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TWO-DIMENSIONAL LOCALIZED MODES IN CONJUGATED POLYMERS: THE NONLINEAR ELECTRON-PHONON COUPLING EFFECT

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The two-dimensional localized modes around a soliton have been investigated by using an extension of Su-Shrieffer-Heeger model, in which is included the nonlinear term of electron-phonon interaction. The results show that there appears an additional localized mode, and the two modes obtained in the previous work without the nonlinear term disappear. Furthermore, the frequencies of the modes are shifted and their localizations are changed after turning on the nonlinear term.

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In recent years, extensive studies of electron-phonon coupling systems have led to a good understanding of various excited states in quasi-one-dimensional conjugated polymers.[1—14] Much of the electronic property in degenerate and nondegenerate conducting polymers is understood in terms of the local excitations such as soliton, polaron and bipolaron. Most of the early theoretical predictions were based on the one-dimensional Su-Shrieffer-Heeger (SSH) model[1] and its continuum TLM model[2], and yield good approximation in many cases, such as spinless electrical conductivity, dimerization amplitude and optical absorption. Furthermore, the present authors have studied the two-dimensional localized modes around a soliton and successfully interpreted the experimental infrared absorption spectra both in lightly and heavily doped trans-polyacetylene.[8,9] However, as we know, the SSH model and its extended model mentioned above include only the linear term of the electron-lattice interactions, neglecting the nonlinear terms. Although the nonlinear terms are smaller than the linear one, in some cases, the terms, especially the square term, have a significant effect as will be proved in this article.

For a π-conjugated system composed of N carbon atoms, we start with the two-dimensional model Hamiltonian with the nonlinear term (only the square term considered) of the electron-phonon coupling interactions:

$$H = -\sum_{n,s}[t_0 - \alpha\delta r_{n+1,n} + \beta(\delta r_{n+1,n})^2](C^+_{n+1,s}C_{n,s} + \text{H.c.}) + \frac{k}{2}\sum_n(\delta r_{n+1,n})^2 + \frac{k'}{2}\sum_n(\delta\theta_n)^2 + \frac{M}{2}\sum_n(\dot{\boldsymbol{r}}_n)^2\,, \tag{1}$$

where $C^+_{n,s}(C_{n,2})$ denotes the creation (annihilation) operator of a π-electron with spin s on the nth site, t_0 is the hopping integral when there is no dimerization, α and β are the coefficients of the linear electron-phonon term and the square term, respectively; k and k' denote the elastic constant of the lattice and the spring constant of the bond-bending term, respectively, $\delta r_{n,n+1}$ is referred to as the change of bond-length between nth and $(n+1)$th sites. The last term is the kinetic energy.

In order to solve Eq.(1), one can express the electronic Hamiltonian using the Wannier basis set, and determine the $\delta r_{n,n+1}$ by the variational method. Then Eq.(1) can be rewritten as the following self-consistent equations:

$$\begin{aligned}
&\varepsilon^s_i\varphi^s_i(n) = -[t_0 - \alpha\delta r_{n,n-1} + \beta(\delta r_{n,n-1})^2]\varphi^s_i(n-1) - [t_0 - \alpha\delta r_{n+1,n} + \beta(\delta r_{n+1,n})^2]\varphi^s_i(n+1)\,,\\
&\delta r_{n+1,n} = \frac{2}{Nk}\sum_n\sum_{i,s(\text{occ})}(\alpha - 2\beta\delta r_{n+1,n})\varphi^s_i(n+1)\varphi^s_i(n) - \frac{2}{k}\sum_{i,s(\text{occ})}(\alpha - 2\beta\delta r_{n+1,n})\varphi^s_i(n+1)\varphi^s_i(n)\,.
\end{aligned} \tag{2}$$

Here the periodic boundary condition has been used, and ε_i^s is the eigenvalue of electron with spin s and $\varphi_i^s(n)$ denotes the nth component of electron eigenfunction with spin s. Solving the self-consistent equations iteratively yields the energy spectra and all the electronic states, and the equilibrium configuration $\delta r_{n+1,n}^0$ of the soliton can be determined by minimizing the energy.

The next step is to calculate the vibrational property. Considering the small disturbance near the equilibrium configuration $\delta r_{n+1,n}^0$ of the soliton, we have

$$\begin{aligned}\delta r_{n+1,n} =& \sin\theta(x_{n+1}-x_n)+(-1)^{n+1}\cos\theta(y_{n+1}\\ &-y_n)+\delta r_{n+1,n}^0\,,\end{aligned}\tag{3}$$

where the coordinate system is chosen as that the direction of the chain is defined as x, and its normal direction is y; θ is half of the bond angle; x_n and y_n are the displacement of the nth carbon atom from the equilibrium position in x and y directions, respectively.

Substitute $\delta r_{n+1,n}$ into Eq.(1) and approximate to second order perturbation,then the total energy can be written as:

$$E = E^0 + \frac{1}{2}\sum_{m,n} V_{mn}^{\alpha\beta}\eta_m^\alpha\eta_n^\beta + \frac{M}{2}\sum_n(\dot{\boldsymbol{r}}_n)^2\,,\tag{4}$$

where α, $\beta = 1, 2$ denote the x and y directions, respectively, thus η_m^1 means x_m and η_m^2 means y_m. E^0 is the static energy of the soliton. The first order term vanishes because the energy is minimum in the equilibrium configuration. $V_{mn}^{\alpha\beta}$ is the vibrational matrix, given as follows

$$V_{mn}^{\alpha\beta} = 2\sum_{i,s(\mathrm{occ})}\sum_{j\neq i}\frac{D_{ij}^{m\alpha}D_{ij}^{n\beta}}{\varepsilon_i^s-\varepsilon_j^s} + 2\sum_{i,s(\mathrm{occ})}N_{i,mn}^{\alpha\beta} + M_{mn}^{\alpha\beta} + M_{mn}^{\prime\alpha\beta}\,.\tag{5}$$

Here

$$\begin{aligned}D_{ij}^{n\alpha} =& C_{ij}^n q_n^\alpha - C_{ij}^{n+1}q_{n+1}^\alpha,\ \text{and}\ q_n^1=\sin\theta, q_n^2=(-1)^n\cos\theta\,,\\ C_{ij}^n =& (\alpha-2\beta\delta r_{n,n-1}^s)[\varphi_i^s(n-1)\varphi_j^s(n)+\varphi_j^s(n-1)\varphi_i^s(n)]\,,\\ N_{i,mn}^{\alpha\beta} =& -2\beta\{[\varphi_i^s(n-1)\varphi_i^s(n)+\varphi_i^s(n)\varphi_i^s(n+1)](\sin^2\theta\delta_{m,n}\delta_{\alpha_1}\delta_{\beta_1}+\cos^2\theta\delta_{m,n}\delta_{\alpha_2}\delta_{\beta_2})\\ &-\sin^2\theta[\varphi_i^s(n)\varphi_i^s(n+1)\delta_{m,n+1}\delta_{\alpha_1}\delta_{\beta_1}+\varphi_i^s(n-1)\varphi_i^s(n)\delta_{m,n-1}\delta_{\alpha_1}\delta_{\beta_1}]\\ &-\cos^2\theta[\varphi_i^s(n)\varphi_i^s(n+1)\delta_{m,n+1}\delta_{\alpha_2}\delta_{\beta_2}+\varphi_i^s(n-1)\varphi_i^s(n)\delta_{m,n-1}\delta_{\alpha_2}\delta_{\beta_2}]\\ &-\sin\theta\cos\theta(-1)^{n+1}[\varphi_i^s(n)\varphi_i^s(n+1)\delta_{m,n+1}\delta_{\alpha_1}\delta_{\beta_2}-\varphi_i^s(n-1)\varphi_i^s(n)\delta_{m,n-1}\delta_{\alpha_2}\delta_{\beta_1}]\\ &-\sin\theta\cos\theta(-1)^{n+1}[\varphi_i^s(n)\varphi_i^s(n+1)\delta_{m,n+1}\delta_{\alpha_2}\delta_{\beta_1}-\varphi_i^s(n-1)\varphi_i^s(n)\delta_{m,n-1}\delta_{\alpha_1}\delta_{\beta_2}]\\ &-\sin\theta\cos\theta(-1)^{n+1}[\varphi_i^s(n-1)\varphi_i^s(n)-\varphi_i^s(n)\varphi_i^s(n+1)](\delta_{m,n}\delta_{\alpha_2}\delta_{\beta_1}+\delta_{m,n}\delta_{\alpha_1}\delta_{\beta_2})\}\,,\\ M_{mn}^{\alpha\beta} =& k[2(\sin^2\theta\delta_{mn}\delta_{\alpha_1}\delta_{\beta_1}+\cos^2\theta\delta_{mn}\delta_{\alpha_2}\delta_{\beta_2})-(\sin^2\theta\delta_{m,n+1}\delta_{\alpha_1}\delta_{\beta_1}+\sin^2\theta\delta_{m,n-1}\delta_{\alpha_1}\delta_{\beta_1})\\ &-(\cos^2\theta\delta_{m,n+1}\delta_{\alpha_2}\delta_{\beta_2}+\cos^2\theta\delta_{m,n-1}\delta_{\alpha_2}\delta_{\beta_2})-\sin\theta\cos\theta(-1)^{n+1}(\delta_{m,n+1}\delta_{\alpha_1}\delta_{\beta_2}\\ &-\delta_{m,n-1}\delta_{\alpha_2}\delta_{\beta_1})-\sin\theta\cos\theta(-1)^{n+1}(\delta_{m,n+1}\delta_{\alpha_2}\delta_{\beta_1}-\delta_{m,n-1}\delta_{\alpha_1}\delta_{\beta_2})]\,,\end{aligned}$$

where $M_{mn}^{\prime\alpha\beta}$ is the bond-bending energy. Readers are referred to Ref.[10] for an explicit expression. In this paper, we only consider the case $k' \ll 1.0$, neglecting the bond bending term.

All vibrational modes can be obtained by diagonalizing the vibrational matrix V_{mn}. The vibrational amplitude G_i corresponding to the frequency ω_i can be expressed as:

$$G_i = (G_i^x, G_i^y) = (X_1^i\cdots X_m^i\cdots X_N^i, Y_1^i\cdots Y_m^i\cdots Y_N^i)\,.$$

Here X_m^i and Y_m^i stand for the vibrational amplitudes of mth site in the x and y directions, respectively.

In the following calculation, we have chosen a ring with 101 carbon atoms, and parameters $t_0 = 2.5\,\mathrm{eV}$, $\alpha = 41.6\,\mathrm{eV/nm}$, $k = 2100\,\mathrm{eV/nm^2}$.[8—10] In order to investigate the effects of the square term of the electron-phonon interactions, the parameter β is varied from zero to $100\,\mathrm{eV/nm^2}$.

Firstly, we discuss the structure of the energy band of a soliton. When $\beta \leq 50\,\mathrm{eV/nm^2}$, all three bound electronic states trapped by a soliton obtained in a weakly coupled system survive after turning on the square term of electron-phonon interaction, but their localizations are changed. It is found that the well-known midgap state becomes more localized with increasing β, and the localizations of the two bound

states near the bottom of valence band and the top of conduction band decrease when the square term parameter β increases. When β >50 eV/nm^2, there exists only the midgap bound electronic state, and the two bound states at the edge of energy band disappear and become extended ones.

Now, we turn to study the localized modes around a soliton. The frequencies of the localized modes for different β are listed in Table 1. The numerical calculations show that all the six localized modes (G_1—G_6), which have been obtained using two-dimensional extended SSH model without the nonlinear term of electron-phonon interaction[8,10], have been found for $\beta \leq$50 eV/nm^2, but both their localizations and frequencies are changed. Furthermore, the localizations of the modes G_3 and G_4 decrease when β increases, and the modes G_1, G_2, G_5 and G_6 have the opposite behavior. The amplitude shape of mode G_1 in the x direction is shown in Fig.1 for $\beta = 0$ and β =25 eV/nm^2 in order to find the trend of localization of mode G_1 with β. For the same reason, Fig.2 shows the amplitude shape of mode G_4 for $\beta = 0$ and β =25 eV/nm^2. From Eq.(1) one can find that the square term of electron-phonon interactions is of the same order as the elastic potential energy, and that the nonlinear electron-phonon interaction decreases the effect of the elastic potential. This should be the crucial factor for changing the localizations and frequencies of the modes. When β >50 eV/nm^2, the modes G_3 and G_4 become extended, only five localized modes have been found, in which G_1, G_2, G_5 and G_6 have their correspondents for $\beta \leq$50 eV/nm^2, and G_3' is an additional localized mode. We find that G_3' has the same parity as G_3, and the localization of the former is strengthened with increasing β. The amplitude shape of mode G_3' for β =75 eV/nm^2 is shown in Fig.3. From Table 1, it is clearly seen that the frequency of mode G_2 increases slightly when β increases, the others, except for G_1 have the opposite behavior. The frequency of the Goldstone mode (G_1) always equals to zero for different β, indicating that G_1 is irrelevant to the nonlinear electron-phonon coupling. Its frequency is not zero after considering the Coulomb pinning effect of the dopant or the soliton on other chains.[8]

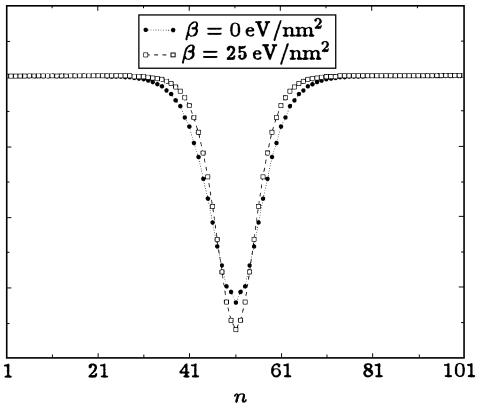


Fig.1. The amplitude shapes of the localized mode G_1 in x direction for $\beta = 0$ eV/nm^2 and β=25 eV/nm^2. The unit of the abscissa is site number n, and the ordinate is in arbitrary units.

Table 1. Calculated frequencies and parity of the localized modes of a soliton for different β (in units of eV/nm^2).

Localized	Parity		Frequencies(ω_i^2/ω_Q^2)				
modes	X	Y	$\beta = 0$	$\beta = 25$	$\beta = 50$	$\beta = 75$	$\beta = 100$
G_1	even	odd	0.000	0.000	0.000	0.000	0.000
G_2	odd	even	0.194	0.195	0.197	0.199	0.200
G_3	even	odd	0.227	0.226	0.225	—	—
G_3'	even	odd	—	—	—	0.282	0.278
G_4	odd	even	0.409	0.399	0.388	—	—
G_5	even	odd	0.450	0.436	0.422	0.408	0.394
G_6	odd	even	0.480	0.461	0.441	0.424	0.405

*Here $\omega_Q = (4k/M)^{1/2}$ is the bare frequency.

It is instructive to compare our results with those of the other models. Sun *et al.*[15] have gained four localized modes using one-dimensional SSH model, which are corresponding to the modes G_1 (Goldstone mode), G_2, $G_3(G_3')$, and G_5 (staggered mode) in our model, respectively, according to the shapes of the X (along the chain) amplitude. Based on our previous works[8—10], we have found the number and frequencies of the localized modes induced by a soliton depend on the linear coupling constant, the bond-

bending term and the hopping term. In this paper, the importance of the nonlinear electron-phonon coupling effect is confirmed. It should be noted that the even modes are infrared active and the odd modes are Raman active. But the nonlinear electron-phonon coupling effect is independent on the odd or even modes according to our calculations.

The conclusion is that the nonlinear electron-phonon coupling has a significant effect on the number and frequencies of the localized modes around a soliton in polyacetylene chains. Finally, we should mention that the exact value of parameter β is unclear. When $\beta \leq 50\,\mathrm{eV/nm^2}$, the SSH model and its extended models are very effective for describing the conjugated polymer systems.

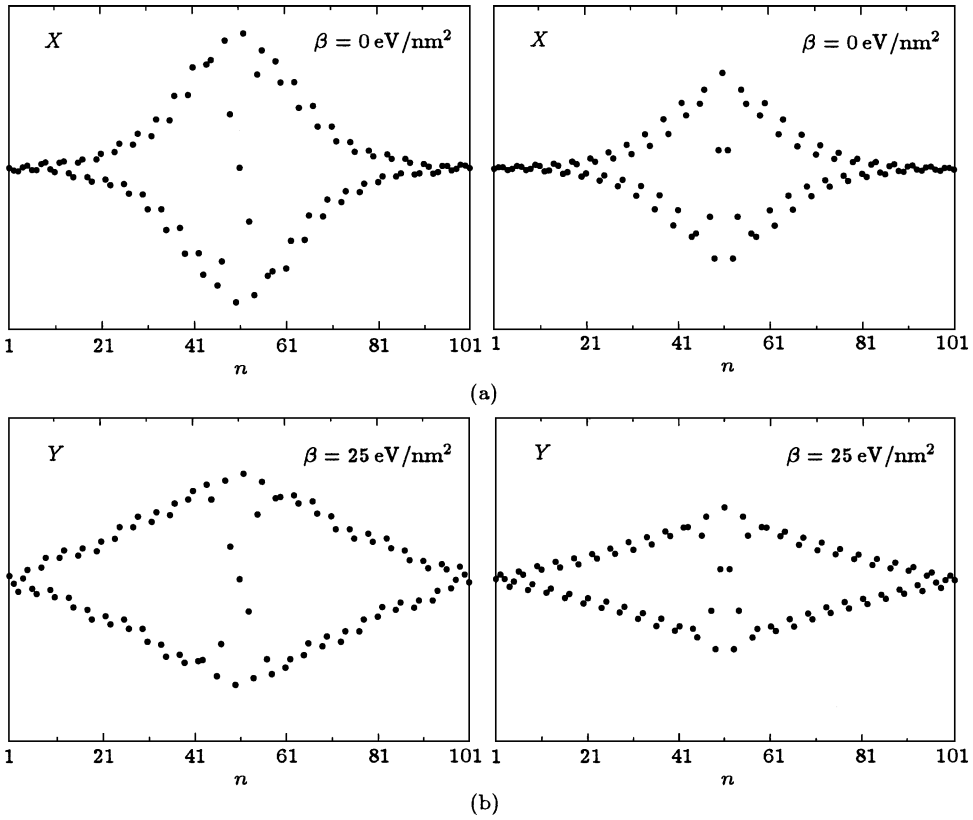


Fig.2. The amplitude shapes of the localized mode G_4 for $\beta = 0\,\mathrm{eV/nm^2}$ (a) and β=25 $\mathrm{eV/nm^2}$ (b). The units of both axes are the same as in Fig.1.

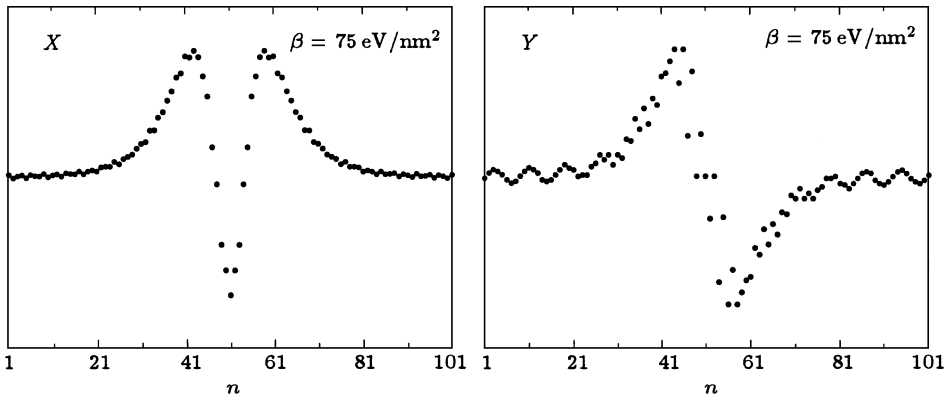


Fig.3. The amplitude shape of the additional localized mode G_3' for $\beta = 75\,\mathrm{eV/nm^2}$. The units of both axes are the same as in Fig.1.

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