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Interchain Coupling and Electronic Band Structure in Polydiacetylenes

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Interchain Coupling and Electronic Band Structure in Polydiacetylenes

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We present a numerical study on an extensioned Su-Schrieffer-Heeger(SSH) model of the effects on interchain coupling interaction on electronic band structure in polydiacetylene (PDA). The results show that the degeneracy of energy levels with respect to different chains is lifted and the energy levels split off due to interchain coupling. the location of energy bands shifts symmetrically and the shape of energy bands changes, especially for the lowest conduction band and the highest valence band. As a result, the energy gap becomes narrower and the total bandwidth gets broader.

Keywords: interchain coupling interaction; polydiacetylene; band structure

INTRODUCTION

Polydiacetylene (PDA) has attracted great interest in its application to nonlinear optical devices because of a fair large third-order nonlinear susceptibility and very fast nonlinear optical response. In the case of practical application of PDA, the information about the electronic energy band structure is very important. Over the

past decades, considerable theoretical efforts[1-3] have been made to understand the electronic band structure, but these descriptions are often restricted to a single isolated chain. Using a Su-Schrieffer-Heeger[4-5] (SSH) type of parameterization, a typical intrachain hopping energy is 2-3 eV, while the inerchain hopping is an order of magnitude or more smaller, perhaps 0.1 eV. At first sight, a single chain description would appear to be a reasonable approximation. There are, however, certain situations in which even small interchain coupling interaction can have a significant effect as demonstrated in this paper. In this paper we will try to add the interchain coupling interaction into Su-Schrieffer-Heeger (SSH) model, and study its effects on the energy band structure.

Theoretical Calculation

Consider two neighboring PDA chains described individually by the SSH Hamiltonian[6]

$$H_i = \sum_{n,s} -t_{i,n,n+1}\left(a^{+}_{i,n,s}a_{i,n+1,s} + h.c\right) + \frac{1}{2}\sum_{n} K_{i,n,n+1}\left(u_{i,n} - u_{i,n+1}\right)^2 \qquad (1)$$

where $t_{i,n,n+1}$ is the nearest-neighbor hopping integral, $u_{i,n,n+1}$ and $a_{i,n}$ are, respectively, the displacement coordinate of carbon along the main chain and the annihilation operator of a π electron on the ith chain at he nth lattice site. For simply the spin indices have been omitted. The geometrical arrangement of PDA chains as obtained from x-ray diffraction[7] is illustrated in Fig.1. One notices that there exists center symmetry between the neighboring chains.

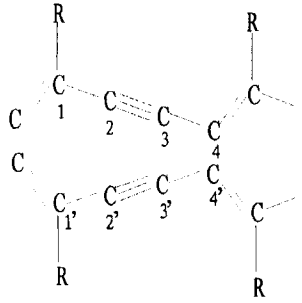

Fig.1 Two neighboring chains of PDA

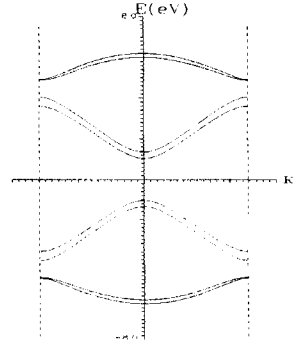

Fig.2 Quantitative energy spectra for PDA when $\rho_2 = \rho_3 = 0$ and $\rho_1 = \rho_4 = \rho'$

The model Hamiltonian in our study can be written as

$$H = H_1 + H_2 + H' \qquad (2)$$

For PDA every C-C bond pair is along the chain, in which there appears an alternation of "double" and "triple" bonds separated by "single" bonds. We assume the following form for the interchain coupling

$$H' = -\sum t_n' \left(c_{1,n}^{+} c_{2,n} + c_{2,n}^{+} c_{1,n} \right) \tag{3}$$

where t_n' is the interchain hopping integral from the site in the first chain to the site in the second chain. Through a series of numerical calculation we can obtain the corresponding electronic eigenvalues and eigenfunction.

Results and Discussions

For convenience of discussion we introduce four new parameters to describe the role of interchain coupling,

$$\rho_1 = \frac{t_1'}{t_{12}}, \quad \rho_2 = \frac{t_2'}{t_{23}}, \quad \rho_3 = \frac{t_3'}{t_{34}}, \quad \rho_4 = \frac{t_4'}{t_{45}} \tag{4}$$

First we take $\rho_1 = \rho_2 = \rho_3 = \rho_4 = \rho$. The calculated results show that degeneracy of the energy levels with respect to different chains is split due to the interchain coupling. The interval between valence band and the interval between conduction band narrow apparently, the lowest conduction band goes down and the highest valence goes up, so that the energy gap becomes narrower while the whole energy bandwidth (from the lowest valence band to the highest conduction band) becomes broader.

Then we discuss the change of energy band when $\rho_2 = \rho_3 = 0$ and $\rho_1 = \rho_4 = \rho'$. It is found that energy bands shift symmetrically all together and the intervals of bands are broader gradually with ρ', and the shapes of the highest valence band and the lowest conduction band varies dramatically, these make the energy spectra become more steeper.

It is of interest to note that the two ends of lowest valence bands and the two ends of the highest conduction bands are fixed separately (Fig.2), so that the energy gap decreases but the whole band width increase. When we take $t_1' = t_2' = t_3' = t_4' = t'$, the fixed ends of bands are separated, and the variations of energy bands are more apparent that the widths of the four bands are broader dramatically, the intervals between bands increase.

According to the theoretical treatment of quantum chemistry, there exist bonding and anti-bonding states in PDA. For the highest occupied orbital of electrons, there are anti-bonds between the "single" bonds and bonds between "triple" bonds; while for the lowest empty orbital, there are bonds between "single" bonds and anti-bonds between "triple" bonds. If bond interactions increase, the orbital energy level descends,

otherwise, the orbital energy level goes up. It can be seen from calculation that the bonding interactions are enhanced and anti-bonding interactions are weakened by interchain coupling interaction, as a result, the shape and location energy bands are changed apparently.

In summary, we study the effects of interchain coupling interaction on the ground states of PDA. It is shown that the degeneracy of energy levels with respect to different chains is lifted due to inrechain interaction. The shapes and locations of energy bands change symmetrically. The highest valence band goes up and the lowest conduction band goes down, which make the gap narrow and the intervals of bands increase. Meanwhile the whole bandwidth increase .It is found that different configuration of interchain coupling result in the different variations of energy spectra of PDA. Therefore, the influence of interchain coupling interaction in PDA could not be neglected. The results described here are potentially important for the interpretation of experimental data.

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