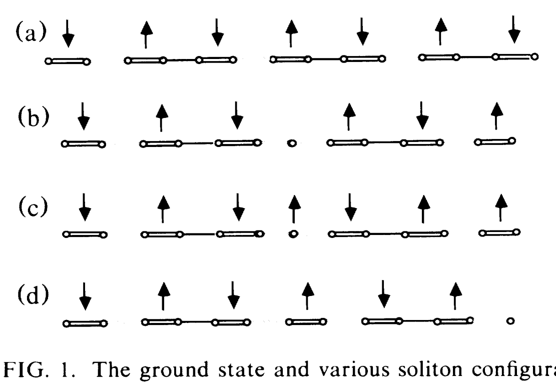

FIG. 1. The ground state and various soliton configurations in the extremely dimerized limit. Double lines, single lines, and broken lines represent strong bonds, weak bonds, and very weak bonds, respectively. Electrons localized on the strong bonds are represented by up and down arrows according to their spins.

This counting argument is correct as far as the expectation value of the spins is concerned. However, although the charge of the soliton is a sharp quantum observable,[5,6] the spin is not. To see this, we define the spin associated with the soliton as $\mathbf{S} = \sum_n f(n)\mathbf{s}(n)$ where $\mathbf{s}(n)$ is the spin density operator and $f(n)$ is a sampling function which is 1 over a region of size L about the soliton, and falls to zero beyond it. The mean square fluctuation of the spin can be computed easily from the spin-spin correlation function $G(n,m) = \langle \mathbf{s}(n) \cdot \mathbf{s}(m)\rangle - \langle \mathbf{s}(n)\rangle \cdot \langle \mathbf{s}(m)\rangle$ according to

$$\langle \Delta \mathbf{S}^2 \rangle = \frac{1}{2} \sum_{n,m} [f(n) - f(m)]^2 G(n,m). \tag{8}$$

In the presence of the soliton, $G(n,m) = G^0(n-m) + F(n,m)$, where G^0 is the correlation function of the perfect spin chain and $F(n,m) \sim G^0(n)G^0(m)$ is the correction due to the presence of the soliton. In the spin-Peierls state $G^0(n)$ is exponentially localized as a result of the gap in the spin-wave spectrum. Thus, for L sufficiently large, the fluctuations associated with the soliton spin are exponentially small. Without the spin-Peierls order, however, $G^0(n) \sim 1/|n|$, and hence the fluctuations are divergent. No particular spin can be associated with the soliton!

We note that in both $(NMP)_x(Phen)_{1-x}TCNQ$ and $Qn(TCNQ)_2$, the x-ray scattering data show the presence of a $4k_F$ distortion, but no $2k_F$ distortion.[10] We thus conclude that these materials are well described by a large-U quarter-filled Peierls-Hubbard model with the spin-Peierls distortion supressed. Experiments by Epstein *et al.*[10] on the magnetic susceptibility have been interpreted in terms of a weakly disordered Heisenberg spin chain, with a defect concentration proportional to the deviation in x from $x=0.5$ (the commensurate value). This has a natural interpretation in terms of a concentration of solitons proportional to $|x-0.5|$. This interpretation is lent further support by the fact that the x-ray scattering shows commensurate lock-in for a finite range of x about $x=0.5$. Experiments on the dielectric response and conductivity have been interpreted in terms of rather mobile, metallic, highly one-dimensional charged carriers in the presence of disorder.[15] The fact that the charge response of the system is characteristic of rather mobile electrons and the spin response is characteristic of an insulator is striking. It has a natural explanation in our model in terms of the almost complete decoupling between charge carriers (solitons) and the spin degree of freedom which occurs when the spin-Peierls transition is suppressed. We will discuss this point in greater detail in a future communication.

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