Two-soliton interaction energy and the soliton lattice in polyacetylene

Y. R. Lin-Liu and Kazumi Maki
Laboratoire de Physique des Solides, Université de Paris-Sud, 91405 Orsay, France*
and Department of Physics, University of Southern California, Los Angeles, California 90007
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Making use of a variational solution $\Delta(x)$ the dimerization pattern, we calculate the interaction energy of two solitons within the Su, Shrieffer, and Heeger model for polyacetylene. It is found that two solitons attract each other in general except for the case of two solitons having the same charge and the case of the spin triplet pair of neutral solitons. We have also studied the electronic structure of a regular array of solitons with the same charge.

I. INTRODUCTION

Recently there has been great interest in solitons in polyacetylene, since the proposal by Rice[1] and Su, Shrieffer, and Heeger (SSH)[2] that solitons will play an important role in the electric properties of doped ones. Su *et al.*[2] have developed a microscopic theory of solitons with the Hamiltonian including both the electronic and lattice distortion terms. While SSH have studied the soliton solution of the above model numerically, Takayama *et al.* (TLM)[3] have shown that the problem can be handled analytically in the continuum limit. Indeed, the continuum approximation should be quite good, as the system is essentially in the weak-coupling limit.

The object of the present work is twofold; first, we examine the interaction between two solitons in the continuum limit of the SSH model; second, we study the electronic properties of the soliton lattice formed by the charged solitons of the same charge. These problems are analyzed by making use of variation solutions, which are asymptotically exact when the distance between two solitons becomes much larger than the soliton size ξ. It is shown that for a large separation d (i.e., $d \gg \xi$), two neutral solitons with opposite spins or two charged solitons with opposite charges attract each other. Also, a neutral soliton and a charged one attract each other, but the interaction energy is one-half of that for two charged solitons of opposite charge. Finally, two charged solitons with the same charge or two neutral solitons with parallel spin configuration (i.e., the spin triplet state) weakly repulse each other.

Because of this, the charged solitons with the same charge tend to form a regular lattice to minimize the interaction energy when the soliton density is increased. Here we neglect the quantum fluctuation of the soliton lattice for simplicity, although it may have quite important consequences. The soliton lattice produces a narrow electron band in the middle of the dimerization energy gap. However, this electron band is either completely occupied for the case of the negatively charged solitons or completely empty for the case of the positively charged solitons. Therefore, the electrons in the narrow band play no role in the magnetic response or in the dc electric response of the system. A probable role of this narrow electron band in the metal-insulator transition of polyacetylene will be discussed later.

II. TWO-SOLITON PROBLEM

We have shown earlier[3] that the SSH model Hamiltonian

$$H = -\sum_{n,s} (t_{n+1,n} C^\dagger_{n+1,s} C_{ns} + \mathrm{H.c.}) + \frac{K}{2} \sum_n (y_{n+1} - y_n)^2 + \tfrac{1}{2} M \sum_n \dot{y}_n^2 \quad (1)$$

with

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

can be transformed into a familiar Hamiltonian[4] in the continuum limit

$$H_c = \frac{\omega_Q^2}{g^2} \int dx\, \Delta^2(x) + \int dx\, \Psi^\dagger(x) \left(-i v_F \sigma_3 \frac{\partial}{\partial x} + \Delta(x) \sigma_1 \right) \Psi(x) , \quad (3)$$

where

$$g = 4\alpha(a/M)^{1/2}, \quad \omega_Q^2 = 4K/M, \qquad \Delta(x) = g(a/M)^{1/2} \tilde{y}(x) , \quad (4)$$

and a is the lattice constant and $\tilde{y}(x)$ is the continuum limit of the dimerization pattern $\tilde{y}_n = (-1)^n y_n$. Here, $C^\dagger_{ns}$ (C_{ns}) is the electron creation (annihilation) operator at the site n, $\Psi(x) \equiv \binom{u(x)}{v(x)}$ is the spinor representation of the electronic field,[5] and σ_i are the Pauli matrices. The functional differentiation of Eq. (3) by Ψ^* and $\Delta(x)$ yields

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$$\epsilon_n u_n(x) = -iv_F \frac{\partial}{\partial x} u_n(x) + \Delta(x) v_n(x) ,$$
$$\epsilon_n v_n(x) = iv_F \frac{\partial}{\partial x} v_n(x) + \Delta(x) u_n(x) , \tag{5}$$

and

$$\Delta(x) = -\frac{g^2}{\omega_Q^2} \sum_{n,s}{}' \operatorname{Re}[v_n^*(x) u_n(x)] , \tag{6}$$

where u_n and v_n are normalized eigenfunctions of Eq. (5). The sum in Eq. (6) runs over up to the Fermi level, which is chosen to be zero. Equations (5) and (6) are very similar to the Bogoliubov-de Gennes equation[4] in the theory of superconductivity, except that the real part of $v_n^*(x)u_n(x)$ appears to the right-hand side of Eq. (6). As pointed out by Horovitz,[6] this reflects the condition that the field $\tilde{y}(x)$ is real in the half-filled band where the charge-density wave is commensurate with the CH group lattice $2k_F = \pi/a$.

It is shown by TLM[3] that the solution $\Delta(x) = \Delta_0 \tanh(x/\xi)$ with $\xi = v_F/\Delta_0$, where $2\Delta_0$ is the dimerization gap and v_F is the Fermi velocity, satisfies the self-consistent equations (5) and (6), yielding the soliton energy

$$E_S = E_{MF}(\Delta(x)) - E_{MF}(\Delta_0) = \frac{2}{\pi}\Delta_0 , \tag{7}$$

where

$$E_{MF}(\Delta(x)) = \sum_{ns}{}' \epsilon_n + \frac{\omega_Q^2}{g^2}\int dx\, \Delta^2(x) . \tag{8}$$

Here again the sum runs over the energy levels below the Fermi level. Furthermore, the bound state at the Fermi level has $\epsilon_n = 0$, and

$$u_n(x) = iv_n(x) = 2^{-1}\xi^{-1/2}\operatorname{sech}(x/\xi) . \tag{9}$$

Therefore, as already noted by Horovitz,[6] the bound state does not contribute to Eq. (6) or to Eq. (7), implying that the neutral and the charge soliton have identical $\Delta(x)$ and E_S, consistent with the numerical result of SSH.[2] Furthermore, the neutral soliton has spin $\frac{1}{2}$, while the charged soliton is spinless.

Here let us consider the two-soliton solution with a variation function

$$\Delta(x) = \Delta_0 \tanh\left(\frac{x - \frac{1}{2}d}{\xi}\right)\tanh\left(\frac{x + \frac{1}{2}d}{\xi}\right) , \tag{10}$$

where d is the distance between two solitons. In the limit of $d \gg \xi$, Eq. (10) approaches asymptotically to the exact solution. Substituting Eq. (10) into Eq. (5), we obtain a coupled equation for $u(x)$ and $v(x)$. The set of equations is separated by introducing $f_\pm = u \pm iv$ as[3,7]

$$\left\{V_F^2 \frac{\partial^2}{\partial x^2} + \epsilon^2 - V_\pm(x)\right\} f_\pm = 0 , \tag{11}$$

where

$$V_\pm(x) = \Delta^2(x) \mp v_F \frac{\partial \Delta(x)}{\partial x} \tag{12}$$

$$= \Delta_0^2\left\{\tanh^2\left(\frac{x - \frac{1}{2}d}{\xi}\right)\tanh^2\left(\frac{x + \frac{1}{2}d}{\xi}\right) \mp \left[\operatorname{sech}^2\left(\frac{x - \frac{1}{2}d}{\xi}\right)\tanh\left(\frac{x + \frac{1}{2}d}{\xi}\right) + \operatorname{sech}^2\left(\frac{x + \frac{1}{2}d}{\xi}\right)\tanh\left(\frac{x - \frac{1}{2}d}{\xi}\right)\right]\right\} . \tag{13}$$

From Eq. (13), we see immediately that $V_+(x)$ has a large potential well at $x = \frac{1}{2}d$, while $V_-(x)$ at $x = -\frac{1}{2}d$. In particular, in the limit $d \gg \xi$, we can approximate Eq. (13) by

$$V_\pm(x) = \Delta_0^2\left[1 - 2\operatorname{sech}^2\left(\frac{x \mp \frac{1}{2}d}{\xi}\right)\right] + O(e^{-2d/\xi}) . \tag{14}$$

This suggests that Eq. (11) can be solved variationally by making use of the solution with the single potential well. Furthermore, we have

$$V_+(x) = V_-(-x) , \tag{15}$$

implying that the energy spectrum of f_- is identical to that of f_+. Therefore, we shall confine ourselves to the f_+ function. The exact solutions of Eq. (11) with

$$V_+^0(x) = \Delta_0^2\left[1 - 2\operatorname{sech}^2\left(\frac{x - \frac{1}{2}d}{\xi}\right)\right] \tag{16}$$

is given as[3]

$$\epsilon_0^2 = 0,\quad f_B^+ = (2\xi_0)^{-1/2}\operatorname{sech}\left(\frac{x - \frac{1}{2}d}{\xi}\right) , \tag{17}$$

$$\epsilon_k^2 = [\Delta_0^2 + (kv_F)^2] ,$$
$$f_k = \{L[1 + (k\xi)^2]\}^{-1/2}\left[-ik\xi + \tanh\left(\frac{x - \frac{1}{2}d}{\xi}\right)\right] e^{ikx} , \tag{18}$$

where there are one bound state [Eq. (17)] and a set of scattering states with wave vector k. Here the scattering state is normalized in the system with length L.

Making use of wave functions given in Eqs. (17) and (18), we calculate the energy spectrum of Eq. (11) when the distance between two-soliton d is much larger than ξ, where we can treat $\delta V_+ = V_+ - V_+^0$ as a small perturbation. We obtain

$$\epsilon_0^2 = (2\xi)^{-1}\int_{-\infty}^{\infty} dx\, \operatorname{sech}^2\left(\frac{x + \frac{1}{2}d}{\xi}\right)\delta V_+(x) = 4\Delta_0^2 e^{-2d/\xi} + O(e^{-4d/\xi}) , \tag{19}$$

and

$$\epsilon_k^2=\Delta_0^2+(v_F k)^2+\frac{1}{L}[1+(k\xi)^2]^{-1}\int_{-\infty}^{\infty}dx\left[\tanh^2\left(\frac{x-\frac{1}{2}d}{\xi}\right)+(k\xi)^2\right]\delta V_+(x)$$

$$=\Delta_0^2+(v_F k)^2+\frac{1}{L}\left[\delta\overline{V}-[1+(k\xi)^2]^{-1}\int_{-\infty}^{\infty}dx\,\mathrm{sech}^2\left(\frac{x-\frac{1}{2}d}{\xi}\right)\delta V_+(x)\right]$$

$$\cong\Delta_0^2+(v_F k)^2+\frac{1}{L}\{\delta\overline{V}-[1+(k\xi)^2]^{-1}(8\xi\Delta_0^2e^{-2d/\xi})\}\,, \tag{20}$$

where

$$\delta V_+(x)=\Delta_0^2\left\{\mathrm{sech}^2\left(\frac{x-d/2}{\xi}\right)\mathrm{sech}^2\left(\frac{x+d/2}{\xi}\right)-\left[1+\tanh\left(\frac{x-d/2}{\xi}\right)\right]\mathrm{sech}^2\left(\frac{x+d/2}{\xi}\right)\right.$$
$$\left.+\left[1-\tanh\left(\frac{x+d/2}{\xi}\right)\right]\mathrm{sech}^2\left(\frac{x-d/2}{\xi}\right)\right\}, \tag{21}$$

and

$$\delta\overline{V}=\int_{-\infty}^{\infty}dx\,\delta V_+(x)=\Delta_0^2\int_{-\infty}^{\infty}dx\,\mathrm{sech}^2\left(\frac{x-d/2}{\xi}\right)\mathrm{sech}^2\left(\frac{x+d/2}{\xi}\right). \tag{22}$$

Equation (19) shows that in the presence of two solitons the bound state at $\epsilon_0=0$ is split into two levels with energy

$$\epsilon_{0\pm}=\pm2\Delta_0e^{-d/\xi}\,. \tag{23}$$

This splitting is due to overlapping of the bound state at $x=\frac{1}{2}d$ and that of $x=-\frac{1}{2}d$.

As to the valence band, the energy shift due to δV is calculated as

$$\delta\epsilon_V=-2\sum_k[\Delta_0^2+(v_F k)^2]^{-1/2}\frac{1}{2L}\{\delta\overline{V}-[1+(k\xi)^2]^{-1}(8\xi\Delta_0^2e^{-2d/\xi})\}$$

$$=-\frac{1}{2\pi}\int_{-\Lambda}^{\Lambda}dk[\Delta_0^2+(v_F k)^2]^{-1/2}\{\delta\overline{V}-[1+(k\xi)^2]^{-1}(8\xi\Delta_0^2e^{-2d/\xi})\}. \tag{24}$$

Here the factor 2 comes from the spin summation. As is easily seen, the first term in Eq. (24) is divergent logarithmically, which is exactly cancelled by one term arising from the lattice distortion energy:

$$E_{\mathrm{lattice}}(\Delta(x))=\frac{\omega_Q^2}{g^2}\int dx\,\Delta^2(x)$$

$$=\frac{\omega_Q^2}{g^2}\Delta_0^2\int dx\left[1-\mathrm{sech}^2\left(\frac{x+\frac{1}{2}d}{\xi}\right)-\mathrm{sech}^2\left(\frac{x-\frac{1}{2}d}{\xi}\right)+\mathrm{sech}^2\left(\frac{x-\frac{1}{2}d}{\xi}\right)\mathrm{sech}^2\left(\frac{x+\frac{1}{2}d}{\xi}\right)\right]. \tag{25}$$

Here use is made of the gap equation (at $T=0$ K):

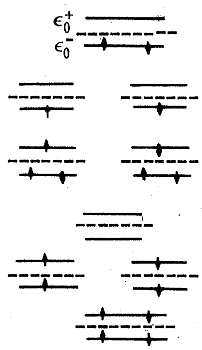
$$1=\frac{1}{\pi v_F}\frac{g^2}{\omega_Q^2}\ln(2\xi\Lambda)\,. \tag{26}$$

Putting together the total energy of the system for a variational function (10), we obtain

$$E_{MF}(\Delta(x))-E_{MF}(\Delta_0)=2E_S+\frac{8}{\pi}\Delta_0e^{-2d/\xi}+\sum_B\epsilon_B\,, \tag{27}$$

where $E_S=(2/\pi)\Delta_0$ is the soliton energy[3] and the last term has to be summed over on occupied bound states. Since the bound-state energy is of order of $e^{-d/\xi}$, the electrons in the bound state have dominant contributions in the interaction energy. The lowest energy state is obtained by putting two electrons in the ϵ_{0-} state.[8] This corresponds to the case of two neutral solitons with opposite spin (i.e., the spin singlet pair) or two charged solitons with opposite charge. The binding energy is given by $-4\Delta_0e^{-d/\xi}$. The second case corresponds to a neutral soliton and a charged soliton. In this case, the total electrons available for the bound states are odd. Therefore, in this case the bound states contribute $-2\Delta_0e^{-d/\xi}$. Finally, for the case of two charged solitons with the same charge or two neutral solitons in the spin triplet state, the electronic energy due to the bound states vanishes. In this case two solitons are repulsive with the interaction energy $(8/\pi)\Delta_0e^{-2d/\xi}$. The charge or spin configurations of two solitons and the related interaction energies are summarized in Table I. Since the spin of

TABLE I. Charge and spin configuration of two solitons and the corresponding interaction energies.

Two solitons Q	Spin	Electron configuration	Interaction energy
+ −	↑ ↓		$-4\Delta_0 e^{-d/\xi}$
+	↑		
+	↓		$-2\Delta_0 e^{-d/\xi}$
−	↑		
−	↓		
+ +			
	↑ ↑		$\frac{8}{\pi}\Delta_0 e^{-2d/\xi}$
	↓ ↓		
− −			

neutral solitons may be flipped in the long run, the repulsive interaction will be effective only for the solitons with the same charge.

III. SOLITON LATTICE

Let us now consider a doped polyacetylene where a number of charged solitons with the same charges are introduced. In such a situation the pinning potentials due to dopants are not negligible, in general. However, we shall consider here the idealized case where the intersoliton interaction is predominant and the solitons form a regular lattice with the distance d. This situation may mimic the more complicated configuration of solitons in a relatively large doping level, although we assume still that $d \gg \xi$. In the present case, a variational function is given by

$$\Delta(x) = \Delta_0 \prod_{n=-\infty}^{\infty} \tanh\left(\frac{x-nd}{\xi}\right). \tag{28}$$

Since the electronic contribution plays the dominant role in the interaction energy, we shall study Eq. (11) with $\Delta(x)$ given by Eq. (28). Substituting Eq. (28) into Eq. (12), we obtain Eq. (11) with

$$\begin{aligned} V_+(x) \cong \Delta_0^2 \Bigg\{ 1 &- 2\sum_n \operatorname{sech}^2\left(\frac{x-(2n+1)d}{\xi}\right) \\ &+ \sum_n \operatorname{sech}^2\left(\frac{x-nd}{\xi}\right)\operatorname{sech}^2\left(\frac{x-(n+1)d}{\xi}\right) \\ &+ \operatorname{sech}^2\left(\frac{x-(2n+1)d}{\xi}\right)\left[1+\tanh\left(\frac{x-2nd}{\xi}\right)\tanh\left(\frac{x-2(n+1)d}{\xi}\right)\right] \\ &- \operatorname{sech}^2\left(\frac{x-2nd}{\xi}\right)\left[1+\tanh\left(\frac{x-(2n-1)d}{\xi}\right)\tanh\left(\frac{x-(2n+1)d}{\xi}\right)\right]\Bigg\}, \end{aligned} \tag{29}$$

where we have neglected the terms of order of $e^{-4d/\xi}$. $V_+(x)$ has the deep potential wells at $x=(2n+1)d$, while $V_-(x)$ has the potential wells at $x=2nd$. Again, the energy spectrum of f_+ is identical to that of f_-, and we shall concentrate on f_+. Let us first consider the bound states in the middle of the dimerization gap in the presence of the soliton lattice. It is quite natural to study the energy spectrum within the tight-binding approximation. Assuming that the bound state is given by

$$\phi_k(x) \sim \sum_n e^{ik(2n+1)d}\operatorname{sech}\left(\frac{x-(2n+1)d}{\xi}\right), \tag{30}$$

we obtain $\epsilon_B(k)$ as

$$\epsilon_B^2(k) = \left[\int dx\left(v_F^2\left|\frac{\partial\phi_k(x)}{\partial x}\right|^2 + V_+(x)|\phi_k(x)|^2\right)\right] \Big/ \int dx\,|\phi_k(x)|^2 \tag{31}$$

$$= 8\Delta_0^2 e^{-2d/\xi}[1-\cos(2ka)] + O(e^{-4d/\xi}) \tag{32}$$

after straightforward but tedious integrals. From Eq. (32), we obtain

$$\epsilon_B(k) = \pm 4\Delta_0 e^{-d/\xi}|\sin(ka)|, \tag{33}$$

and

$$-\frac{\pi}{2d} < k < \frac{\pi}{2d}.$$

The bound states form a narrow one-dimensional band with half-width $4\Delta_0 e^{-d/\xi}$, which is the energy splitting in the presence of two solitons. Furthermore, the electrons in the narrow band are completely inert, as the band is either completely filled (the negatively charged soliton lattice) or completely empty (the postiviely charged soliton). (In this circumstance the electric conduction is still dominated by moving solitons.) The energy between solitons is due to the continuum electron state as well as the lattice-distortion terms. The total energy of the system is then given

$$E_{s1}=n_s\left(E_S+\frac{16}{\pi}\Delta_0 e^{-2d/\xi}+O(e^{-4d/\xi})\right) , \quad (34)$$

where $n_s=d^{-1}$ is the soliton density.

IV. CONCLUDING REMARKS

We have studied the interaction between two solitons by making use of a variational function. We find that two solitons attract each other except for the case of two charged solitons of the same charge or two neutral solitons with a triplet spin. Therefore for solitons with the same charge it is possible to form a regular soliton lattice when the soliton density is sufficiently high. In this circumstance, the bound states at the center of the dimerization gap form a narrow electron band which is completely inert to low-frequency external perturbation. However, when one neutral soliton is introduced in the above soliton lattice, which will provide an electron or a hole in the narrow band, and which is active both electrically and magnetically, the energy required to introduce a neutral soliton is now

$$\delta E=E_S+\frac{16}{\pi}\Delta_0 e^{-2d/\xi}-4\Delta_0 e^{-d/\xi} , \quad (35)$$

where $E_S=(2/\pi)\Delta_0$, and the last term arises from the hole at the top of the narrow band or the electron at the bottom of the same band associated with the neutral soliton. Then, when the soliton density is such that $\delta E<0$, it is energetically favorable to introduce neutral solitons in the soliton lattice. This implies a possibility of a new type of the metal-insulator transition in polyacetylene, where the electrons in the narrow band suddenly become metallic. If we assume that Eq. (35) is still valid for such soliton densities, the critical soliton density $n_s^{cr}=d_c^{-1}$ is determined from

$$\delta E=0 \quad \text{or} \quad d=\xi\ln[\pi+(\pi^2-8)^{1/2}] \cong 1.5\xi . \quad (36)$$

This corresponds to $n_s^{cr}\simeq 10^{-1}$ if we take $\xi\simeq 7a$, where a is the distance between two neighboring (CH) groups. Although the critical soliton density obtained here appears to be too large compared with the experiments[9] on doped solitons, the approximation used ($d\gg\xi$) is certainly no longer valid in this short distance. Therefore, in order to determine the critical soliton concentration, more refined treatment of the soliton lattice is necessary.

As already mentioned in the introduction, we have also neglected the effect of fluctuations of the soliton lattice. Inclusion of the fluctuation effect will also modify the critical density given above. These are some of the most urgent questions, which require further clarification.

Note added in proof. In a recent publication S. A. Brazouskii [Zh. Eksp. Teor. Fiz. 78, 677 (1980)] has also considered the interaction between two solitons and obtained similar results.

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*Laboratoire associé au C.N.R.S.
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