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Zero-Point Motions in Trans-Polyacetylene*

FU Rong-tang(傅荣堂), RAO Xue-song(饶雪松), SUN Xin(孙鑫)
Department of Physics, Fudan University, Shanghai 200433
Y.Kawazoe
Institute for Materials Research, Tohoku University, Sendai 980-77, Japan

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In order to substantiate the applicability of the Takayama-Lin-Liu-Maki model to conducting polymer, the Su-Schrieffer-Heeger model is generalized to include the effects of lattice zero-point motions on electronic properties. Beyond the treatment of the white-noise approximation, some significant electronic properties of Peierls-Fröhlich states are documented. The finding shows that the correlation of lattice motions suppresses the effects of zero-point motions on the electronic properties more seriously.

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In the last decade, Peierls instability of ground states was always suggested to survive in one-dimensional systems. Most treatment was discussed within a rigid lattice or Born-Oppenheimer approximation. Lattice zero-point motion was a little documented. Recently, McKenzie and Wilkins[1,2] pointed out that in many of low-dimensional materials the bond alternation u_0, which causes the electronic gap, is comparable to the zero-point motions of the lattice δu. Lattice zero-point motions should have some significant effects on the electronic properties, like that smearing out of an inverse square-root singularity of density of states at $\omega = 2\Delta$, and the reasonable absorption tail below the gap. Their results seem to incorporate with some experiments.

In their works, the extensive studies should be expected to improve in two aspects. First, the continuum Takayama-Lin-Liu-Maki (TLM) approximation is a good model just for the long-wave features. But, the bond alternation, which is a prominent feature of conjugated polymer, cannot be announced properly in the continuum limit. Formally, the discrete Su-Schrieffer-Heeger (SSH) model[3] is a primitive way to show the electron–phonon interaction in polymer, especially for polyacetylene. Second, the bonds in polymer are correlated to each other: if one bond is disturbed by some influences such as dopant, defect or zero-point motions, the bond distortion will spread out in polymer to cover an area. However, white-noise approximation is correct only if bonds distort independently. Then, an essential issue is still open, how to treat the zero-point motions of polymer beyond the white-noise approach? In this paper, we will declare that the white-noise treatment overestimates the effects of zero-point motions seriously in trans-polyacetylene.

In trans-polyacetylene, there exist many interesting properties of electronic states. Charge transfer from photo-induced or doped process produces the nonlinear excitations such as soliton, polaron and bipolaron. Many treatments focused on static electronic states and bond relaxation in the presence of the mean-field approximation and electron–electron interaction. Here, we apply the discrete SSH Hamiltonian with the commonly accepted parameters instead of the continuum TLM limit to describe the electron–lattice interaction, which was demonstrated to be a good description within the mean-field approximation in the preceding studies, [3]

$$\hat{H} = \sum_{n,\sigma}[t_0 - \alpha(u_{n+1} - u_n)](\hat{c}^{\dagger}_{n+1,\sigma}\hat{c}_{n,\sigma} + \text{H.c.}) + \frac{K}{2}\sum_n (u_{n+1} - u_n)^2, \quad (1)$$

where t_0, α, and K denote the hoping coefficient of π electrons, the electron–lattice interaction and the elastic constant, respectively, $\hat{c}^{\dagger}_{n,\sigma}$ and $\hat{c}_{n,\sigma}$ are creation and annihilation operators of π electron at site n, u_n the distorted displacement of lattice at site n. They are given by

$$t_0 = 2.5 \text{ eV}, \qquad \alpha = 4.1 \text{ eV/Å}, \qquad K = 21.0 \text{ eV/Å}^2.$$

In the mean-field limit, the optical absorption $\alpha(\omega)$ is expected to be zero for frequencies less than the gap, 2Δ, and contains an inverse square-root singularity at $\omega = 2\Delta$. There exists an obvious confliction with the experimental absorption tail in many quasi-one-dimensional materials.

Since phonon frequencies are much smaller than the electronic energy gap, this means that the scattering possibilities of phonons on the electronic states at the Fermi surface are so small that each phonon can propagate freely except for the thermal scattering. The perturbation theory is then identical to that for an electronic system where u_n is a random static potential, with mean $\langle u_n \rangle = u_0$. It is easy to show that, for dispersionless phonons (single frequency), the potential has white-noise bond correlation at the temperature $T = 0\,\text{K}$:

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$$\langle u_n u_{n'} \rangle = u_0^2 + (\delta u)^2 \delta_{n,n'}. \quad (2)$$

The bond correlation represents bond-disorder, δu means the amplitude of zero-point motions, which is dependent on the specific materials, e.g., given by $\delta u = [\hbar/(2M\omega_{2k_F})]^{1/2}$ for mono-mode and dispersionless phonon. In trans-polyacetylene, δu is comparable to $u_0 = 0.04$ Å.

The model of static white-noise disorder in the Peierls-Fröhlich state has been studied extensively. In the self-consistent Born approximation all diagrams with non-crossing impurity lines are summed. This approximation gives reasonably accurate results except well below the gap or for strong disorder. Exact expressions for the density of states and the localization length can be obtained by several different techniques (e.g., Fokker-Planck equations, supersymmetry).[4-7] One of these formulae is used in Refs. 1 and 2 to calculate analytically some electronic properties with the continuum limit. Beyond this level , to establish the discrete model seems too difficult to retain the accurate properties. A new treatment is represented to treat the discrete SSH model numerically in our report.

In our numerical calculations, 1000 random independent white-noise distributions with average bond length $\langle u_n \rangle = (-1)^n u_0$ (u_0 the dimerization) and average square-root δu are extracted to simulate the static random potential to express the bond-disorder induced by zero-point motions. The statistical average approach at $T = 0$K is used to calculate the electronic properties which are given below:

(1) Density of states: The density of states $\rho(E)$ is primitively written as

$$\rho(E) = \sum_i \delta(E_i - E), \quad (3)$$

where i is the index of electronic states, E_i the energy of the corresponding state. The summation of δ function means the number of states with the fixed energy E. We apply a direct way to analyze the density of states with the standard random sampling method. Our results show that the bond disorder removes the inverse-square-root-singularity at $\omega = 2\Delta$ in density of states and produces a tail below the energy gap (Fig. 1). The band gap survives in zero-point motions. For trans-polyacetylene, i.e., $\delta u \simeq u_0$, the subgap tail is comparable to the experimental value.[2]

(2) Conductivity: The electronic properties of disorder systems, such as amorphous solid, present a great challenge both to analytical theory and to numerical calculation. There, the conductivity is a comparatively complicated quantity to be calculated. Stein *et al.*[8] have made a direct numerical evaluation of the Kubo-Greenwood formula using a technique based on the recursion method. We do not want to follow their approach because of the complicated consideration for current–current interaction. The zero-order current–current interaction is considered in the present work and expected to analyze the effect of zero-point motions on the conductivity qualitatively. In SSH model, the conductivity at frequency ω is given by the Kubo-Greenwood formula:

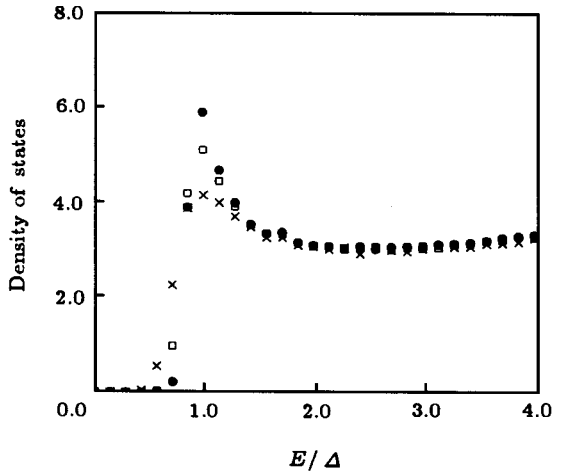

Fig. 1. For the zero-point motions $\delta u = 0.04$ Å, the density of states is calculated with the assumed exponential correlation length (chain length $N = 400$). Cross, open sqnare, and closed circle signals represent the density of states with the correlation length $L = 0, 1, 2$ (undimerization bond length a in unit).

$$\sigma(\omega) \propto \frac{1}{\omega} \sum_{\alpha,\beta} |\langle \alpha | \boldsymbol{e} \cdot \boldsymbol{J} | \beta \rangle|^2 \cdot \{ f(E_\alpha)[1 - f(E_\beta)] \delta(E_\alpha - E_\beta - \hbar\omega) + f(E_\beta)[1 - f(E_\alpha)] \delta(E_\beta - E_\alpha - \hbar\omega) \}, \quad (4)$$

where $\boldsymbol{J}$ is the current operator of electronic states, $\boldsymbol{e}$ the direction of the applied field, f the Fermi-Dirac occupation function, α and β are label energy eigenstates, and the others have their conventional meanings. Only the conductivity at the zero temperature for one-dimensional system is considered in this paper. The current operator of the discrete SSH model is written as

$$\hat{J} = \sum_n [t_0 - \alpha(u_{n+1} - u_n)](\hat{c}^\dagger_{n+1,\sigma} \hat{c}_{n,\sigma} - \hat{c}^\dagger_{n,\sigma} \hat{c}_{n+1,\sigma}). \quad (5)$$

Given the static configuration, the electronic states can be solved by the formal diagonalization of Hamiltonian matrix, and the zero-order matrix of current is easily retained. In our result, the characteristic of conductivity is like that happens in density of states(Fig. 2): zero-point motions move the conductivity threshold from conducting bottom $\omega = 2\Delta$ into the midgap, and there appears the obvious subgap tail.

(3) Localization length: Localization length represents the localizing feature and gives information about the transportation of electronic states in attempting to discriminate between extended and localized states. The definition about localization length

with the participation ratio reads

$$L^{-1}(E) = \sum_n |\psi_n(E)\psi_n^*(E)|^2, \qquad (6)$$

where $\psi_n(E)$ is the wannier wavefunction corresponding to energy eigenvalue E at site n. In trans-polyacetylene, the localization length decreases more rapidly below the conducting band, this means that the electronic states in the subgap region are more localized than in the conducting band.

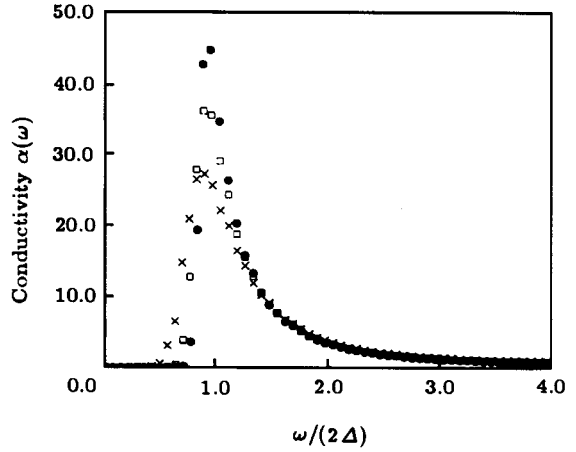

Fig. 2. For the zero-point motions $\delta u = 0.04$ Å, the conductivity is calculated with the assumed exponential correlation length (chain length $N = 400$). Cross, open square, and closed circle signals represent the conductivity with the correlation length $L = 0, 1, 2$ (undimerization bond length a in unit).

For trans-polyacetylene, strong dispersion of phonon exists so that the correlation of bond is expected to be an important effect. Beyond the white-noise approximation, we combine linearly the independent white-noise distribution to form the correlated bond distribution near the white-noise distribution region to treat the assumed exponential correlation of a static random potential: $\overline{u}_n = u_n - (-1)^n u_0$

$$\langle \overline{u}_n \overline{u}_{n'} \rangle = \begin{cases} A(\delta u)^2 \exp(-|n-n'|a/L), & L > 0, \\ (\delta u)^2 \delta_{n,n'}, & L = 0, \end{cases} \qquad (7)$$

where L is the assumed correlation length, a undimerization bond length, A is a constant which keeps the phonon zero-point energy conserved. We rewrite Eq. (7) as a matrix form. Denote the vector $U = \{\overline{u}_1, \overline{u}_2, ..., \overline{u}_n\}$, then Eq. (7) reads $U^{\mathrm{T}}U = (\delta u)^2 V$ (the matrix V represents the correlation). And the independent white-noise distribution basis, i.e., $U^0 = \{\overline{u}_1^0, \overline{u}_2^0, ..., \overline{u}_n^0\}$, satisfies the condition $U^{0T}U^0 = (\delta u)^2 I$, where I means the unitary matrix. The correlated bond distribution U is combined linearly with the independent white-noise basis U^0 near the white-noise distribution region: $U^{\mathrm{T}} = TU^{0\mathrm{T}}$ (T transformation matrix). Thus, T matrix can be obtained from $V = T^{\mathrm{T}}T$, finally the correlated bond distribution reads $U = U^0 T^{\mathrm{T}}$.

The electronic properties via density of states, conductivity and localization length are calculated with the reasonable bond-disorder parameter $\delta u = 0.04$ Å for trans-polyacetylene (Figs. 1–3). Our results show that the effect of zero-point motions is suppressed seriously by the correlation of bond alternation. In physical viewpoint, bond correlation always keeps the neighboring bond moving in phase to some extent, but for the independent white-noise correlation (correlation length is zero), the neighboring bond moves freely so that the effect of zero-point motions is always overestimated.

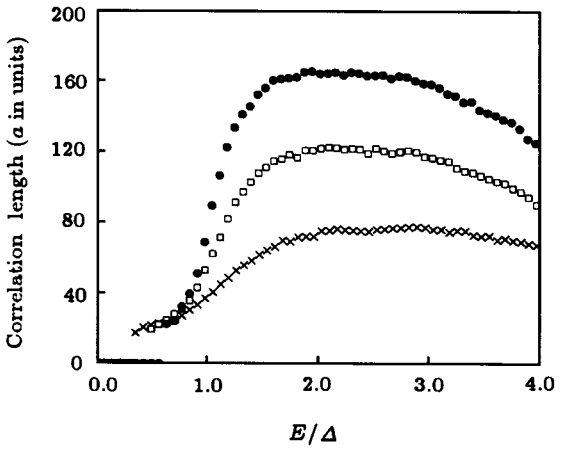

Fig. 3. For the zero-point motions $\delta u = 0.04$ Å, the localization length is calculated with the assumed exponential correlation length (chain length $N = 400$). Cross, open circle, and closed circle signals represent the localization length with the correlation length $L = 0, 1, 2$ (undimerization bond length a in unit).

In conclusions, we find that the subgap states were much more strongly localized than the states above the gap besides the removal of an inverse square-root singularity of density of states at $\omega = 2\Delta$ and the absorption tail below the gap. Meanwhile the correlated bond motions suppress more seriously the effect of zero-point motions.

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