



Communication

Polarons in endohedral $\text{Li}^+@C_{60}^-$ dimers and in 1D and 2D crystalsYoshiyuki Kawazoe^{a,b}, Vladimir R. Belosludov^{a,c,*}, Ravil K. Zhdanov^{c,d}, Rodion V. Belosludov^d^a New Industry Creation Hatchery Center, Tohoku University, 980-8579, 6-6-10, Aza-Aoba, Aramaki, Aoba-ku, Sendai, Japan^b Department of Physics and Nanotechnology, SRM University, 603203 Chennai, Tamil Nadu, India^c Nikolaev Institute of Inorganic Chemistry SB RAS, Lavrentiev av. 3, Novosibirsk 630090, Russia^d Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

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ABSTRACT

The electron charge distribution and polaron formation on the carbon sites of dimer clusters $\text{Li}^+@C_{60}^-$ and of 1D or 2D $\text{Li}^+@C_{60}^-$ periodic systems are studied with the use of the generalized Su–Schrieffer–Heeger model with respect to the intermolecular and intramolecular degrees of freedom. The charge distributions over the molecular surface and Jahn–Teller bond distortions of carbon atoms are calculated using the self-consistent iterative methods. Polarons formed in periodic 1D and 2D systems (chains and planar layers) as well as in dimer cluster system are examined. In the periodic systems polaron formation may be described by the cooperative Jahn–Teller effect. Orientation of the polarons on the molecule surface depends on the doping of the system, moreover, electron doping changes the energy levels in the system.

1. Introduction

Many researchers in their works tried to explain the nature of the unique behavior of pure fullerene systems and fullerenes doped by metal atoms. As one of the possible variants of doping, metal atoms can be arranged outside the fullerene cages of C_{60} dimers and crystals. The strong correlation of π -electrons in these systems has been suggested by researches, moreover, the interaction of that π -electrons with the intramolecular distortions of the fullerenes has been mentioned. In the particular case of a single C_{60} molecule, the formation of a polaron by means of electron-lattice interactions by self-trapped electron, transferred from the metal atom arranged outside the fullerene, by the Jahn–Teller (JT) distortions of C_{60} structure has shown [1–7]. According these studies, upon a polaron formation C_{60} the molecule distorts and additional charge is almost completely accumulated on equatorial belt of the C_{60} molecule. In the three dimensional potassium-doped K_nC_{60} ($n = 1, 2, 3, 4$) crystals the electronic structure influenced by the cooperative JT effect were studied using the generalized Su–Schrieffer–Heeger (SSH) model [8] for the intermolecular and intramolecular degrees of freedom. It was shown that only the cooperative JT effect can explain the existence of metallic and insulating phases in these compounds [9,10].

In the case of endohedral doping the insertion of a metal atom into the C_{60} cage is one of the most attractive methods to tune the electronic properties without changing the exterior framework of the resulting products, called ‘endohedral metallofullerenes’ (EMF). The EMFs have

attracted wide interest during recent years, not only in physics and chemistry but also in interdisciplinary areas [11].

Many studies on various EMFs have been conducted due to their unique electronic structure, formally determined by an electron transfer from the inner metal atom to the outer fullerene cage [12,13]. Formation of the isolation of an ion-encapsulated fullerene as a SbCl_6^- salt $[\text{Li}^+@C_{60}](\text{SbCl}_6^-)$ and crystal structure of polar cationic metallofullerenes has been reported [11]. Later, lithium-ion-encapsulated C_{60} radical anion $\text{Li}^+@C_{60}^-$ was synthesized and the dimerized structure of $\text{Li}^+@C_{60}^-$ connected by a single C–C bond was determined in the co-crystal with nickel octaethylporphyrin [14]. Also in this work [14] the structural features were confirmed by DFT calculations. As noted in Popov et al. [13] work the ionic conjecture for EMFs, which is widely used, is only a formal one and should not be understood as an exact formulation. There are numerous studies which show that the ionic model is oversimplified. An overview of the electronic structure and bonding in EMFs and the discussion of the factors which determine the stability of the isomers of EMFs are presented in work [13]. Many calculations were performed to investigate influence of an endohedral atom on the structural and electronic properties of EMF [15–19].

The main purpose of the present work is to study properties of polaron states in a dimer cluster $\text{Li}^+@C_{60}^-$ and in 1D and 2D $\text{Li}^+@C_{60}^-$ crystals with the use of the generalized SSH model for the intermolecular and intramolecular degrees of freedom. Electron charge distributions over the molecular surface, energy levels, and JT distortions of

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carbon atom positions in C₆₀ are calculated self-consistently for these systems.

2. The model of endohedral metallofullerenes

Our calculations are performed in the framework of the generalized SSH model [6]. Earlier this model has been applied successfully for isolated fullerene molecules and dimers.

The model Hamiltonian can be written as:

$$H = \frac{K}{2} \sum_n \sum_{\langle ij \rangle} (d_{ij}^n)^2 + \frac{K'}{2} \sum_{\langle nn' \rangle} \sum_{\langle ij \rangle} (d_{ij}^{nn'})^2 - \left(\frac{1}{2} \sum_{nn'} \sum_{\langle ij \rangle} t_{ij}^{nn'} a_{ni}^{*n} a_{nj}^n + H. c. \right), \quad (1)$$

where K and K' are spring constants; $a_{n'j}$ and a_{ni}^* are operators of annihilation and creation of electron on carbon site of n -th molecule; intramolecular hopping integrals for n -th molecule are represented by $t_{ij}^{nn} = (t - \alpha d_{ij}^n)$ for the nearest neighbour atoms and 0 otherwise; d_{ij}^n is the change in bond lengths between sites i and j of the molecule n ; intermolecular hopping integrals from molecule n to n' are given by $t_{ij}^{nn'} = (T - \alpha' d_{ij}^{nn'})$ for nearest neighbour atoms and 0 otherwise; $d_{ij}^{nn'}$ is the change in bond lengths between sites i in the molecule n and j in the molecule n' ; α and α' are the electron-lattice coupling constants.

Eigenvalues of this Hamiltonian can be found in the one-electron approximation of the wave function. In this case the electron eigenfunction $\psi_{i\mu}^n$ at the site i corresponding to the energy level $\epsilon_{i\mu}$ can be found from the Schroedinger equation:

$$H\psi_{i\mu}^n = \epsilon_{i\mu}\psi_{i\mu}^n, \quad (2)$$

The energy within the generalized SSH model E^{SSH} can be calculated as the sum of levels occupied by electrons $\sum_{\mu}^{occ} \epsilon_{i\mu}^n$ and the energy connected with changes of bonds between carbon atoms d_{ij}^n and $d_{ij}^{nn'}$:

$$E^{SSH} = \sum_{\mu}^{occ} \epsilon_{i\mu}^n + \frac{K}{2} \sum_n \sum_{\langle ij \rangle} (d_{ij}^n)^2 + \frac{K'}{2} \sum_{\langle nn' \rangle} \sum_{\langle ij \rangle} (d_{ij}^{nn'})^2, \quad (3)$$

$$d_{ij}^n = \frac{2\alpha}{K} \sum_{\mu}^{occ} \psi_{i\mu}^{*n} \psi_{i\mu}^n + \frac{2\alpha}{90 K N_b} \sum_{\langle ij \rangle} \sum_{\mu k s}^{occ} \psi_{i\mu}^{*n} \psi_{i\mu}^n, \quad (4)$$

where N_b is the number of fullerenes in the system. In this paper $N_b = 2$ for the case of dimer clusters and $N_b = 1$ in all other cases.

$$d_{ij}^{nn'} = \frac{2\alpha'}{K'} \sum_{\mu}^{occ} \psi_{i\mu}^{*n} \psi_{i\mu}^{n'}, \quad (5)$$

The Coulombic interaction energy of the system:

$$U^{Coul} = \sum_{\langle MM' \rangle} \frac{e_{M+}^2}{|r_{M+} - r_{M'+1}|} + \sum_{\langle nM \rangle} \frac{e_{M+} e_{ni}}{|r_{M+} - r_{ni}|} + \sum_{\langle nM \rangle} \frac{e_{ni} e_{n'i}}{|r_{ni} - r_{n'i}|}, \quad (6)$$

where M index corresponds to metal ion. Charges on atoms can be evaluated from electron eigenfunctions:

$$e_{ni} = -en_i^n = -e \sum_{\mu}^{occ} \psi_{i\mu}^{*n} \psi_{i\mu}^n, \quad (7)$$

Van der Waals (vdW) energy is:

$$U^{vdW} = \sum_{ij} \left[-\frac{A}{|\vec{r}_i - \vec{r}_j|^6} + B \exp(-a|\vec{r}_i - \vec{r}_j|) \right]. \quad (8)$$

$A = 421 \text{ kcal/mole} \cdot \text{\AA}^6$, $B = 71,600 \text{ kcal/mole}$, and $a = 3.68 \text{ \AA}^{-1}$ are parameter of the vdW interaction [20].

The nonlinear system of Eqs. (2), (4) and (5) is closed and its

solution allows self-consistent determination of all unknown parameters.

More detailed formalism and description of the used model can be found in the Harigaya work [2], Belosludov et al. works [6,7].

3. Results and discussion

In order to match the experimental values of bond lengths for doped and undoped fullerene molecules we used the following parameters; $\alpha = 6.31 \text{ eV/\AA}$, $K = 52.5 \text{ eV/\AA}^2$, and $t = 2.5 \text{ eV}$. These parameters have been validated in our previous works [6,7]. For complex systems built from many C₆₀ molecules the parameters of inter C₆₀ bonds (K' , α' , and T) play very significant role. In this work we fixed $\alpha' = \alpha$ and $K' = K$ and varied only spring constant T for inter-C₆₀ bonds related to electron correlation strength. This constant depends on the distance between fullerene particles and we focused in the current work on the case of weak interaction strength where no chemical bonds is formed between the nearest fullerenes. For the real systems these parameters for the each case should be obtained separately, nevertheless it is possible to assume that parameters should not vary much from one system to another.

All inter-C₆₀ bonds are formed by carbon atoms common for two adjusted hexagons in each C₆₀ molecule.

We calculated the SSH energy relative to isolated ($T = 0 \text{ eV}$) state energy for dimer, chain, and planar layer cases for undoped (Fig. 1) and doped systems as a function of the spring constant T . The SSH model contribution into the energy (3) is a few orders of magnitude greater than the electrostatic and vdW contributions, hence, the latter can be neglected. According to our calculations for the doped C₆₀ systems, the SSH energy is always positive and increases in magnitude with increasing spring constant T value. In contrast with the doped state, the SSH energy of undoped state can be negative, as can be seen in Fig. 1 this dependence has a minimum around 1.2 eV. In other words, such configuration is more energetically favourable than isolated fullerenes.

First principle calculation of C₆₀ undoped dimer system [21] have shown that binding energy in this case is 0.413 eV with energy gap 1.7981 eV. Within the SSH model, this binding energy is reached at two spring constant values 0.37 and 1.72 eV, while the energy gap at this points are 2.04 and 1.36 eV, respectively. Despite that SSH model a simple model in comparison with *ab initio* calculations, the results obtained by both methods are still close. Results for $T = 0.37 \text{ eV}$ agree of those in work [21].

Here we have selected two T values for our further calculation: $T = 0.25 \text{ eV}$ and $T = 0.75 \text{ eV}$ that are not differ much to $T = 0.37 \text{ eV}$.

Besides, according to our calculations it is energetically favourable to form the doped system. For single C₆₀ doped system, formation energy is 29.252 eV, and almost total of these value given by the SSH model. For other doped systems the formation energy is also positive, but it depends on the spring constant T : increase of T causes reduction

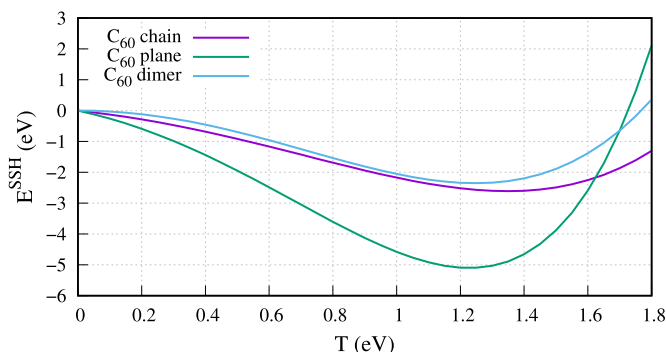


Fig. 1. SSH energy relative to isolated (spring constant $T = 0 \text{ eV}$) state energy in dependence on T parameter for undoped C₆₀ chain, plane, and dimer.

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