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Polymer-C₆₀ excitation mixing

Natalie A. Gunko, Slava V. Rotkin *

Ioffe Physico-Technical Institute, Politehnicheskaya 26, St. Petersburg 194021, Russian Federation

Abstract

The one-electron spectrum of C₆₀ cluster which is coupled to PPV chain is calculated. It shows that non-rigid band scheme has to be considered for this composite system. The splitting of states in the closest valence and conduction bands is discussed. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

This work was inspired by our desire to clarify the situation with the electronic and electron-hole excitations in composed material which is a polymer doped with fullerene clusters. This problem becomes interesting by virtue of a recent progress in the photovoltaic device fabrication on the basis of different fullerene-polymer composites. These materials possess a number of useful conducting and photoconducting properties [1]. The pure polymeric material (without fullerene doping) is a photoconductor, though doping essentially enhances it sometimes.

Charge transfer processes are of particular interest because the critical point [1] for the photoconductivity is the process of the recombination of electron-hole pairs created on the polymer chain by a photon of the proper energy. While the pair experiences twin-recombination (that means that the same electron and hole that were created by the

photon recombine by radiation or other ways), no photocurrent would be generated. The only non-twin-recombination contributes to the photore-sponse. The role of the fullerene cluster is to collect electrons from (or to donate holes to) a polymer chain.

It is well known that doping of the fullerene with alkaline metals results in a simple population of the highest unoccupied level of C₆₀ by electrons that are donated by the metal atoms. The electronic structure is well described by the rigid band scheme. This paper is aimed at giving a simple description of the fullerene doping of a PPV polymer (as an example of composite material) and to discuss the rigid band approximation in this case. We suppose a polymer excitation to be rather delocalized along the chain, while C₆₀ charge carrier wave function is known to be localized on a single cluster even in a pristine fullerene crystal. We consider the infinite PPV chain (for the sake of simplicity) coupled with a single C₆₀ cluster. In this case, we suspect that some change in conduction and valence bands will occur.

We used a simple Huckel-like model to calculate the PPV one-electron states as well as C₆₀

*Corresponding author. Tel.: +7-812-247-9367; fax: +7-812-247-1017; e-mail: rotkin@theory.ioffe.rssi.ru

states in a general approach. The main simplification is that the hopping energy is taken to be the same for both materials. Harnessing of this assumption seems to be natural for π -electron system which will only be considered below.

2. Coupling of one-electron states

The calculated one-electron spectrum is used only for a purpose of a schematic sketch of the process of rehybridization of states in the composite material. Of course, more accurate calculation has to include the Coulomb interaction as well as the electron–phonon coupling which are known to be important for the pristine polymer and C_{60} as well. However, the one-electron picture of the mixing of states seems to be a very ocular demonstration to present it here.

Let us find the electronic structure of the pure polymer chain and the pure fullerene cluster within the simplest approach: the tight-binding (TBA) Huckel model with the same hopping parameter β for both materials as well as the same zero energy level. This model gives the π -electron spectrum of C_{60} with a high accuracy. It will be seen that further refining of the model is possible but it would overdraw the exactness of consideration.

A spectrum of C_{60} TBA-Hamiltonian is known to be solved analytically because of the very high symmetry of the cluster [2–7]. It contains 60 levels with the proper degeneracy from 1 to 5. Of course, the spin degeneracy is not included here. We will not consider a spin–orbit coupling, therefore, below we will omit the spin index and the corresponding degeneracy of levels if it does not cause a misunderstanding. The levels around the Fermi energy are 5-fold (H_u), 9-fold ($H_g + G_g$) degenerate occupied levels, and 3-fold (T_{1u}), 3-fold (T_{1g}) and 5-fold (H_g) degenerate unoccupied levels. Within this energy region some polymer bands occur.

Our toy model represents the one-electron band structure of the PPV-chain by 4 occupied (valence) and 4 empty (conduction) bands. Two of them have no dispersion in k , wavenumber along the chain. As usual, we suggested periodic boundary conditions. The Fourier-transformed Hamiltonian is easy to solve analytically. The uppermost va-

lence band and lowermost conduction band intersect the fullerene cluster levels. That means that one expects these levels to be mixed if some coupling between PPV-chain and C_{60} is switched on. There is no experimental evidence for the actual geometrical structure of the compound material which defines the strength of the coupling. We suppose the simplest case of bond–bond or hexagon–hexagon coupling. That means that we include the additional terms to TBA Hamiltonian describing a resonance between some neighboring atoms. The resulting Hamiltonian in the secondary quantization reads as:

$$H = \beta \left(\sum_{g \in Y, f \in \mathcal{N}} c_f^\dagger c_g + \sum_{r \in \mathcal{P}, q \in \mathcal{M}} c_q^\dagger c_r + A \sum_{g \in \mathbf{S}, r \in \mathcal{S}} c_g^\dagger c_r + \text{h.c.} \right), \quad (1)$$

where $g \in Y$ denotes the summation over all sites of the lattice of the Y (icosahedral) C_{60} cluster, and $f \in \mathcal{N}$ stands for the summation over all nearest neighbors of the site g . As usual c_g is an operator destroying the electron in the state localized on the site g . The second sum goes over all the eight atoms of the elementary unit of the PPV-chain: $r \in \mathcal{P}$, and $q \in \mathcal{M}$ over all their neighboring atoms. The proper phase multiplier is added to the bond connecting different monomers (not shown explicitly). Here we include the coupling between components with the strength A in the last term. The indices \mathbf{S}, \mathcal{S} denote sets of common points in the C_{60} and the polymer, respectively. We calculated the energy levels of the system as well as the eigen-states (as the vector in the space of electrons sitting on a site). The code is available from authors upon request.

As a result we obtained one-electron spectra of the composite system: the C_{60} -PPV-chain. Depending on the used coupling scheme, the different level anticrossing occurs. One can easily trace all bands, but we are mainly interested in the states lying near the Fermi level. We mentioned that 3 different electron levels of C_{60} intersect the conduction band of PPV, and 3 hole states (forming only two levels due to occasional degeneracy of G_g and H_g states) are within the valence band.

The most important mixing occurs for the hexagon–hexagon coupling. We considered the fullerene cluster connected with the hexagon of the PPV-monomer (plane-to-plane). The valence band state (the 1-fold state for each point of the Brillouin zone) is completely changed due to the interaction with the C_{60} 5-fold hole level, with the symmetry notation H_u . The symmetry of fullerene cluster is lowered due to the interaction. Consequently, we expected the level to be split, which is seen in Fig. 1. Moreover, the valence band of the PPV is split too. This effect is quite pronounced at the coupling parameter being about $\beta/2$.

The interesting behavior of the lowermost empty level of the C_{60} is found (the 3-fold level of symmetry T_{1u} which is well known to be of the most importance for all doped fullerene materials). This level does not even cross the conduction band of the pristine PPV. However, the wavefunction of the electron in this state is p -like. This means that as for an atom it has three x, y, z orbits. Evidently, such a state has to couple readily despite the non-resonant character of the mixing. Indeed, the level splits at the comparatively small coupling parameter into 1- and 2-fold states, that is typical for an axial perturbation. The splitting is larger on the Brillouin zone boundary, $k \rightarrow \pi/a$, where a is the PPV-monomer-cell period. The similar situation is for the second empty level of C_{60} (T_{1g} , which is very close by symmetry to the first but has a different parity in the single cluster spectrum).

For the case of bond–bond coupling, we get a splitting of the C_{60} levels smaller than for the hexagon–hexagon model. Nonetheless, the anti-crossing behavior of the PPV valence and conduction band is clear from Fig. 2. In general, the picture is the same with exception of some details. For example, the T_{1u} mode remains unchanged even at strong coupling. The valence band of the PPV is not split but only mixed with all the hole levels of C_{60} crossed.

3. Concluding remarks

The one-electron picture presented in the paper does not really reflect the actual electron spectrum of the composite material because the electron–

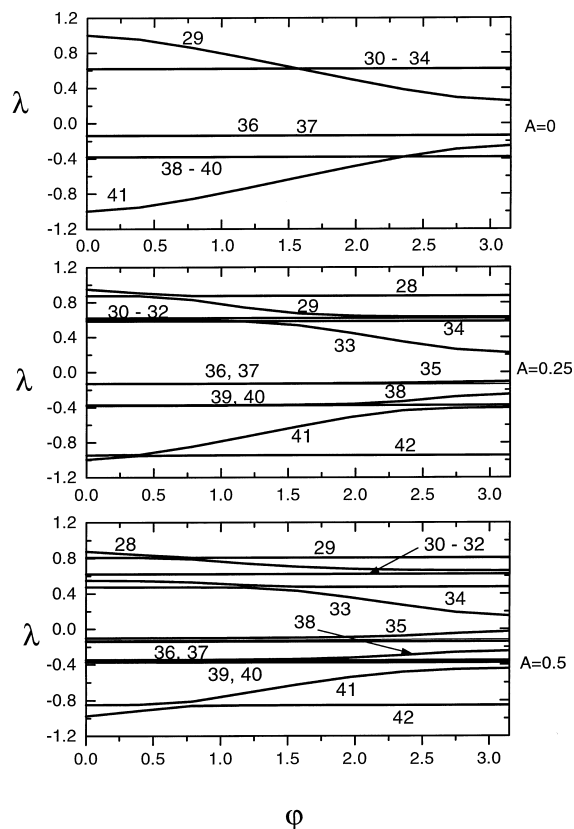


Fig. 1. The one-electron spectrum of C_{60} –PPV-chain. The eigen values of TBA matrix are shown ($E = -\beta\lambda$). The Hamiltonian includes the coupling according to the hexagon–hexagon scheme which means that some TBA hopping integral, β_1 , is added between six-membered-ring (6MR) of C_{60} and 6MR of PPV monomer. The parameter $A = \beta_1/\beta$ gives the strength of coupling. From top to bottom, it changes from 0 to 0.5. All 68 levels and their wavevectors were calculated. Only the central energy region near the Fermi level is shown. The pristine material reveals two bands of PPV and three C_{60} levels crossing them (top). The mixing of bands is described in the text.

electron and electron–phonon interactions were neglected. However, we conclude that even this simplest analysis shows that the process of fullerene doping of the conductive polymer material cannot be considered in the rigid band approximation.

The band structure of the composite material depends essentially on the geometrical structure of the bonding between the polymer chain and the fullerene cluster, that was neglected in the previous consideration. Despite the very symmetrical shape

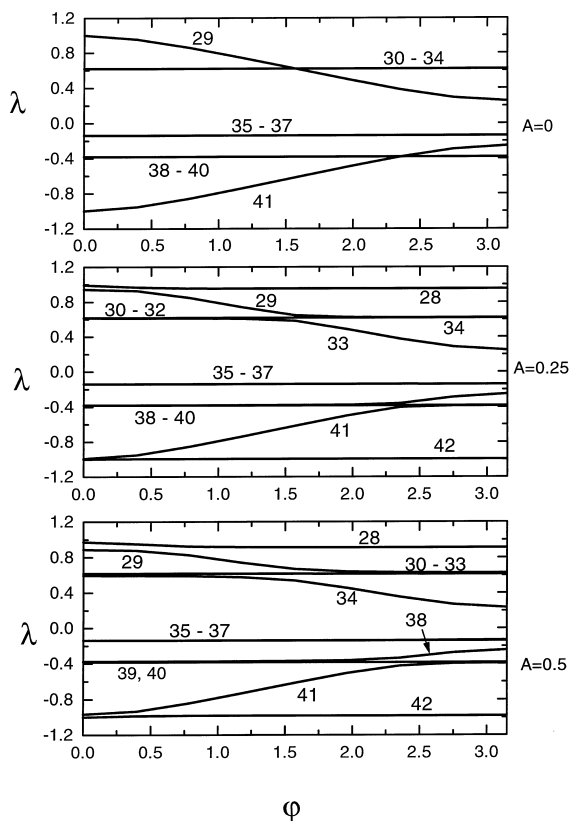


Fig. 2. The mixing of C_{60} levels with polymer-chain valence and conduction bands calculated at different schemes of coupling 'bond-bond'. The general structure of band is the same. The energy divided by $-|\beta|$ is plotted versus k , wavenumber of excitation.

of the fullerene cluster, it cannot be treated as a perfect sphere. Moreover, the high symmetry leads to the high degeneracy of the levels in the pristine C_{60} , which is lowered when the coupling is switched on.

We found even in the simplest Huckel model that the valence band of the material splits into two parts due to the strong coupling with the occupied level of the C_{60} in the case of the hexagon-hexagon coupling scheme. Like for a local impurity level lying within the band in a crystal, the local hole level (H_{ii}) of the C_{60} creates some gap

within the PPV valence band. At the same time, the lowermost unoccupied level of the fullerene which does not even cross the conduction band, experiences the symmetry lowering and splitting like a shallow donor. According to the one-electron picture, the electron-hole pair excited on the PPV-chain can be decoupled through an electron transfer to this donor level. The electron loses some energy (less about the hopping parameter β in the point $k = \pi/a$) which should be further compared with the bonding energy of the exciton-polariton in the polymer. If the shallow donor level lies below the exciton level position, the exciton autoionization may occur.

In order to discuss the carrier transfer process more exactly, we need to solve the Coulomb Hamiltonian with the electron-phonon interaction, which can be in principle done using the similar technique of group expansion of the lattice Hamiltonian [8]. We will discuss this in detail elsewhere.

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