Solitons in polyacetylene: A comment

Baruch Horovitz
Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104
*and Department of Nuclear Physics, The Weizmann Institute of Science, Rehovot, Israel**
(Received 7 December 1979)

Recent soliton solutions in a charge-density-wave condensate in both the incommensurate and the commensurate half-filled band are considered. Neutral solitons exist in both cases while the charged soliton exists only in the commensurate case. Inclusion of exchange Coulomb interaction leads to a complex order parameter and then the charged solitons become phase solitons.

Takayama, Lin-Liu, and Maki (TLM)[1] have recently found a remarkable analytic solution for solitons in a condensed charge-density-wave system. Their model is a continuum version of the theory of solitons in polyacetylene studied by Su, Schrieffer, and Heeger (SSH).[2]

TLM applied their solution to a neutral soliton in an incommensurate system. Here we extend their result by considering the following: (a) effects of commensurability when the electron band is half-filled; (b) the possibility of charged solitons; (c) effects of Coulomb exchange interaction. We find that the TLM solution does not describe charged solitons in an incommensurate system, but it does describe both neutral and charged solitons in the commensurate system. When Coulomb exchange interaction is included in a Hartree-Fock scheme, the TLM solution is still valid for neutral solitons. However, charged solitons in the commensurate system are described by a complex order parameter and correspond to phase solitons.

The SSH model Hamiltonian of a one-dimensional electron-phonon system is written as

$$\mathcal{H}=\sum_{n,s} t_{n+1,n} C^{\dagger}_{n+1,s} C_{n,s} + \text{H.c.} + \tfrac{1}{2}K \sum_{n} (y_{n+1}-y_n)^2 + \tfrac{1}{2}M \sum_{n} \dot{y}_n^2 \tag{1}$$

with

$$t_{n+1,n} = -t_0 - \alpha (y_{n+1}-y_n), \tag{2}$$

where $C^{\dagger}_{n,s}$ creates an electron of spin s on the nth site and y_n is the ion displacement. The transfer integral $t_{n+1,n}$ is modulated by the electron-phonon coupling α, while M and K are the ion mass and force constant, respectively.

The continuum limit is obtained by decomposing the electron field in the form

$$C_{n,s} = u_s(n) e^{ik_F na} - iv_s(n) e^{-ik_F na}, \tag{3}$$

where a is the lattice constant and k_F the Fermi wave vector. The relevant electronic states are those near the Fermi level and therefore the fields $u(n)$, $v(n)$ are slowly varying and considered independent. This approximation leads to the Luttinger model and to most other models on one-dimensional electron system.[3]

The phonon field is also decomposed as

$$y_n = \frac{1}{4\alpha'} [\Delta^{\dagger}(n) e^{2ik_F na} + \Delta(n) e^{-2ik_F na}] \tag{4}$$

with $\Delta(n)$ again a slowly varying field and $\alpha' = \alpha \sin k_F a$.

The Hamiltonian (1) can now be written in terms of the slowly varying fields and a continuum notation $x = na$ is used. We use a parameter η which has two values: $\eta = 1$ for a commensurate system $k_F = \pi/2a$ and $\eta = 0$ for an incommensurate one, i.e., k_F is far from $\pi/2a$ and terms involving $\exp(4ik_F a)$ are rapidly oscillating and neglected. Terms involving $\exp(2ik_F na)$ are neglected in both cases.

Define a dimensionless electron-phonon coupling

$$\lambda = 4\alpha^2 a/(\pi v_F K), \tag{5}$$

where $v_F = 2t_0 a$ and the Hamiltonian becomes

$$\mathcal{H} = \sum_s \int dx \Big[-iv_F \Big(u_s^{\dagger}(x) \frac{\partial}{\partial x} u_s(x) - v_s^{\dagger}(x) \frac{\partial}{\partial x} v_s(x) \Big) + [\Delta^{\dagger}(x) + \eta \Delta(x)] u_s^{\dagger}(x) v_s(x) + [\Delta(x) + \eta \Delta^{\dagger}(x)] v_s^{\dagger}(x) u_s(x) \Big] + (2\lambda \pi v_F)^{-1} \int dx [2\Delta^{\dagger}(x)\Delta(x) + \eta \Delta^2(x) + \eta \Delta^{\dagger 2}(x)]. \tag{6}$$

The field $\Delta(x)$ is time independent, which is a mean-field Hartree approximation.

The equations of motion for $u(x)$ and $v(x)$ yield single-particle wave functions which satisfy

$$-iv_F\frac{\partial}{\partial x}u_{n,s}(x)+\tilde{\Delta}^\dagger(x)v_{n,s}(x)=\epsilon_n u_{n,s}(x)\,,$$
$$iv_F\frac{\partial}{\partial x}v_{n,s}(x)+\tilde{\Delta}(x)u_{n,s}(x)=\epsilon_n v_{n,s}(x)\,. \tag{7}$$

The off-diagonal element in the electron wave equation is defined as the order parameter

$$\tilde{\Delta}(x)=\Delta(x)+\eta\Delta^\dagger(x)\,, \tag{8}$$

which is explicitly related to the ion displacement.

The variation of $\mathcal{H}$ with respect to $\Delta(x)$ gives the self-consistency equation

$$\tilde{\Delta}(x)=-\lambda\pi v_F\left(\sum_{n,s}u^*_{n,s}(x)v_{n,s}(x)+\eta\sum_{n,s}v^*_{n,s}(x)u_{n,s}(x)\right), \tag{9}$$

where the summation is on occupied states.

When $\tilde{\Delta}(x)$ is slowly varying Eqs. (7) and (9) can be solved by a Green's function method.[4] In a spinor representation (u,v) Eq. (7) defines a Green's function by

$$\left(i\frac{\partial}{\partial t}+iv_F\sigma_3\frac{\partial}{\partial x}-\mathrm{Re}\tilde{\Delta}(x)\sigma_1-\mathrm{Im}\tilde{\Delta}(x)\sigma_2\right)G(xt,x't')=\delta(x-x')\delta(t-t')\,, \tag{10}$$

where σ_i are Pauli matrices. Equation (9) reduces to

$$\tilde{\Delta}(x)=\tfrac{1}{2}i\lambda\pi v_F\mathrm{Tr}\{[\sigma_1(1+\eta)+i\sigma_2(1-\eta)]\,G(xt,xt)\}\,. \tag{11}$$

This equation is precisely the self-mass equation in the Hartree approximation.[4] The problem can now be solved by a derivative expansion of the Green's function. This expansion assumes $v_F\partial\tilde{\Delta}/\partial x\ll\tilde{\Delta}^2$ and clearly breaks down if $\tilde{\Delta}(x)$ vanishes at some point in space.

Let us first consider the incommensurate case $\eta=0$. TLM show that the ground state has $\Delta=\Delta_i$, where

$$\Delta_i=We^{-1/\lambda}\,, \tag{12}$$

and W is the bandwidth. The soliton solution, found by TLM, is

$$\Delta(x)=\Delta_i\tanh(\Delta_i x/v_F)\,. \tag{13}$$

The electron system has one bound state (two spin states) with energy $\epsilon_b=0$ and eigenfunction

$$iv_b(x)=u_b(x)=(\Delta_i/4v_F)^{1/2}\,\mathrm{sech}(\Delta_i x/v_F)\,. \tag{14}$$

In addition, there are extended states with energies outside the gap $\pm\Delta_i$. Equation (9) is satisfied by (11) if the soliton is neutral, i.e., the occupancy ν_b of the bound level is $\nu_b=1$ while both spin states of the levels below the gap are occupied. Since $u_b(x)v_b(x)$ is imaginary, when $\nu_b=1$ it is cancelled by the extended states so that $\tilde{\Delta}(x)$ in Eq. (9) is real. For a charged soliton $\nu_b=0,2$ and this cancellation is not complete, suggesting that the solution for $\Delta(x)$ is complex.

When $\Delta(x)$ is complex and does not pass through the point $\Delta=0$ one may consider the derivative expansion method. The excess charge is given by[4]

$$\delta\rho=e\phi'(x)/\pi\,, \tag{15}$$

where $\Delta=|\Delta|\exp(i\phi)$. For the incommensurate system (and no interchain coupling) $\int\phi'^2(x)dx$ must be minimized. The charge $\pm e$ would then correspond to $\phi(x)=\pi x/L$ where L is the length of the system. This has the effect of redefining the Fermi level.

Consider next the $\eta=1$ case. The umklapp terms, i.e., those which multiply η, describe interactions which are important only in the commensurate phase. In the incommensurate phase $\Delta^\dagger(x)$ scatters a $-k_F$ electron into a $+k_F$ electron, while in the commensurate phase it can also scatter a $+k_F$ electron into a $+3k_F$ electron which is the same as a $-k_F$ electron.

The crucial effect of the umklapp term in Eq. (9) is that all imaginary terms cancel. Thus for the potential (13) the contributions of the bound state (14) in Eq. (9) is canceled for any occupation of the bound state. The only contribution to Eq. (9) is then the real part of the sum with the extended states, and the TLM solution is valid for all the occupations of the bound state $\nu_b=0,1,2$. The only change is the replacement $\lambda\to2\lambda$ so that the ground state has $\Delta=\Delta_c$ with

$$\Delta_c=We^{-1/2\lambda}\,, \tag{16}$$

and the soliton solution (13) and (14) is valid with Δ_c replacing Δ_i. Thus for the half-filled band case the TLM solution is valid (except for a redefinition of the coupling) for both the neutral and charged solitons. This is in agreement with the SSH results.

Let us now consider the effects of adding a Coulomb interaction between electrons, in the Hartree-Fock approximation.

$$\mathcal{H}_{\mathrm{Coul}}=\sum_{n,n'}V(n-n')C^\dagger_nC_nC^\dagger_{n'}C_{n'}\,. \tag{17}$$

We assume that the potential has a long range r_0 with $a\ll r_0\ll v_F/\Delta_c$. Substituting Eq. (3) in (17) we obtain the following type of terms: (a) terms with only u electrons or only v electrons—these can renormalize v_F but do not affect the off-diagonal potential and we neglect them; (b) terms with three u electrons and one v electron or vice versa—these terms involve a phase factor $\exp(\pm2ik_Fna)$ with fast oscillations and can be neg-

lected; (c) scattering of $u \to v$ and $v \to u$—this involves the $2k_F$ component of the interaction, i.e., a phase factor of $\exp[\pm 2ik_F(n-n')a]$; since the interaction is long range this term is also neglected; (d) scattering of two u electrons into v states or vice versa—this umklapp process involves a phase factor of $\exp[\pm 2ik_F(n+n')a]$ and is also neglected; and (e) scattering with small momentum transfer, which is the only terms that we keep:

$$\mathcal{H}_{\text{Coul}} = 2\gamma\pi v_F \sum_{s,s'} \int dx u_s^\dagger(x) u_s(x)\, v_{s'}^\dagger(x) v_{s'}(x)\,; \tag{18}$$

since the fields $u(x), v(x)$ are varying slowly on the scale of r_0 we assumed a local interaction in (18).

The final assumption is that the system is charge neutral on the scale of the coherence length v_F/Δ so that the direct Coulomb interaction in (18) is canceled while the exchange decoupling gives

$$\mathcal{H}_{\text{Coul}}^{\text{ex}} = -2\gamma\pi v_F \sum_s \int dx [u_s^\dagger(x) v_s(x) \langle v_s^\dagger(x) u_s(x)\rangle + v_s^\dagger(x) u_s(x) \langle u_s^\dagger(x) v_s(x)\rangle]\,. \tag{19}$$

The total Hamiltonian of Eq. (19) and Eq. (6) leads to Eq. (7) except that now the order parameter $\tilde{\Delta}(x) \to \tilde{\Delta}_s(x)$ is given by

$$\begin{aligned}\tilde{\Delta}_s(x) &= \Delta(x) + \eta\Delta^\dagger(x) - 2\gamma\pi v_F \sum_n u_{n,s}^*(x) v_{n,s}(x) \\ &= -\lambda\pi v_F \left(\sum_{n,s} u_{n,s}^*(x) v_{n,s}(x) + \eta \sum_{n,s} v_{n,s}^*(x) u_{n,s}(x) \right) - 2\gamma\pi v_F \sum_n u_{n,s}^*(x) v_{n,s}(x)\,.\end{aligned} \tag{20}$$

The ground state is symmetric with respect to the spin, and for $\eta = 0$, or $\eta = 1$,

$$\Delta_i = We^{-1/(\lambda+\gamma)} \quad (\eta = 0)\,, \tag{21}$$

$$\Delta_c = We^{-1/(2\lambda+\gamma)} \quad (\eta = 1)\,. \tag{22}$$

The neutral soliton solution (13) is valid provided that one of the spin states $(\uparrow \pm \downarrow)/\sqrt{2}$ is occupied. Then $\tilde{\Delta}(x)$ is independent of s and (13) is valid with Δ_i for $\eta = 0$ and Δ_c replacing Δ_i for $\eta = 1$.

However, the charged soliton is not given by the solution (13) even for $\eta = 1$. The last term of (20) generates an additional imaginary part when $\nu_b = 0, 2$ which is not canceled by an umklapp term. Note that for an on-site interaction $V(n-n') \sim \delta(n-n')$ the umklapp process [term of type (d)] must be retained and will keep the order parameter real. However, if the interaction is long range the umklapp term does not compensate the direct scattering and the order parameter becomes complex.

Since the singular point $\tilde{\Delta} = 0$ can be avoided one can try the derivative-expansion method. This indeed has been done[5] and has led to an effective phase-amplitude Hamiltonian which has phase solitons.[5,6] A phase soliton has charge $\pm e$ and spin 0, i.e., it is the charged SSH soliton when the interaction (19) is added.

The phase soliton width increases with γ so that the derivative expansion is justified for $\gamma \gg \lambda$. However, even for $\beta = \lambda/[\gamma(2\lambda+\gamma)] = 1.5$ the total soliton width is[6] $\sim 4v_F/\Delta_c$ and the multisoliton solutions have even smaller derivatives.

Perturbation expansion around the solution (13) for small γ yields also a complex $\tilde{\Delta}(x)$ with $\mathrm{Im}\tilde{\Delta}(x) \sim \gamma \operatorname{sech}^2(xv_F/\Delta_c)$. Therefore the solution does not pass through $\tilde{\Delta} = 0$, probably for all γ, i.e., it is a phase soliton.

The solutions of the phase-amplitude Hamiltonian[5,6] show that for $\beta > 1.48$ phase solitons attract each other. In this case a system with finite density of phase solitons will separate into two phases: one phase with a high density of charged solitons, and a second commensurate phase with no solitons.

These results are consistent with experiments on doped polyacetylene. Here we assume that the dopant ions are sufficiently mobile and stay near the charged solitons, so that the system is charge neutral on the scale of the coherence length. The phase with the solitons is conducting while the rest of the polymer is insulating. Thus the system is described as metallic particles embedded in an insulating medium. This is consistent with infrared data[7] and with the temperature dependence of the conductivity.[8]

ACKNOWLEDGMENTS

I am deeply indebted to Professor J. R. Schrieffer for his hospitality at the University of Pennsylvania and for many fruitful discussions. I have also benefitted from discussions with W. P. Su, S. Kivelson, Professor A. J. Heeger and Professor J. A. Krumhansl.

*Present address.

[1]H. Takayama, Y. R. Lin-Liu, and K. Maki, Phys. Rev. B 21, 2388 (1980).
[2]W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. 42, 1698 (1979).
[3]For reviews see: *Highly Conducting One Dimensional Solids*, edited by J. T. Devreese, R. P. Evrard, and V. E. van Doren (Plenum, New York, 1979).
[4]B. Horovitz and J. A. Krumhansl, Solid State Commun. 26, 81 (1978).
[5]B. Horovitz, Solid State Commun. 34, 61 (1980).
[6]M. Grabowsky, K. R. Subbaswamy, and B. Horovitz, Solid State Commun. (in press).
[7]C. R. Fincher, Jr. *et al.*, Phys. Rev. B 20, 1589 (1979).
[8]Y. Tomkiewicz, T. D. Schultz, H. B. Brom, T. C. Clarke, and G. B. Street, Phys. Rev. Lett. 43, 1532 (1979).