Doping Effects and Electronic States in C$_{60}$-Polymers

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Abstract

Band structures of C$_{60}$-polymers are studied changing conjugation conditions and the electron number. We use a Su-Schrieffer-Heeger type semiempirical model. In the neutral C$_{60}$-polymer, electronic structures change among direct-gap insulator and the metal, depending on the degree of conjugations. The C$_{60}$-polymer doped with one electron per one molecule is always a metal. The energy difference between the highest-occupied state and the lowest-unoccupied state of the neutral system becomes smaller upon doping owing to the polaron effects. The C$_{60}$-polymer doped with two electrons per one C$_{60}$ changes from an indirect-gap insulator to the direct-gap insulator, as the conjugations become stronger.

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1. Introduction

Recently, it has been found that the linear $C_{60}$-polymer is realized in alkali-metal doped $C_{60}$ crystals: $A_1C_{60}$ ($A$ = K, Rb, Cs) [1-4], and much attention has been focused on their solid state properties. One electron per one $C_{60}$ is doped in the polymer chain. It seems that Fermi surfaces exist in high temperatures, but the system shows antiferromagnetic correlations in low temperatures than about 50K [1]. The structure of the $C_{60}$-polymer is displayed in Fig. 1(a). The $C_{60}$ molecules are arrayed in a linear chain. The bonds between $C_{60}$ are formed by the [2+2] cycloaddition mechanism.

Several calculations of the electronic structures have been performed. For example, a tight-binding calculation of a linear chain [5] has been reported, and the relation to the antiferromagnetic ground state has been discussed. A semiempirical tight-binding model [6] analogous to the Su-Schrieffer-Heeger (SSH) model [7] of conjugated polymers has been proposed, and the possibility of the charge density wave state has been pointed out. The band calculation by the first principle method has also been done [8]. The electronic structures can become three dimensional when distances between $C_{60}$-polymer chains are short, while they remain one dimensional when the distances are longer.

The above works have been focused upon electronic structures of the $C_{60}$-polymer doped with one electron per one $C_{60}$. The electronic structures may depend sensitively upon the conjugation conditions even in the neutral polymer, because the several bonds connecting neighboring molecules are largely distorted and the mixing between $\sigma$- and $\pi$-orbitals will change only by slight change of the bond structures [2]. We would like to study effects of the change of the conjugation conditions by introducing a phenomenological parameter
in a tight-binding model. The model is an extension of the SSH-type model which has been applied to C$_{60}$ [9,10] and C$_{70}$ [10,11] molecules. We look at electron densities, and band structures, in order to discuss metal-insulator changes and polaron effects. We note that the calculations of the neutral system have been reported in [12]. We, however, include the results in order to discuss systematic variations from the neutral system to the doped systems.

The main conclusions are as follows: (1) In the neutral C$_{60}$-polymer, electronic structures change among direct-gap insulators and the metal, depending on the degree of conjugations. The high pressure experiments may be able to change conjugation conditions in the chain direction, and the electronic structure changes could be observed. (2) The C$_{60}$-polymer doped with one electron per one molecule is always a metal. The energy difference between the highest-occupied state and the lowest-unoccupied state of the neutral system becomes smaller upon doping owing to the polaron effects. (3) When the C$_{60}$-polymer is doped with two electrons per one C$_{60}$, the system is insulating. When the conjugation in the direction of the polymer chain is smaller, it is a direct-gap insulator. The energy gap becomes indirect when the conjugation is stronger.

In the next section, our tight-binding model is introduced and an idea of changing conjugation conditions is discussed. The section 3 is devoted to numerical results. The paper is closed with a short summary in section 4.

2. Model

We would like to apply an SSH-type model to a C$_{60}$-polymer. In the previous works [9-11], we have proposed the extended SSH model to C$_{60}$ and C$_{70}$. In C$_{60}$,
all the carbon atoms are equivalent, so it is a good approximation to neglect the mixing between $\pi$- and $\sigma$-orbitals. The presence of the dimerization and the energy level structures of the neutral C$_{60}$ molecule can be quantitatively described by the calculations within the adiabatic approximation. In C$_{70}$, the molecular structure becomes longer, meaning that the degree of the mixing between $\pi$- and $\sigma$-characters are different depending on carbon sites. In this respect, the extended SSH model does not take account of the difference of the mixings. However, it has been found [10,11] that qualitative characters of the electronic level structures are reasonably calculated when the extended SSH model is applied to the C$_{70}$. This is a valid approach because the energy positions of the $\sigma$-orbitals are deep enough and their effects can be simulated by the classical springs in the first approximation.

In this paper, we assume the same idea that the lattice structures and the related molecular orbitals of each C$_{60}$ molecule in the C$_{60}$-polymer can be described by the SSH-type model with one orbital per one lattice site. However, the mixings between the $\pi$- and $\sigma$-orbitals near the four bonds, $\langle i, j \rangle$ ($i, j = 1 - 4$), shown in Fig. 1(a) are largely different from those of regions far from the four bonds. We shall shed light on this special character of bondings between neighboring C$_{60}$. Electronic structures would be largely affected by changes of conjugation conditions around the four bonds. We shall introduce a semiempirical parameter $a$ as shown in the following Hamiltonian:

$$
H_{\text{pol}} = a \sum_{l, \sigma} \sum_{\langle i, j \rangle = (1,3), (2,4)} (-t + \alpha y_{l,(i,j)}) (c^\dagger_{l,i,\sigma} c_{l+1,j,\sigma} + \text{H.c.}) \\
+ (1 - a) \sum_{l, \sigma} \sum_{\langle i, j \rangle = (1,2), (3,4)} (-t + \alpha y_{l,(i,j)}) (c^\dagger_{l,i,\sigma} c_{l,j,\sigma} + \text{H.c.}) \\
+ \sum_{l, \sigma} \sum_{\langle i, j \rangle = \text{others}} (-t + \alpha y_{l,(i,j)}) (c^\dagger_{l,i,\sigma} c_{l,j,\sigma} + \text{H.c.})
$$
where \( t \) is the hopping integral of the system without the dimerization in the isolated \( C_{60} \) molecule; \( \alpha \) is the electron-phonon coupling constant which changes the hopping integral linearly with respect to the bond variable \( y_{l,\langle i,j \rangle} \), where \( l \) means the \( l \)th molecule and \( \langle i,j \rangle \) indicates the pair of the neighboring \( i \) and \( j \)th atoms; the atoms with \( i = 1 - 4 \) are shown by numbers in Fig. 1(a) and the other \( i \) within \( 5 \leq i \leq 60 \) labels the remaining atoms in the same molecule; \( c_{l,i,\sigma} \) is an annihilation operator of the electron at the \( i \)th site of the \( l \)th molecule with spin \( \sigma \); the sum is taken over the pairs of neighboring atoms; and the last term with the spring constant \( K \) is the harmonic energy of the classical spring simulating the \( \sigma \)-bond effects.

As stated before, the parameter \( a \) controls the strength of conjugations in the chain direction. When \( a = 1 \), the bonding between atoms 1 and 2 (and also 3 and 4) is completely broken and the orbitals would like \( \pi \)-orbitals of the bonding between atoms 1 and 3 (and atoms 2 and 4). The bond between the atoms 1 and 3 (and that between the atoms 2 and 4) becomes the classical double bond. As \( a \) becomes smaller, the conjugation between the neighboring molecule decreases and the \( C_{60} \) molecule becomes mutually independent. In other words, the interactions between molecules become smaller. When \( a = 0 \), the \( C_{60} \) molecules are completely isolated each other. The band structures of the \( C_{60} \) polymer will change largely depending on the conjugation conditions. This problem is the central issue of this paper. We note that the operator at the lattice sites of the four membered rings is one of the relevant linear combinations of the effective \( \sigma \)-like components, assuming a possibility of local \( \sigma \)-conjugations at the four membered rings. The similar assumption of the \( \sigma \)-
conjugation has been used in Si-based polymers, for example, in [13]. We, however, use the term “conjugation” for simplicity in this paper, because the local $\sigma$-conjugations can be regarded as a part of the global conjugations which are extended over the system.

In the literature [6], the possibility of charge density wave states has been taken into account by regarding two molecule pair as a unit cell. In contrast, our interests are focused on the one-dimensional band structure in the spatially homogeneous system, so we do not consider the doubled unit cell. The present unit cell consists of one C$_{60}$ molecule. Using the lattice periodicity, we skip the index $l$ of the bond variable $y_l(i,j)$. In other words, all the molecules in the polymer are assumed to have the same lattice structure. The bond variables are determined by using the adiabatic approximation in the real space. The same numerical iteration method as in [10] is used here. We will change the parameter, $a$, within $0 \leq a \leq 1.0$, and the excess electron number per one C$_{60}$, $N_{\text{ex}}$, is varied as $N_{\text{ex}} = 0, 1, \text{ and } 2$. The other parameters, $t = 2.1\text{ eV}$, $\alpha = 6.0\text{ eV/Å}$, and $K = 52.5\text{ eV/Å}^2$, give the energy gap $1.904\text{ eV}$ and the difference between the short and bond lengths $0.04557\text{ Å}$ for a C$_{60}$. We shall use the same parameter set here.

3. Numerical Results

Figures 1(b), (c), and (d) show the excess electron distribution for the three conjugation conditions, $a = 0.5, 0.8, \text{ and } 1.0$. The labels of sites, A-I, are shown in Fig. 1(a). Due to the reduced symmetry of the polymer chain, mutually symmetry equivalent sites have the same electron density. The each
label represents the site with the different electron density. The white bars are for the case $N_{\text{ex}} = 1$ and the black bars are for $N_{\text{ex}} = 2$. The excess electron density at the sites A is the largest for all the displayed cases. The bond alternation patterns are largely distorted near these sites, so the electron density change is the largest too. In Fig. 1(b), the densities at sites D, F, and H, are relatively larger. In Figs. 1(c) and (d), the densities are larger at sites D and I. In this way, the sites, where excess electrons prone to accumulate and thus the dimerization patterns are highly distorted, are spatially localized in the molecular surface. This is one of the polaron effects, which we have discussed in [10]. Here, we do not show dimerization patterns for simplicity. We only note that the distortion of the dimerization is larger where the change of the electron density is larger. The polaronic distortion pattern is different from that in the isolated $C_{60}$, and this is owing to the difference in the symmetry group. Tanaka et al [5] have drawn a schematic figure where the electron density change is the largest at the molecule center, but the present result does not agree with this feature. Numerical calculations are necessary in order to derive the actual distributions. They have not calculated the electron distributions in [5].

Next, we discuss band structures of electrons in detail. Figures 2, 3, and 4 display the band structures for the conjugation parameters, $a = 0.5, 0.8$, and 1.0, respectively. Figures (a), (b), and (c) are for $N_{\text{ex}} = 0, 1$, and 2, respectively. In each figure, the unit cell is taken as unity, so the first Brillouin zone extends from $-\pi$ to $\pi$. Due to the inversion symmetry, only the wavenumber region, $0 \leq k \leq \pi$, is shown in the figures. We note that the band structures of the neutral system have been reported in [12]. They are shown again in
order to discuss doping effects.

Figures 2(a), (b) and (c) show the band structures of the polymer for 

$a = 0.5$ and with $N_{ex} = 0$, 1, and 2, respectively. In Fig. 2(a), the highest

fully occupied band is named as “HOMO”, and the lowest empty band as

“LUMO”. There is an energy gap about 0.8 eV at the zone center. The

system is a direct gap insulator. When doped with one electron per $C_{60}$, the

system is a metal as shown by the presence of the Fermi surface in Fig. 2(b).

The system is an insulator again when $N_{ex} = 2$, as shown in Fig. 2(c). Here, the energy gap is at the boundary of the Brilloune zone, i.e., at $k = \pi$.

As increasing the parameter $a$, the overlap of the HOMO band and LUMO band appears in the neutral system. This is shown for $a = 0.8$ in Fig. 3(a).

There are Fermi surfaces, so the system changes into a metal. If $a$ increases further, the positions of the previous HOMO band and LUMO band are reversed as shown for $a = 1.0$ in Fig. 4(a). The system becomes a direct gap insulator again. The energy gap is at $k = \pi$.

When $N_{ex} = 1$, the system is always a metal when $a$ varies. The representative cases, $a = 0.8$ and 1.0, are displayed in the Figs. 3(b) and 4(b). The number of the Fermi surface is two or four, depending upon the parameter $a$. However, the metallic property is obtained for all the $a$ we take. We also find that the HOMO band and LUMO band of the neutral system shift into the energy gap upon doping. The positions of the other energy bands do not change so largely. This is due to the polaronic distortion of the lattice, which we have discussed in the calculation of an isolated molecule [9,10].

When $N_{ex} = 2$, the system turned out to be always an insulator. For smaller $a$, for example, $a = 0.5$ and 0.8, the energy gap appears at $k = \pi$. For
larger $a$, for example, $a = 1.0$ [Fig. 4(c)], the energy gap becomes an indirect gap. The polaronic distortion becomes larger as the doping concentration increases. Thus, the intrusions of the HOMO and LUMO bands of the neutral system become larger, too.

The above variations of the energy gap are summarized for the cases $N_{\text{ex}} = 0$ and 2, where a finite energy gap appears for a certain $a$ value. The results are shown in Figs. 5(a) and (b). The white (black) squares indicate that the system is a direct gap insulator where there is a energy gap at $k = 0$ ($\pi$). The squares with the plus mean that the system is an indirect gap insulator. The crosses are for metals. In the neutral system $N_{\text{ex}} = 0$ [Fig. 5(a)], the energy gap decreases almost linearly for smaller $a$. The system changes into a metal as $a$ increases, and finally an energy gap appears again. As has been discussed in [2], the conjugations between the bonds, $\langle 1, 2 \rangle$ and $\langle 3, 4 \rangle$, might be weak. So, we can assume that the larger parameter $a$ is reasonable for the real $C_{60}$-polymer. There would be a good possibility that the realistic $a$ is in the region where we can expect metallic and insulating behaviors. Therefore, it would be interesting to do experiments which give a high pressure to neutral systems in order to change conjugation conditions. For $N_{\text{ex}} = 2$ shown in Fig. 5(b), the system is a direct gap insulator with the energy gap at $k = \pi$ up to $a \sim 0.9$. The system turns into an indirect gap insulator near $a = 1.0$.

4. Summary

We have studied the variations of the band structures of the $C_{60}$-polymer. We have changed conjugation conditions and the electron number. A semiem-
A theoretical model with SSH-type electron-phonon interactions has been proposed. Electron densities and band structures have been shown extensively, in order to discuss metal-insulator changes and polaron effects. A possibility of observing electronic structure changes in high pressure experiments has been pointed out.

Recently, the other new phases of C_{60} systems have been reported [14-16]. They are synthesized at high pressures. Two dimensional polymer structures [15] have been proposed and a tight-binding calculation [17] has been already reported. The work which extends the present calculations to the novel two dimensional structures has been reported separately [18].
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Figure Captions

Fig. 1. (a) The crystal structure of the C$_{60}$ polymer. The labels, A-I, indicate carbon atoms whose charge densities are not equivalent due to the symmetry. These labels are used in (b), (c), and (d). The conjugations along four bonds, which connect carbon atoms with labels, 1-4, are controled by the parameter $a$ in eq. (1). And, the excess electron distribution is shown for the three conjugation conditions, (b) $a = 0.5$, (c) 0.8, and (d) 1.0. The white bars are for the case $N_{ex} = 1$ and the black bars are for $N_{ex} = 2$.

Fig. 2. Band structures of the C$_{60}$-polymer of the case $a = 0.5$. The excess electron number per one C$_{60}$ is (a) 0, (b) 1, and (c) 2, respectively. In (a), the highest fully occupied band is named as “HOMO”, and the lowest empty band as “LUMO”. The lattice constant of the unit cell is taken as unity.

Fig. 3. Band structures of the C$_{60}$-polymer of the case $a = 0.8$. The excess electron number per one C$_{60}$ is (a) 0, (b) 1, and (c) 2, respectively. The lattice constant of the unit cell is taken as unity.

Fig. 4. Band structures of the C$_{60}$-polymer of the case $a = 1.0$. The excess electron number per one C$_{60}$ is (a) 0, (b) 1, and (c) 2, respectively. In (a), the highest fully occupied band is named as “HOMO”, and the lowest empty band as “LUMO”. The lattice constant of the unit cell is taken as unity.

Fig. 5. The variations of the energy gap plotted against $a$. The cases $N_{ex} = 0$
and 2 are shown in (a) and (b), respectively. The white (black) squares indicate that the system is a direct gap insulator where there is a energy gap at \( k = 0 \) (\( \pi \)). The squares with the plus symbol mean that the system is an indirect gap insulator. The crosses are for metallic cases.