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Electron-electron interactions and solitons in polyacetylene

Shi-jie Xie and Liang-mo Mei
Department of Physics, Shandong University, Jinan 250100, People's Republic of China

Xin Sun
Department of Physics, Fudan University, Shanghai 200433, People's Republic of China

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The electron-electron interactions and the creation energy of a soliton in highly conducting polymers were calculated by using a correlated-basis-function method with a general screening Coulomb potential within the Kronig-Penny-model framework. Our results showed that even when the electron-electron interactions are considered, solitons are still the main charge carriers. The strong long-range electron-electron interaction is seen to reduce the creation energy of a soliton. A comparison with results based on the Hubbard model has been made. The limitations of the Hubbard model in this application were discussed.

I. INTRODUCTION

In recent years highly conducting polymers have attracted the attention of physicists and chemists because of their inherent conduction properties and vast potential for applications. Physical phenomena in conducting polymers that have been studied are primarily those related to the one-dimensional character of these materials. The concept of a soliton, as a nonlinear excitation of lattice defects, has also been extensively applied.[1] In fact, it has been found that the charged carriers in conducting polymers have many interesting characteristic, which cannot be explained with conventional theory for electric conduction. For example, the charged carriers in conducting polymers may have no spin, unlike electrons (or holes) in metals or semiconductors.

In 1979, Su, Schrieffer, and Heeger (SSH) set up a soliton theory[2] that clarified the physics of charged-carrier conduction in conducting polymers. The key point is that ε_s (soliton creation energy) $< \Delta$ (electron or hole excited energy). If $\varepsilon_s > \Delta$, it would be more difficult to excite a soliton than to excite an electron (or hole). In such a case, solitons could not be the main carriers in conducting polymers, although a soliton excited state might also exist. SSH theory gave

$$\varepsilon_s = \frac{2}{\pi}\Delta \tag{1}$$

and proved that solitons are mainly charged carriers in conducting polymers. However, in SSH theory only the electron-lattice interactions were evaluated, while the electron-electron interactions were neglected entirely. Many experiments[3,4] have shown the importance of electron-electron interactions in conducting polymers. So a Hubbard model and its extended form[5]

$$H_{ee} = U_0 \sum_{i,s} n_{i,s} n_{i,s} + \sum_{i,j,s,s'} V_{i,j} n_{i,s} n_{j,s'} \tag{2}$$

have been commonly used to describe the *e-e* interactions in polymers as well as in transition metals, heavy-fermion systems, etc. Soos and Ramasesha[6] calculated regular and alternating Hubbard and Pariser-Pan-Pople (PPP) chains and rings through a real-space basis of valence-bond (VB) diagrams and pointed out that molecular correlations contrast sharply with uncorrelated descriptions of topological solitons. Several authors have calculated the soliton creation energy in *trans*-polyacetylene based on the Hubbard model. But the results are contradictory to each other. The calculations of Campbell, Degrand, and Mazumdar[7] and Hirsch and Grabowski[8] with the Monte Carlo method showed that the *e-e* interactions made the soliton creation energy decrease. It would be favorable to the excitation of a soliton in polymer. However, the calculations of Kuprievich with the antisymmetrized product of strongly orthogonal geminals (APSG) method[9] and Kivelson *et al.* with a perturbation method[10] showed that the *e-e* interactions made the soliton creation energy increase so much that the criterion $\varepsilon_s < \Delta$ could no longer be satisfied.

In this paper the electron-electron interactions and soliton creation energy in *trans*-polyacetylene were calculated by using a general screening Coulomb potential and a correlated-basis-function method within the Kronig-Penny-model framework. The results presented here are helpful in clarifying the nature of the effect of electron-electron interactions on solitons.

II. SCREENING COULOMB POTENTIAL

In fact, because of the screening effect, the electron-electron interactions in polyacetylene generally contain two physical parameters: the interaction strength U and interaction range Λ. So it will be suitable to use a screening Coulomb potential, i.e.,

$$V(x,x') = \frac{U}{[1+(x-x')^2/a^2]^{1/2}} \exp\left[-\frac{\beta|x-x'|}{a}\right], \tag{3}$$

where U is the *e-e* interaction strength, a is the lattice spacing, and β is the screening factor, with interaction range $\Lambda = a/\beta$. Its equivalent form can be written in a second-quantized representation with the Wannier function

$$H_{ee} = \sum_{i,j,m,n,s,s'} V(i,j,m,n) a^{\dagger}_{i,s} a^{\dagger}_{j,s'} a_{m,s'} a_{n,s} , \tag{4}$$

where $V(i,j,m,n)$ is the matrix element of the interaction $V(x,x')$,

$$V(i,j,m,n) = \int dx \int dx' \Phi_i^*(x) \Phi_j^*(x') \times V(x,x') \Phi_m(x') \Phi_n(x) , \tag{5}$$

and $a_{i,s}$ ($a^{\dagger}_{i,s}$) is the electron annihilation (creation) operator with spin s on site i. The one-center term $V(i,i,i,i)$ is the on-site repulsion U_0, the two-center diagonal term $V(i,j,j,i)$ is the site-charge repulsion $V_{i,j}$, the exchange term $V(i,j,i,j)$ is the bond-charge repulsion $W_{i,j}$, and the remaining off-diagonal term of the two-center term $V(i,i,i,j)$ is the site-bond interaction $X_{i,j}$.[11] These four terms among $V(i,j,m,n)$ will be the most important. Obviously, $W_{i,j}$ and $X_{i,j}$ are both neglected in the Hubbard model, and in the Kivelson-Su-Schrieffer-Heeger model,[10] $X_{i,j}$ is neglected. In order to examine the intensity of each of these four terms in polyacetylene, we carried out a calculation by taking the ground-state orbital in a square potential well as the Wannier function $\Phi_n(x)$. For *trans*-polyacetylene the well depth V_0 and width b used here are 40 eV and 0.6 Å, respectively; the lattice constant $a = 1.22$ Å.[11] The results are shown in Fig. 1. One can see that the on-site repulsion U_0 is always larger than other three terms. In general cases, the two-center diagonal term $V_{i,j}$ is larger than the exchange term $W_{i,j}$ or the site-bond term $X_{i,j}$. However, $V_{i,j}$ will be weakened with an increase of the screening factor β and be smaller than $X_{i,j}$ as $\beta \geq 4$. For *trans*-polyacetylene, β is equal to 1.7.[11] In this case the off-diagonal terms $W_{i,j}$ and $X_{i,j}$ are comparable to $V_{i,j}$, and so neither $W_{i,j}$ nor $X_{i,j}$ can be neglected. So we will use the general form (3) with a correlated-basis-function (CBF) method (in coordination space) to study the soliton creation energy and soliton's localization in polyacetylene, rather than the Hubbard model.

III. CORRELATED-BASIS-FUNCTION METHOD

The eigenvalue equation of the non-electron-electron interaction Hamiltonian H_0 is

$$H_0 \phi_k(x) = \varepsilon_k \phi_k(x) , \tag{6}$$

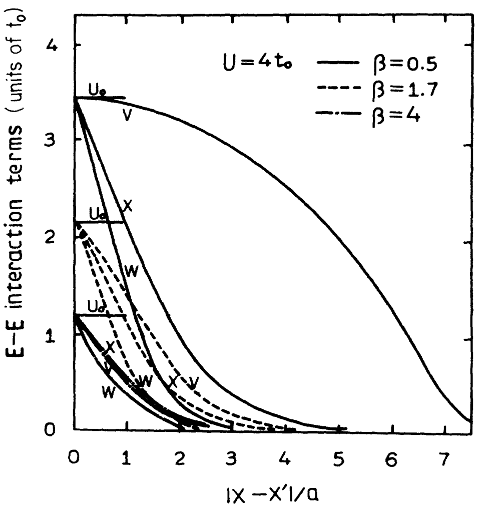

FIG. 1. Electron-electron interaction terms U_0, V, W, and X as a function of $|X-X'|/a$. β is the screening factor.

where ε_k is energy spectrum and $\phi_k(x)$ the Bloch wave function. Then the ground state of the N-particle interaction Hamiltonian $H(=H_0+V)$ can be formally written as the Jastrow wave function[12]

$$\Psi(1,2,\ldots,N) = D[\phi_k] \exp\left[\tfrac{1}{2}\sum_{i,j} u_{ij}\right] , \tag{7}$$

where $D[\phi_k]$ is the wave function of the ground state of H_0 and $u_{i,j}$ is an unknown function, which represents the electron-electron correlation induced by e-e interactions. So it is called a correlation factor and can be determined through variation with the total energy of a system.

In a system with a wideband, such as polyacetylene, a tight-binding method may be not a good approximation. A general Hamiltonian of electron-lattice interactions should be used, and it could be written as

$$H_0 = \sum_i \left[-\frac{\hbar^2}{2m} \nabla_i^2 + \sum_j V_0(x_i - X_j) \right] , \tag{8}$$

where $V_0(x_i - X_j)$ is the potential produced by the atom on X_j and exerting on the electron at x_i. Then the complete Hamiltonian of a one-dimensional system is

$$H = H_0 + \tfrac{1}{2}\sum_{i,j} V(x_i - x_j) + \tfrac{1}{2}k\sum_j (X_{j+1} - X_j - a)^2 . \tag{9}$$

The last term is the elastic energy of the lattice distortion.

From (7) and (9), the energy of ground state can be obtained,[10]

$$\begin{aligned} E &= \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle \\ &= \sum_{\text{occ}} \varepsilon_k + \tfrac{1}{2}\int d1 \int d2 [P(1) - n_0] V(1,2) [P(2) - n_0] + \tfrac{1}{2}\int d1 \int d2\, P(1) P(2) V(1,2) [g(1,2) - 1] \\ &\quad + \frac{\hbar^2}{8m} \int d1 \int d2\, P(1,2) (\nabla_1 u_{12})^2 + \frac{\hbar^2}{8m} \int d1 \int d2 \int d3\, P(1,2,3) (\nabla_1 u_{12}) (\nabla_1 u_{13}) + \tfrac{1}{2}k \sum_j (X_{j+1} - X_j - a)^2 , \end{aligned} \tag{10}$$

where n_0 is the average density of electrons and $P(1,2,\ldots,n)$ is the n-particle distribution,

$$P(1,2,\ldots,n)=\frac{n!}{(N-n)!}\frac{\int|\Psi(1,2,\ldots,N)|^2 d_{n+1}\cdots d_N}{\int|\Psi(1,2,\ldots,N)|^2 d_1\cdots d_N}\ . \tag{11}$$

The two-particle distribution can be expressed as

$$P(1,2)=P(1)P(2)g(1,2)\ , \tag{12}$$

where $g(1,2)$ is the e-e correlation function, and the one-particle distribution P(1) is the electron density.

In (10) the second term is the electrostatic energy, the third term the exchange energy, the fourth and fifth terms both are correlation energy, and the last term the elastic energy. In polyacetylene each atom has only one π electron, and the interaction range Λ is the order of the lattice constant a; the electron density is not high. There is little chance for three or more electrons to be found close to one another. So the three- or multiple-body correlation are much less important than the two-body correlation. Then the n-particle distribution function ($n>2$) can be expanded in terms of the two-body correlation function $g(1,2)$ and its convolution integral (the convolution approximation).[12]

The correlation function $g(1,2)$ can be obtained by using the CBF method. It is determined by the equations

$$P(1|\eta)=P(1|0)\exp\left\{\int_0^{\eta}d\eta'\int d2\,u_{12}\frac{P(1,2|\eta')}{P(1|\eta')}+\tfrac{1}{2}\int_0^{\eta}d\eta'\int d2\int d3\,u_{23}\left[\frac{P(1,2,3|\eta')}{P(1|\eta')}-P(2,3|\eta')\right]\right\}\ , \tag{13}$$

$$\begin{aligned}P(1,2|\eta)=P(1,2|0)\exp\Bigg\{&\eta u_{12}+\int_0^{\eta}d\eta'\int d3(u_{13}+u_{23})\frac{P(1,2,3|\eta')}{P(1,2|\eta')}\\&+\tfrac{1}{2}\int_0^{\eta}d\eta'\int d3\int d4\,u_{34}\frac{[P(1,2,3,4|\eta')-P(1,2|\eta')P(3,4|\eta')]}{P(1,2|\eta')}\Bigg\}\ ,\end{aligned} \tag{14}$$

where $P(1|0)$ and

$$P(1,2|0)=P(1|0)P(2|0)g_0(1,2)$$

are the density and two-particle distribution function of noninteracting electrons, respectively:

$$P(1|0)=2\sum_k|\phi_k(x_1)|^2\ , \tag{15}$$

$$g_0(1,2)=1-\frac{1}{2}\frac{\left|2\sum_k\phi_k^*(x_1)\phi_k(x_2)\right|^2}{p(1|0)p(2|0)}\ . \tag{16}$$

Thus $P(1)$ and $P(1,2)$, corresponding to $\eta=1$, can be calculated by solving the coupled integral equations (13) and (14).

IV. CALCULATIONS AND RESULTS

From above formulas, the static lattice configurations (ground state or soliton state) can be theoretically determined through minimizing the total energy (10) with respect to X_j and u_{ij}. Choosing different U and β, one can get the dependence of the site coordinate X_j and soliton creation energy ε_s on the interaction strength and screening factor β. In order to make the calculations more transparent, a square well was taken as the lattice potential $V(x_i-X_j)$, in which the center site is at X_j with height V_0 and width b. A hyperbolic tangent function was chosen as the soliton configuration,

$$X_j=(-1)^j u\tanh(1/\xi)\ , \tag{17}$$

where u is the dimerization and ξ is the soliton half width; both are affected by e-e interactions.

Further, generally speaking, e-e interactions give a greater effect on $P(x)$ rather than on $g(x_i,x_j)$, and so we took $g(x_1,x_2)\approx g_0(x_1,x_2)$ in the calculation and, correspondingly,

$$P(x_1,x_2)\approx P(x_1)P(x_2)g_0(x_1,x_2)\ . \tag{18}$$

The total energy of a *trans*-polyacetylene chain, including electron-electron interactions as well as electron-lattice interactions, have been calculated; the ground state and soliton excitation have also been obtained. The parameters used here are $V_0=40$ eV, $b=0.6$ Å, $a=1.22$ Å, $k=55.76$ eV/A^2, the bandwidth $4t_0=15$ eV, and the electron-lattice coupling constant $\delta=0.29$.[12] $L=41a$ ($N_L=41$) was chosen as the length of the chain, which is rather larger than the soliton width.[1]

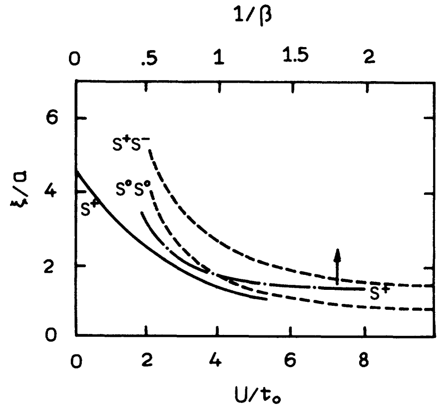

FIG. 2. Soliton width ξ vs e-e interaction strength U [$\beta=1.5$ (solid line)] and vs inverted screening factor β [$U=2t_0$ (dot-dashed line)]; the dashed line shows the results ($g=0.5$) from Ref. 9.

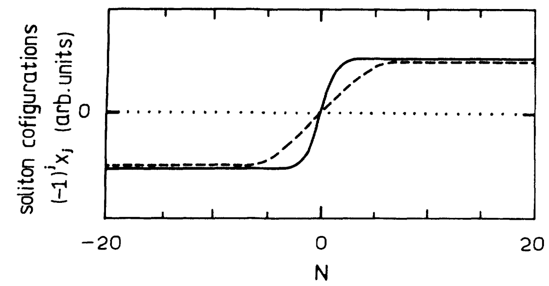

FIG. 3. Configuration of a positive soliton located in the center of a polyacetylene chain: solid line, with *e*-*e* interactions ($U=4t_0, \beta=1.5$); dashed line, without *e*-*e* interactions.

The soliton half width ξ versus the *e*-*e* interaction strength U and screening factor β are shown in Fig. 2. The configurations of a polyacetylene chain with a positive soliton ($N=N_L-1$) located in the center are shown in Fig. 3. The soliton width (2ξ) decreases monotonously with an increase of either the interaction strength U or the interaction range Λ ($=a/\beta$). It means that soliton localizations are strengthened by *e*-*e* interactions. When $U \geq 4t_0$, soliton is almost localized on a single site. Since all electron-electron interaction terms are included here, the change of ξ with U is rather smooth, and a reasonable value of the soliton width at $U=0$ ($\xi=\xi_0$) can be obtained. It could be proved by the measurement of a negative spin density of solitons.

In order to provide a clearer picture, the change of soliton creation energy due to electron-electron interactions was calculated:

$$\delta\varepsilon_s=(E_s'-E_D')-(E_s-E_D) , \tag{19}$$

where E_s' and E_D' are the total energy of a soliton and the energy of a dimerization chain, respectively, in which *e*-*e* interactions are included, and E_s and E_D are without *e*-*e* interactions. E_D' and E_D have been converted into those with the same chain lengths as solitons. The calculation of a positively charged soliton S^+ showed that in the range $\beta \leq 2.5$ the inequality

$$\delta\varepsilon_s<0 \tag{20}$$

is always satisfied, for any U (see Fig. 4). It indicates that in a polyacetylene chain electron-electron interactions lower the soliton creation energy and the formatting of a soliton state is more favorable than that of an electron state. In the meantime the soliton creation energy decreases with an increase of both the *e*-*e* interaction strength U and interaction range Λ. For example, if $U=2t_0$ and $\beta=1.7$, the soliton creation energy will be lowered by 50%.

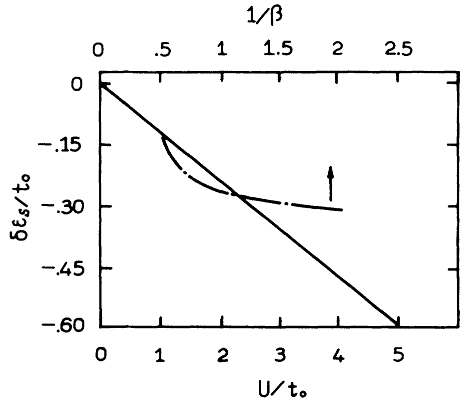

FIG. 4. $\delta\varepsilon_s$ (the change of soliton creation energy) vs the *e*-*e* interaction strength U [$\beta=1.5$ (solid line)] and inverted screening factor β [$U=2t_0$ (dot-dashed line)].

V. SUMMARY

A general screening Coulomb potential was used here. It contains the off-diagonal terms as well as the diagonal terms and is suitable to be used to describe a system with a wideband. A long chain length (41a), which is longer than those in other calculations, was assumed in the calculation. So it would be better to study a nonperiodic system. The CBF calculations here have shown that a strong long-range electron-electron interaction is favorable to soliton creation. So solitons are found to be the stable excitations and the main carriers in polyacetylene.

ACKNOWLEDGMENT

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