Effects of the next-nearest-neighbor hopping interactions on the two-dimensional localized modes of *trans*-$(CH)_x$ around a soliton

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We have studied the effects of next-nearest-neighbor hopping interactions on the two-dimensional localized modes around a soliton using a two-dimensional extension of the Su-Schrieffer-Heeger model. The results show that (1) for a negative-charged soliton, one additional mode has been found, and one of the localized modes obtained in an earlier work without next-nearest-neighbor hopping interactions disappears; (2) for a positive-charged soliton, all six localized modes always survive, but their localizations are strengthened and the frequencies slightly decrease; (3) for a neutral soliton, seven localized modes have been found.

Up to now, the Su-Schrieffer-Heeger (SSH) model[1] and its extensional model[2] are very popular models with which to study the nonlinear excitations in polyacetylene, and many significant results have been given.[1-7] Xing Biao and the present authors have assessed the influence of polyacetylene configuration on the localized modes around a soliton or a polaron and found some results.[8,9] The vibration of carbon perpendicular to the chain is comparable to that along the chain for most of the modes. Several additional localized modes, which depend on the bond-bending term, have been found. However, the SSH model and its extensional models only include the first-neighbor hopping interactions. Considering the peculiar geometry of polyacetylene and the short C-C bond lengths, the next-nearest-neighbor hopping interactions cannot be neglected. The configuration of trans-$(CH)_x$ is shown in Fig. 1. In this paper, we will study effects of the next-nearest-neighbor hopping interactions on the two-dimensional (2D) localized modes based on our previous work.[9]

Instead of the standard SSH model, we start from the two-dimensional extension of the SSH model that includes next-nearest-neighbor hopping interactions and investigate the small oscillation around a soliton.

The model Hamiltonian is given as

$$H=-\sum_{n,\sigma}\sum_{j=1}(t_j-\alpha_j\delta r_{n+j,n})(c^{\dagger}_{n+j,\sigma}c_{n,\sigma}+\text{H.c.})+\frac{k}{2}\sum_n(\delta r_{n+1,n})^2+\frac{k'}{2}\sum_n(\delta\theta_n)^2+\frac{M}{2}\sum_n(\dot{\mathbf{r}}_n)^2\ , \quad (1)$$

where k, k', and M have the same meanings as in our previous papers,[8,9] $\delta r_{n+j,n}$ denotes the change of distance from the equilibrium position between the nth and the $(n+j)$th site. t_j is the resonance integral between original and the jth (CH) group for the undimerized chain, and α_j is the corresponding electron-phonon coupling constant. The Hamiltonian does not include the long-range elastic interactions. It is easy to show that they can be taken into account by using an effective elastic constant.[10] In the following calculation, we consider the first-neighbor and the next-nearest-neighbor hopping interactions, then the Eq. (1) can be rewritten

$$H=-\sum_{n,\sigma}(t_1-\alpha_1\delta r_{n+1,n})(c^{\dagger}_{n+1,\sigma}c_{n,\sigma}+\text{H.c.})+\frac{k}{2}\sum_n(\delta r_{n+1,n})^2+\frac{k'}{2}\sum_n(\delta\theta_n)^2-\sum_{n,\sigma}(t_2-\alpha_2\delta r_{n+2,n})(c^{\dagger}_{n+2,\sigma}c_{n,\sigma}+\text{H.c.})+\frac{M}{2}\sum_n(\dot{\mathbf{r}}_n)^2\ , \quad (2)$$

where t_1 and α_1, t_2 and α_2 denote constants of the first-neighbor and the next-nearest-neighbor hopping interactions, respectively.

A static solution of soliton can be determined by the following self-consistent equations:

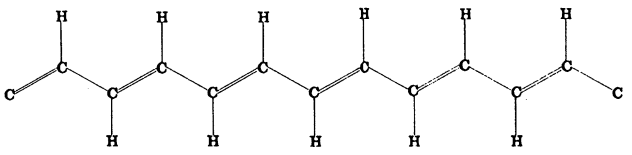

FIG. 1. The configuration of trans-$(CH)_x$. Bond lengths approximately equal 1.47 and 1.33 Å, alternatively, and bond angles equal 120°, which change little in the case of dimerization and undimerization.

$$\varepsilon_i^\sigma \psi_i^\sigma(n) = -(t_1-\alpha_1\delta r_{n,n-1})\psi_i^\sigma(n-1)-(t_1-\alpha_1\delta r_{n+1,n})\psi_i^\alpha(n+1)$$
$$-(t_2-\alpha_2\delta r_{n,n-2})\psi_i^\sigma(n-2)-(t_2-\alpha_2\delta r_{n+2,n})\psi_i^\sigma(n+2)\ ,$$

$$\delta r_{n+1,n} = -\frac{2}{k}\left[\sum_{\substack{i,\sigma \\ (occ)}}\{\alpha_1\psi_i^\sigma(n+1)\psi_i^\sigma(n)+\alpha_2\sin\theta[\psi^\sigma(n+2)\psi^\sigma(n)+\psi^\sigma(n-1)\psi^\sigma(n+1)]\}\right.$$
$$\left.-\frac{1}{N}\sum_{\substack{i,n,\sigma \\ (occ)}}\{\alpha_1\psi_i^\sigma(n+1)\psi_i^\sigma(n)+\alpha_2\sin\theta[\psi^\sigma(n+2)\psi^\sigma(n)+\psi^\sigma(n-1)\psi^\sigma(n+1)]\}\right]\ , \tag{3}$$

$$\delta r_{n+2,n} = \sin\theta\delta r_{n+2,n+1}+\sin\theta\delta r_{n+1,n}\ ,$$

where the periodic boundary condition has been used. ε_i^σ is the eigenvalue of electron with spin σ and $\psi_i^\sigma(n)$ denotes the nth component of electron eigenfunction with spin σ. θ is half of the bond angle and equals 60°.

Now, we consider the small vibration around the soliton, expanding $\delta r_{n+1,n}$ near the equilibrium configuration $\{\delta r_{n+1,n}^s\}$

$$\delta r_{n+1,n} = \sin\theta(x_{n+1}-x_n)+(-1)^{n+1}\cos\theta(y_{n+1}-y_n)+\delta r_{n+1,n}^s\ , \tag{4}$$

where the coordinate is chosen as that shown in Fig. 1. The direction of chain is defined as x, the normal direction is y. Then the total energy can be written as

$$E = E^s+\tfrac{1}{2}\sum_{m,n} V_{mn}^{\alpha\beta}\eta_m^\alpha\eta_n^\beta+\frac{M}{2}\sum_n(\dot{\mathbf{r}}_n)^2\ , \tag{5}$$

where $\alpha,\beta=1,2$ denote the x direction and y direction, respectively. E^s is the energy of the soliton:

$$\eta_m^1 = x_m\ ,\quad \eta_m^2 = y_m\ ,$$

$$V_{mn}^{\alpha\beta} = 2\sum_{\substack{i,\sigma \\ (occ)}}\sum_{j\neq i}\frac{D_{ij}^{m\alpha}D_{ij}^{n\beta}}{\varepsilon_i-\varepsilon_j}+M_{mn}^{\alpha\beta}+M_{mn}'^{\alpha\beta}\ ,$$

$$D_{ij}^{n\alpha} = [\alpha_1 C_{ij}^n+\alpha_2\sin\theta(E_{ij}^{n+1}+E_{ij}^n)]q_n^\alpha-[\alpha_1 C_{ij}^{n+1}+\alpha_2\sin\theta(E_{ij}^{n+2}+E_{ij}^{n+1})]q_{n+1}^\alpha\ , \tag{6}$$

$$q_n^1 = \sin\theta\ ,\quad q_n^2 = (-1)^n\cos\theta\ ,$$

$$C_{ij}^n = \psi_i(n)\psi_j(n-1)+\psi_j(n)\psi_i(n-1)\ ,\quad E_{ij}^n = \psi_i(n)\psi_j(n-2)+\psi_j(n)\psi_i(n-2)\ ,$$

$$M_{mn}^{\alpha\beta} = k[2(\sin^2\theta\delta_{mn}\delta_{\alpha1}\delta_{\beta1}+\cos^2\theta\delta_{mn}\delta_{\alpha2}\delta_{\beta2})-\sin^2\theta\delta_{m,n+1}\delta_{\alpha1}\delta_{\beta1}+\sin^2\theta\delta_{m,n-1}\delta_{\alpha1}\delta_{\beta1}$$
$$-(\cos^2\theta\delta_{m,n+1}\delta_{\alpha2}\delta_{\beta2}+\cos^2\theta\delta_{m,n-1}\delta_{\alpha2}\delta_{\beta2})-\sin\theta\cos\theta(-1)^{n+1}(\delta_{m,n+1}\delta_{\alpha1}\delta_{\beta2}-\delta_{m,n-1}\delta_{\alpha2}\delta_{\beta1})$$
$$-\sin\theta\cos\theta(-1)^{n+1}(\delta_{m,n+1}\delta_{\alpha2}\delta_{\beta1}-\delta_{m,n-1}\delta_{\alpha1}\delta_{\beta2})]\ , \tag{7}$$

TABLE I. Dependence of frequencies of localized vibrational modes around the negative-charged soliton on the parameter ρ.

Localized mode	Parameter ρ			
	$\rho=0.0$	$\rho=0.05$	$\rho=0.1$	$\rho=0.2$
G_1	0.000	0.000	0.000	0.000
G_2	0.194	0.193	0.192	0.183
G_3	0.227	0.227	0.227	0.224
G_4	0.409	0.406	0.400	
G_5	0.450	0.449	0.445	0.430
G_6	0.480	0.475	0.470	0.452
G_7			0.303	0.300

TABLE II. Dependence of frequencies of localized vibrational modes around the positive-charged soliton on the parameter ρ.

Localized mode	Parameter ρ			
	$\rho=0.0$	$\rho=0.05$	$\rho=0.1$	$\rho=0.2$
G_1	0.000	0.000	0.000	0.000
G_2	0.194	0.193	0.192	0.187
G_3	0.227	0.227	0.226	0.224
G_4	0.409	0.409	0.407	0.393
G_5	0.450	0.449	0.445	0.430
G_6	0.480	0.479	0.477	0.466

TABLE III. Dependence of frequencies of localized vibrational modes around the neutral soliton on the parameter ρ.

Localized mode	Parameter ρ			
	$\rho=0.0$	$\rho=0.05$	$\rho=0.1$	$\rho=0.2$
G_1	0.000	0.000	0.000	0.000
G_2	0.194	0.194	0.193	0.193
G_3	0.227	0.227	0.227	0.225
G_4	0.409	0.407	0.403	0.385
G_5	0.450	0.449	0.445	0.430
G_6	0.476	0.474	0.473	0.458
G_7			0.300	0.298

where $\{M'^{\alpha\beta}_{mn}\}$ is the bond-bending energy. Readers are referred to Ref. 9 for its explicit expression. In the paper, we only consider the case $k' \ll 1.0$, neglecting the bond-bending term.

We take a ring of 101 atoms, and the parameters[9] are $t_1=2.5$ eV, $\alpha_1=4.16$ eV/Å, and $K=21$ eV/Å^2. In order to study the effects of the second-neighbor hopping interactions, the parameter $\rho=t_2/t_1=\alpha_2/\alpha_1$ varies from zero to 0.2 in our calculation.

All vibrational modes can be obtained by diagonalizing the matrix $\{V_{mn}\}$. The numerical calculation shows that six localized modes (G_1-G_6) have been found for $\rho=0.05$ (see Tables I–III), and they are just the modes found for $\rho=0.0$.[9] It is worth noting from Table I that the localization of mode G_4 around the negative-charged soliton is weakened by turning on the next-nearest-neighbor hopping term, the other modes have opposite behaviors.

When $\rho=0.1$, for the negative-charged soliton, seven localized modes have been found, and six of them have existed in the case of $\rho=0.0$. G_7 is an additional mode. The localization of mode G_4 becomes more weak. The shape of mode G_4 is shown for $\rho=0.0$, $\rho=0.1$ in Figs. 2(a) and 2(b). For the positive-charged soliton, all six localized modes exist. No other additional modes occur, but their localizations are strengthened and the frequencies are decreased (see Table II). In the case of a neutral soliton, seven modes (G_1-G_7) have been found, and G_7 is a localized mode (see Table III). When $\rho=0.2$, six localized modes around the negative-charged soliton have been found (see Table I), and, again, five of them are the modes found for $\rho=0.0$. The mode G_4 become an extended mode. For the positive soliton and the neutral soliton, the number of localized modes does not change, compared to the case of $\rho=0.1$. Nevertheless, their localizations are changed and the frequencies move slightly.

It is worth noting that the modes G_1-G_3 and G_5 and G_6 always survive and the frequencies of all modes slight-

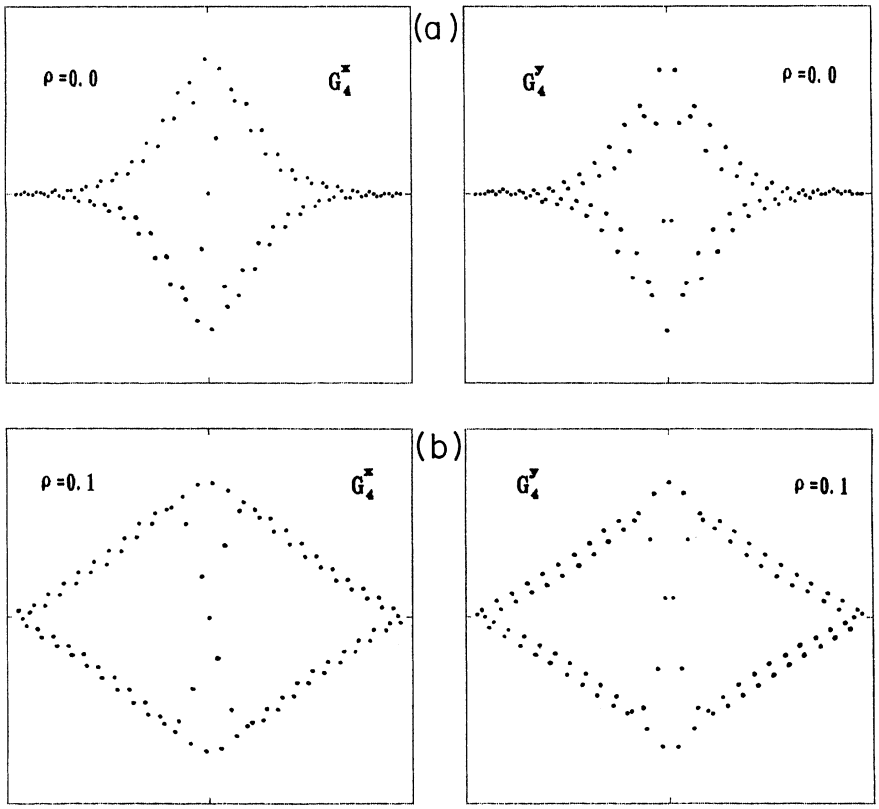

FIG. 2. (a) The shape of the localized mode G_4 around a negative-charged soliton for $\rho=0.0$. The unit of the abscissa is site number n, and the ordinate is in an arbitrary unit. (b) The shape of the localized mode G_4 around a negative-charged soliton for $\rho=0.1$. The units of both axes are the same as in (a).

ly decrease with increasing ρ. At the same time, the amplitudes of both directions for most of modes become much nearer. Thus we can conclude that the number and frequencies of localized modes depend not only on the first-neighbor hopping interactions and the bond-bending term,[9] but also on the long-range hopping interactions. Besides, they are related to type of the solitons.

Finally, we should mention that the exact values of parameters t_2 and α_2 are unclear. When $\rho \leq 0.05$, the SSH model and its extensional models are very effective for studying the properties of nonlinear excitations in polyacetylene.

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