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Polaron in a one-dimensional C₆₀ crystal

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Polaron states in a linear chain of fullerenes have been investigated using the Su-Schrieffer-Heeger model supplemented by the Hubbard on-site Coulomb energy. The model is solved numerically within the adiabatic approximation. In this study, the electron charge distribution over the molecular surface, Jahn-Teller distortions of bonds between carbon atoms, and the density of electron states have been calculated self-consistently for a linear chain of C₆₀ molecules with one extra electron or hole. It is shown that the structure of an electron or hole polaron in the chain differs from the structure of the polaron in a single molecule. These distinctions are caused by both the conjugation of π electrons on the nearest-neighbor molecules and electron-electron correlation. Finally, the critical value of the intermolecular hopping integral for the existence of a self-trapped charge carrier due to the lattice distortion has been determined.

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I. INTRODUCTION

The outstanding discovery¹ of the fullerene has created a new field of research at the boundary of chemistry and condensed-matter physics, and the properties of the C₆₀ molecule and C₆₀ solids have been the subject of much attention from both experimental and theoretical viewpoints. The theoretical interests lie in investigating the bonding character and stability of the isolated fullerene and heterofullerene molecules and C₆₀ solids,²⁻⁴ the reactivity of the C₆₀ fullerene,⁵ and insertion of different atoms in C₆₀ fullerene cages.⁶⁻⁸ Solid C₆₀ is a molecular crystal bound by van der Waals forces and its properties reflect both the properties of individual C₆₀ molecules as well as the solid. However, the electronic configuration of crystal C₆₀ is fundamentally different from usual molecular crystals because of the conjugated character of the bonds in solid C₆₀. In the C₆₀ molecule, as well as in conjugated polymers, the chemical bonding inside the molecule leads to one unpaired electron (π electron) per carbon atom. These π electrons delocalize on the quasi-two-dimensional surface of the C₆₀ molecule and can move between molecules in solid C₆₀. In spite of the fact that π conjugation between C₆₀ molecules is much weaker than inside the C₆₀ molecule, solid C₆₀ as crystal has remarkable physical properties.

Among different properties, the unusual behavior of fullerenes as a function of alkali-metal doping has been extensively studied.⁹ For example, A₃C₆₀ (A = K, Rb, or Cs) is a superconductor, whereas A₄C₆₀ and A₆C₆₀ are insulators. KC₆₀ shows a metallic temperature dependence of the electrical conductivity, while RbC₆₀ is an insulator at ambient pressure but under pressure it transforms to a metallic phase.¹⁰ A dimer phase for Li_xC₆₀ ($x \leq 1$) has been identified.¹¹ Until now many experimental and theoretical investigations aimed at revealing the nature of the unique behavior of pure and doped C₆₀ solids have been conducted. The studies have suggested that pure and doped C₆₀ solids

are strongly correlated π electron systems and that π electrons interact with the intramolecular distortions of the C₆₀ molecules. This is due to the narrow bandwidth compared with the strong intramolecular Coulomb repulsion and the presence of Jahn-Teller (JT) distortions in the C₆₀ molecule. Several theoretical studies have shown that an electron (hole) doped in a C₆₀ molecule is self-trapped by the JT distortions of its structure, forming a polaron by means of electron-lattice interactions.¹²⁻¹⁴ Polaron states in a linear chain of fullerenes caused by the cooperative Jahn-Teller effect¹⁵ have been reported. In accordance with the Landau concept of the polaron (an electron that can be trapped by digging its own hole in a crystal),¹⁶ from these studies it follows that upon addition of an electron the C₆₀ molecule distorts and additional charge is almost completely accumulated in an equatorial ring circling the C₆₀ molecule, i.e., a molecular polaron forms. Therefore, one could expect that the properties of the doped C₆₀ solids will be determined by the properties of the molecular polarons of individual molecules. However, theoretical investigations conducted up to the present have revealed some interesting collective properties connected both with the conjugated character of bonds between molecules in C₆₀ solids and with the strong correlation of π electrons. For example, calculations of the electronic structure of C₆₀ solids with full-potential and all-electron *ab initio* formalism^{17,18} have shown that the electronic structure is sensitive to the orientation of the fullerenes in the crystal.

Variation in the band structures of one- and two-dimensional C₆₀ polymers with changes in the π conjugation was studied using a semiempirical model with Su-Schrieffer-Heeger-type electron-phonon interactions.^{19,20} It has been found that the electronic structures change from direct-gap insulators to metals, depending on the degree of π conjugation. The C₆₀ polymer doped with one electron per molecule is always a metal whereas doping with two electrons C₆₀ can change the electronic structure from an indirect-gap insulator to a direct-gap insulator, as the conjugations become stronger.²¹ The band reconstruction of A_nC₆₀ ($n = 1, 2, 3, 4$)

(Ref. 22) and the electronic structure of linear chains of fullerenes^{23,24} caused by the cooperative Jahn-Teller effect were studied using a generalized Su-Shrieffer-Heeger (SSH) model for the intermolecular and intramolecular degrees of freedom. It was shown that only the cooperative Jahn-Teller effect can explain the existence of metallic and insulating phases in these compounds. The JT distortions can arise in A_4C_{60} with strong electron correlation and change a Mott-Hubbard insulator into a band insulator.²⁵ Inhomogeneous charge distribution among carbon atoms in A_3C_{60} appears with JT distortions.²⁶ Models with Coulomb interactions were used for calculation of the electronic structure of C_{60} polymers and a phase diagram was obtained by changing the Coulomb interaction strengths and the parameter of π conjugation between C_{60} molecules.²⁷ It was found that antiferromagnetism can be described by this model. Using a model with electron-electron and electron-phonon interactions, it was shown²⁸ that both interactions are important for explanation of observed anomalies in the alkali-metal-doped A_xC_{60} . JT distortion of the C_{60} molecule could create an effective electronic interaction that would modulate electron-electron repulsion, so that A_3C_{60} is metallic and superconducting, while A_4C_{60} and A_6C_{60} are insulating²⁹. As shown by experiment,³⁰ dynamic JT distortions can induce attractive electronic interactions in odd-electron systems. Since π electrons in electron- (hole-) doped C_{60} solids are strongly correlated, the interplay between an electron-phonon interaction and electron-electron repulsion may be important in understanding the origin of high-temperature superconductivity at finite doping. For low doping of C_{60} solids and weak π conjugations between C_{60} molecules one could suggest that electrons form polarons on single molecules. Will the molecular polarons remain such with increasing conjugation strength and doping level? Does the electron correlation and conjugation of π electrons have a strong effect on the conditions under which polarons can form? These questions are important to understand the nature of the unusual physical properties of doped C_{60} solids.

We, therefore, investigate the role of electron correlation, conjugation of π electrons and level of doping on formation of polarons in C_{60} solids. For description of the polaron we use a generalized SSH model for the intermolecular and intramolecular degrees of freedom including a Hubbard-type on-site interaction. Our previous results show that this model satisfactorily describes the physical picture of the phenomena as well as several properties of the fullerene compounds.^{15,22-24}

II. MODEL

The model Hamiltonian for the C_{60} crystal including electron correlation can be written as the sum of the extended SSH Hamiltonian²² and the Hubbard interaction term:

$$H = H_{ph} + H_{el-ph} + H_{el-el}, \quad (1)$$

$$H_{ph} = \frac{K}{2} \sum_n \sum_{\langle ij \rangle} (d_{ij}^n)^2 + \frac{K'}{2} \sum_n \sum_{\langle ij \rangle} (d_{ij}^{n,n'})^2 \quad (2)$$

$$H_{el-ph} = -\frac{1}{2} \sum_{n,n' \langle ij \rangle s} t_{ij}^{n,n'} a_{nis}^\dagger a_{n'is} + \text{H.c.}, \quad (3)$$

$$H_{el-el} = U \sum_{ni} a_{ni\uparrow}^\dagger a_{ni\uparrow} a_{ni\downarrow}^\dagger a_{ni\downarrow}. \quad (4)$$

Here a_{nis}^\dagger creates a π electron of spin s on the i th carbon atom of the n th molecule; intramolecular hopping integrals for the n th molecule are represented by $t_{ij}^{nn} = t - \alpha d_{ij}^n$ for nearest-neighbors and 0 otherwise; d_{ij}^n is the change in bond length between sites i and j of molecule n ; intermolecular hopping integrals from molecule n to n' are given by $t_{ij}^{nn'} = T - \alpha' d_{ij}^{n,n'}$ for nearest-neighbors and 0 otherwise; $d_{ij}^{n,n'}$ is the change in bond length between sites i in molecule n and j in molecule n' ; α and α' are the electron-lattice coupling constants; and U is the on-site Hubbard electron-electron interaction. In the approximation where displacements of carbon atoms caused by intramolecular and intermolecular vibrations are ignored, H_{ph} is the bond-stretching energy of the crystal with spring constants K and K' .

For simplicity, we have not considered electron-electron interactions among electrons located at different sites. It can be supposed that this interaction will merely "renormalize" t and U .³¹ As usual we treat the above Hamiltonian in the adiabatic approximation.

In the one-electron approximation the wave function ψ_{is}^n of a π electron with spin s on carbon atom i of molecule n can be represented by $\psi_{is}^n = a_{nis}^\dagger |0\rangle$ ($|0\rangle$ is the ground state of the system without π electrons). The electron eigenfunction $\psi_{\mu is}^n$ at site i corresponding to the energy level ε_μ can be found from the Schrödinger equation,

$$H \psi_{\mu is}^n = \varepsilon_\mu \psi_{\mu is}^n \quad (5)$$

The model is treated in the Hartree-Fock approximation,

$$\begin{aligned} & \sum_{ni} a_{ni\uparrow}^\dagger a_{ni\uparrow} a_{ni\downarrow}^\dagger a_{ni\downarrow} \\ & \equiv \sum_{ni} (n_{i\uparrow}^n a_{ni\downarrow}^\dagger a_{ni\downarrow} + n_{i\downarrow}^n a_{ni\uparrow}^\dagger a_{ni\uparrow}) - \sum_{ni} n_{i\uparrow}^n n_{i\downarrow}^n \\ & \quad + \sum_{ni} (a_{ni\uparrow}^\dagger a_{ni\uparrow} - n_{i\uparrow}^n)(a_{ni\downarrow}^\dagger a_{ni\downarrow} - n_{i\downarrow}^n) \\ & \equiv \sum_{ni} (n_{i\uparrow}^n a_{ni\downarrow}^\dagger a_{ni\downarrow} + n_{i\downarrow}^n a_{ni\uparrow}^\dagger a_{ni\uparrow}) - \sum_{ni} n_{i\uparrow}^n n_{i\downarrow}^n. \end{aligned} \quad (6)$$

In the Hartree-Fock approximation, $H \Rightarrow H_{HF}$,

$$\begin{aligned} H_{HF} = & - \sum_{n,n' \langle ij \rangle s} t_{ij}^{n,n'} a_{nis}^\dagger a_{n'is} + \text{H.c.} \\ & + U \sum_{ni} (n_{i\uparrow}^n a_{ni\downarrow}^\dagger a_{ni\downarrow} + n_{i\downarrow}^n a_{ni\uparrow}^\dagger a_{ni\uparrow}). \end{aligned} \quad (7)$$

Equation (5) can be written as

$$\begin{aligned}
& - \sum_j (t - \alpha d_{kj}^n) \psi_{\mu j \uparrow}^n - \frac{1}{2} \sum_j [(T - \alpha' d_{kj}^{n,n-1}) + (T - \alpha' d_{kj}^{n,n+1})] (\psi_{\mu j \uparrow}^{n+1} + \psi_{\mu j \uparrow}^{n,n-1}) + U n_{\mu k \downarrow}^n \psi_{\mu k \uparrow}^n = \varepsilon_\mu \psi_{\mu k \uparrow}^n, \\
& - \sum_j (t - \alpha d_{kj}^n) \psi_{\mu j \downarrow}^n - \frac{1}{2} \sum_j [(T - \alpha' d_{kj}^{n,n-1}) + (T - \alpha' d_{kj}^{n,n+1})] (\psi_{\mu j \downarrow}^{n+1} + \psi_{\mu j \downarrow}^{n,n-1}) + U n_{\mu k \uparrow}^n \psi_{\mu k \downarrow}^n = \varepsilon_\mu \psi_{\mu k \downarrow}^n. \quad (8)
\end{aligned}$$

Here $n_{i\uparrow(\downarrow)}^n$ is the electron density on the i th carbon atom of the n th molecule with spin up (down). The total energy of the system is

$$\begin{aligned}
E(\{d_{ij}^n\}, \{d_{ij}^{n,n'}\}, \{n_{js}^n\}) \\
= \sum_{\mu}^{occ} \varepsilon_\mu(\{d_{ij}^n\}, \{d_{ij}^{n,n'}\}, \{n_{js}^n\}) + \frac{K}{2} \sum_{n(ij)} (d_{ij}^n)^2 \\
+ \frac{K'}{2} \sum_{n,n'(ij)} (d_{ij}^{n,n'})^2 + U \sum_{ni} n_{i\uparrow}^n n_{i\downarrow}^n. \quad (9)
\end{aligned}$$

We determine the lowest energy state using the variational theorem,

$$\frac{\partial E(\{d_{ij}^n\}, \{d_{ij}^{n,n'}\}, \{n_{js}^n\})}{\partial d_{ij}^n} = 0, \quad \frac{\partial E(\{d_{ij}^n\}, \{d_{ij}^{n,n'}\}, \{n_{js}^n\})}{\partial d_{ij}^{n,n'}} = 0, \quad (10)$$

under conditions $\sum_{(ij)} d_{ij}^n = 0$, and

$$\frac{\partial E(\{d_{ij}^n\}, \{n_{js}^n\})}{\partial n_{is}^n} = 0. \quad (11)$$

From Eq. (10) one can obtain d_{ij}^n and $d_{ij}^{n,n'}$,

$$d_{ij}^n = -\frac{2\alpha}{K} \sum_{\mu s}^{occ} \psi_{\mu is}^* \psi_{\mu js}^n + \frac{2\alpha}{90K} \sum_{\langle ij \rangle} \sum_{\mu s}^{occ} \psi_{\mu is}^* \psi_{\mu s \uparrow}^n, \quad (12)$$

$$d_{ij}^{n,n'} = -\frac{2\alpha'}{K'} \sum_{\mu s}^{occ} \psi_{\mu is}^* \psi_{\mu js}^{n'}, \quad (13)$$

and from Eq. (11),

$$n_{is}^n = \sum_{\mu}^{occ} \psi_{\mu is}^* \psi_{\mu is}^n. \quad (14)$$

The nonlinear system of equations (8), (12), and (13) is closed and its solution allows self-consistent determination

of the electron structure of a one-dimensional C₆₀ crystal, the distributions of bond lengths between carbon atoms, and the charge densities with spins up and down on each site. For an ideal crystal one can use translational symmetry to reduce the system of $120N$ (N is the number of C₆₀ molecules in the crystal) equations to a system of 120 equations, because the unit cell contains one C₆₀ molecule. In the case of crystal doping by one electron (hole) and creation of a polaron, the translational symmetry is broken and, in general, in order to find a solution, the system of $120N$ equations has to be solved. Thus, to study polaron formation, it is necessary to consider a larger cell than the basic unit cell. We have therefore constructed a supercell of m unit cells consisting of m C₆₀ molecules and one excess electron (hole). In this case the system of $120N$ equations is reduced to a system of $120m$ equations. The value of m is determined from the condition that the resulting system of equations would permit description of the creation of polaron in the C₆₀ crystal to a reasonable degree of approximation. It is convenient to introduce in this case two indices n and l for molecules in the crystal supercell instead of one index n . Thus ψ_{is}^{nl} is the eigenfunction of an electron at site i of the l th ($l=1, 2, \dots, m$) molecule in supercell n ($n=1, 2, \dots, N_c$) of the crystal. Using the Fourier transformation for a one-dimensional crystal

$$\psi_{js}^{nl} = \frac{1}{\sqrt{N_c}} \sum_q \psi_{js}^l(q) e^{iqa_c n}, \quad (15)$$

where N_c is the number of supercells, $a_c = ma$ is the length of the supercell, a is the length of the unit cell, q is the modulus of the reciprocal lattice vector. Applying the translational symmetry, $\psi_{is}^{nl} = \psi_{is}^l$ and $d_{ij}^{nl} = d_{ij}^l$, $d_{ij}^{n,l,nl+1} = d_{ij}^{l,l+1}$. The system of equations (8) can be presented in the matrix form as

$$\begin{bmatrix} A + C_\downarrow & 0 \\ 0 & C_\uparrow + A \end{bmatrix} \begin{bmatrix} \psi_{\mu \uparrow} \\ \psi_{\mu \downarrow} \end{bmatrix} = \varepsilon_\mu(q) \begin{bmatrix} \psi_{\mu \uparrow} \\ \psi_{\mu \downarrow} \end{bmatrix}, \quad (16)$$

where

$$\psi_{\mu s} = \begin{bmatrix} \psi_{\mu s}^1(q) \\ \psi_{\mu s}^2(q) \\ \psi_{\mu s}^3(q) \\ \vdots \\ \psi_{\mu s}^{m-1}(q) \\ \psi_{\mu s}^m(q) \end{bmatrix}, \quad A = \begin{bmatrix} A^1 & B^{12} & 0 & \dots & 0 & 2 \cos(qa_c) B^{1m} \\ B^{21} & A^2 & B^{23} & 0 & \dots & 0 \\ 0 & B^{32} & A^3 & B^{34} & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & \dots & \dots & \dots & A^{m-1} & B^{mm-1} \\ B^{m1} 2 \cos(qa_c) & 0 & \dots & \dots & B^{m-1m} & A^m \end{bmatrix}, \quad (17)$$

$$C_s = \begin{bmatrix} C_s^1 & 0 & \dots & \dots & \dots & 0 \\ 0 & C_s^2 & 0 & \dots & \dots & 0 \\ 0 & 0 & C_s^3 & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & \dots & \dots & 0 & C_s^{m-1} & 0 \\ 0 & \dots & \dots & \dots & 0 & C_s^m \end{bmatrix}, \quad (18)$$

$$C_s^k = \begin{bmatrix} n_{1s}^k & 0 & \dots & \dots & \dots & 0 \\ 0 & n_{2s}^k & 0 & \dots & \dots & 0 \\ 0 & 0 & n_{3s}^k & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & \dots & \dots & 0 & n_{59s}^k & 0 \\ 0 & \dots & \dots & \dots & 0 & n_{60s}^k \end{bmatrix}.$$

Here N is the number of molecules in the crystal, A^l is the 60×60 matrix corresponding to the hopping of electrons between carbon atoms inside the l th fullerene molecule: $A_{ij}^l = t - \alpha d_{ij}^l$ for nearest-neighbors of the i th and j th carbon atoms of the l th molecule. B^{ll+1} is a 60×60 matrix that describes electron hopping between nearest-neighbor fullerene molecules l and $l+1$: $B_{ij}^{ll+1} = T - \alpha' d_{ij}^{ll+1}$ for nearest-neighbors of the i th carbon atom on the l th molecule and the j th carbon atom on the $l+1$ th molecule and 0 otherwise.

From Eqs. (12)–(14) one can obtain d_{ij}^l and $d_{ij}^{l'}$,

$$d_{ij}^l = -\frac{2\alpha}{KN_c} \sum_{\mu s q}^{occ} \psi_{\mu is}^{*l}(q) \psi_{\mu js}^l(q) + \frac{2\alpha}{90KN_c} \sum_{\langle ij \rangle}^{occ} \sum_{\mu s q} \psi_{\mu is}^{*l}(q) \psi_{\mu js}^l(q), \quad (19)$$

$$d_{ij}^{l'} = -\frac{2\alpha'}{K'N_c} \sum_{\mu s q}^{occ} \psi_{\mu is}^{*l}(q) \psi_{\mu js}^{l'}(q), \quad (20)$$

III. RESULTS AND DISCUSSION

As was described above, in order to solve the problem of the existence of one polaron in the C_{60} chain we have used the approximation in which the possibility of the existence of a polaron in a supercell was considered. The one-dimensional chain was modeled by means of defining the supercell from three, five, seven, or nine fullerene molecules. In our calculations the parameter of the intermolecular electron hopping T was varied from $0.01t$ to $0.4t$ (t is the value of intramolecular hopping integral). The system (16) of self-consistent equations was solved numerically by ordinary iteration techniques. The calculations were conducted in 61 points in the Brillouin zone in the reciprocal space.

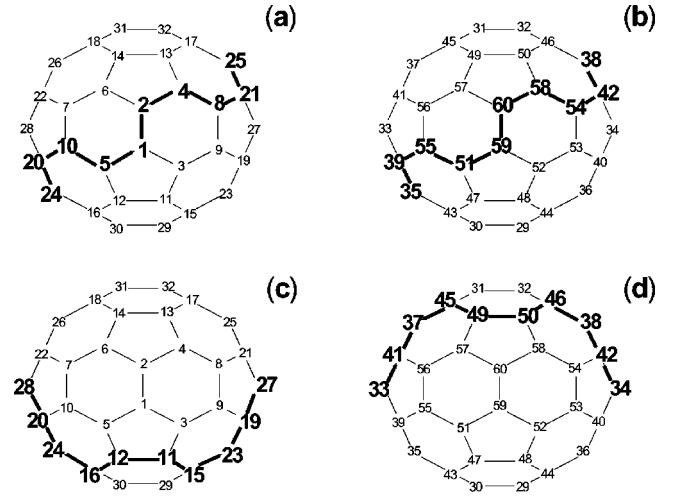


FIG. 1. Numbering of carbon atoms in the C_{60} molecule. Bold numbers show atoms on which the main part of the charge is concentrated after formation of a string polaron. The heavy curves indicate the path in which dimerization is suppressed for the string polaron. (Ref. 13) Front (a) and back (b) views of an electron or hole polaron on single C_{60} . Front (c) and back (d) views of a hole polaron in a linear chain for $T/t=0.1$ and $U=0$.

The interatomic distances and charges on the central C_{60} molecule were initially set to the values corresponding to an isolated charged molecule. Those of the other molecules were initially set to the values of an isolated neutral molecule. These values were determined from the calculations of the electronic structure and bond lengths between carbon atoms for isolated charged and neutral C_{60} molecules, respectively. The initial bond lengths between atoms in the neutral molecule were equal. In the case of charged molecule the initial bond lengths were taken as the calculated bonds for the neutral molecule.

Following Ref. 14 we have numbered the 60 carbon atoms per C_{60} molecule as indicated in Fig. 1. Bonds between carbon atoms are numbered as shown in Table I. The numeration of bonds is chosen so that the first 30 bonds separate the pentagons from the hexagons and the remaining 60 bonds separate the hexagons.

For the neutral C_{60} molecule in the case where electron-electron interaction is neglected, $U=0$ and with the parameters $t=2.5$ eV and $\alpha=6.31$ eV/Å,^{12,32,33} $K=49.7$ eV/Å,¹² $K'=K$, $\alpha'=\alpha$ two distinct bond lengths exist. Bonds separating the pentagons and hexagons become longer than the bonds separating the hexagons, and changes in the bond lengths are identical to previous results.^{12,13,34} The calculated width of the energy band gap in the electron spectrum of the neutral C_{60} molecule is equal to 2.25 eV, which agrees well with the experimental photoelectron and inverse-photoelectron spectra for solid C_{60} (Ref. 35) as well as earlier calculations.^{13,14,36} In the case of $U \neq 0$, for $0 \leq U \leq 2t$ in the neutral molecule, the bond lengths and energy gap in the electronic spectrum are the same as in the case $U=0$. With increasing U , the behavior of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels in the electronic spectrum is linear and identical to previous results.³⁶

TABLE I. Numbering of bonds in the linear chain.

k	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
i	1	3	4	5	6	11	12	13	14	19	20	21	22	27	28	29	31	35	36	37	38	43	44	45	46	51	52	54	56	59
j	2	9	8	10	7	15	16	17	18	23	24	25	26	34	33	30	32	39	40	41	42	47	48	49	50	55	53	58	57	60
k	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
i	1	1	2	2	3	4	5	6	7	7	8	8	9	10	11	13	15	15	16	16	17	17	18	18	19	20	21	22	23	24
j	3	5	4	6	11	13	12	14	10	22	9	21	19	20	12	14	23	29	24	30	25	32	26	31	27	28	27	28	36	35
k	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
i	25	26	29	30	31	32	33	33	34	34	35	36	37	38	39	40	41	42	47	47	48	49	49	50	51	52	53	55	57	58
j	38	37	44	43	45	46	39	41	40	42	43	44	45	46	55	53	56	54	48	51	52	50	57	58	59	59	54	56	60	60

For the C₆₀ molecule with one extra charge, in the case where $U=0$, the same bond lengths between carbon atoms and electronic spectrum as in earlier reports^{12,14} have been obtained. Using the notation described above for the carbon atoms (Fig. 1) and bonds (Table I), the distribution of excess charge and relative changes in bond lengths are shown in Fig. 2. It is seen that upon electron as well as hole doping there occurs a nonhomogeneous distribution of excess charge on the molecule and dimerization is suppressed on the bonds that connect sites with maximum values of extra charge [Figs. 1(a,b)], which corresponds to formation of a string polaron.¹³

Upon addition of extra charge in a one-dimensional C₆₀ crystal under weak conjugation ($T/t \ll 1$) a polaron is formed on the central molecule in the supercell, and with increasing conjugation there occurs a redistribution of charge on the other molecules in the supercell. This is accompanied by changes in the bond lengths between carbon atoms and in the electronic structure of the fullerene chain.

In Figs. 3–8 we show the results of calculations of the charge distribution, changes in the bond lengths, and electron density of states in a supercell consisting of three C₆₀ molecules for different doping levels and values of the parameters T/t and U .

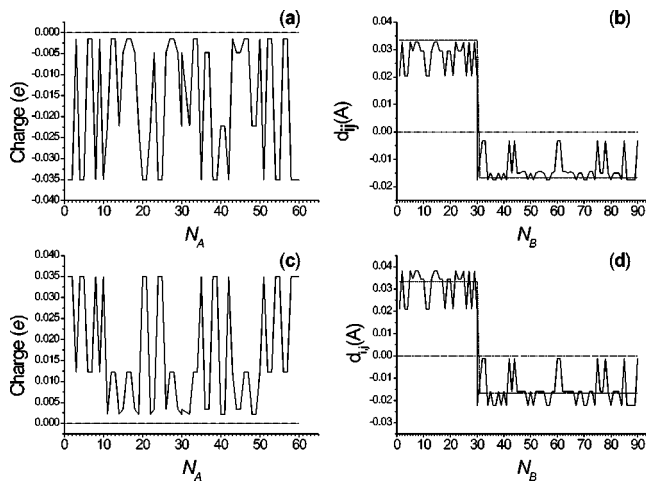


FIG. 2. Charge distribution and distortions in bond lengths d_{ij} on a single molecule C₆₀ in the cases of electron (a), (b) and hole (c), (d) doping. The numeration of the atoms (N_A) and bonds (N_B) corresponds to numberings indicated in Fig. 1 and Table I, respectively. Dotted lines indicate results for the neutral single molecule.

For small values of the parameter T/t extra charge is localized on the central molecule. For $U=0$ distribution of the excess electron [Fig. 3(a)] and distortions in the bond lengths [Fig. 4(a)] in this molecule differ slightly from the case of the isolated fullerene [Figs. 2(a,b)], and some spreading of the string polaron occurs. The behavior of all considered quantities for the end molecules is the same as for the isolated neutral molecule. Taking the Hubbard interaction into account produces an insignificant influence on the charge distribution in the system and has very little influence on the bond lengths [Figs. 3(b) and 4(b)]. In the case of hole doping for $U=0$, distribution of the excess charge on the central molecule [Fig. 5(a)] and changes in the bond lengths [Fig. 6(a)] in this molecule also differ from the case of the isolated molecule [Figs. 2(c,d)], while the end molecules remain neutral. Figures 1(c,d) show the change in distribution of the hole polaron on the surface of the central molecule in supercell as compared with the isolated fullerene (Fig. 1). Inclusion of the Hubbard interaction qualitatively changes the picture of Figs. 1(c,d) to that of Figs. 1(a,b) [see also Figs. 5(b) and 6(b)].

Increasing the parameter T/t leads to disappearance of the

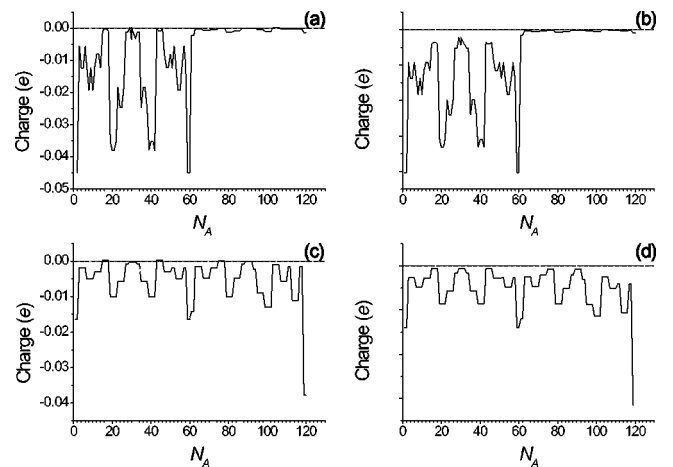


FIG. 3. Charge distribution of carbon atoms in the chain modeled by a system of three periodically repeated C₆₀ molecules with one extra electron: (a) $U=0$, $T/t=0.1$; (b) $U=2t$, $T/t=0.1$; (c) $U=0$, $T/t=0.4$; (d) $U=2t$, $T/t=0.4$. The results are shown only for the central molecule (atom numbers 1–60) and one end molecule (atom numbers 61–120). The results for both end molecules are identical.

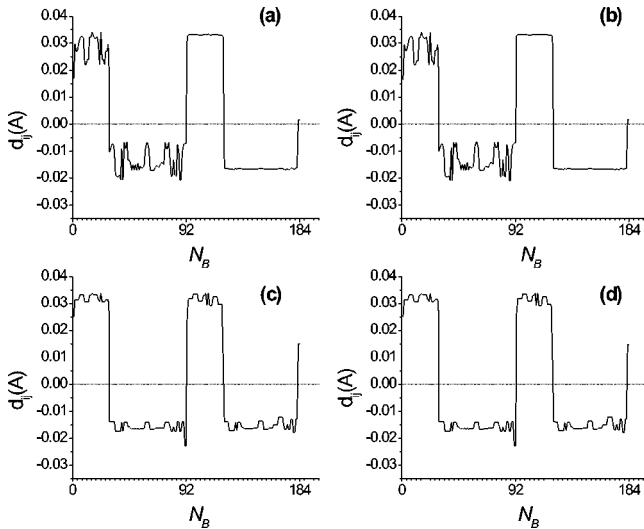


FIG. 4. Change in bond length d_{ij} in the chain modeled by a system of three periodically repeated C_{60} molecules with one additional electron. The results are shown only for the central (atom numbers 1–90) and one end molecule (atom numbers 93–182). Bonds 91 and 92 link the central and end molecules; while bonds 183 and 184 connect the end molecules of neighboring supercells in the chain. The results for both end molecules are identical.

polaron. The atomic charge distribution differs in the cases of electron and hole doping. In both cases the charge distribution on all molecules is similar but on the bonds linking the end molecules of neighboring supercells the value of extra charge is maximal and it changes most significantly with inclusion of the Hubbard interaction [Figs. 3(c,d) and 5(c,d)]. Distortions in the intramolecular bond lengths are nearly the same and do not depend on the doping level. However, the bonds linking the central molecule with the end molecules are shortened, while the bonds between the end molecules in neighboring supercells are stretched, which leads to a net contraction of the supercell. Account of the

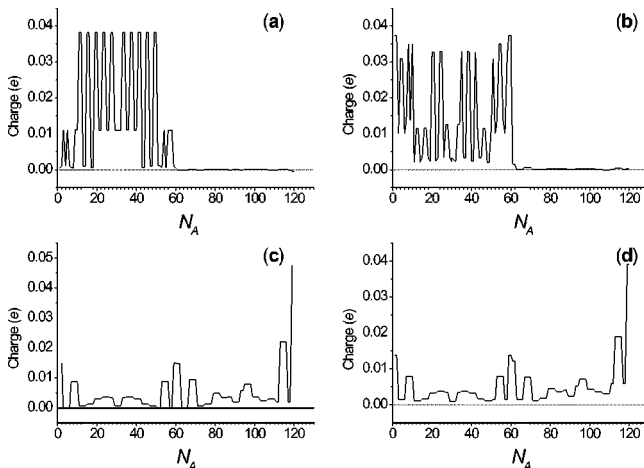


FIG. 5. Charge distribution for carbon atoms in the chain modeled by a system of three periodically repeated C_{60} molecules with one additional hole. The numeration of atoms is the same as in Fig. 3.

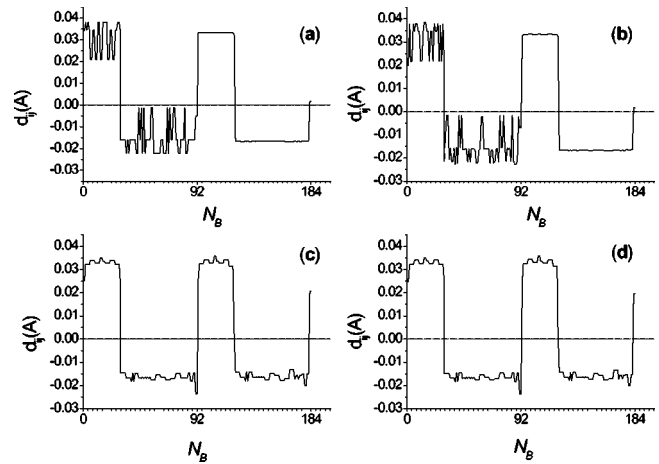


FIG. 6. Change in bond length d_{ij} in the chain modeled by a system of three periodically repeated C_{60} molecules with one additional hole. The numeration of atoms is the same as in Fig. 4.

Hubbard interaction has practically no influence on the bond lengths [Fig. 4(c,d) and 6(c,d)].

The densities of electron states for electron and hole doping with $U=0$ in comparison with the neutral chain are shown on Fig. 7. The electronic structure of the chain is reconstructed. In the case of the neutral chain [Fig. 7(a)], the interaction between different C_{60} molecules implies that, distinct from an isolated molecule, the gap in electronic spectrum is narrowed to 1.78 eV and doubly degenerate energy levels are split from the corresponding HOMO and LUMO levels of the single molecule. Upon addition of one electron (hole) to the system these split levels become closer. The extra electron (hole) occupies one of the levels and the split-

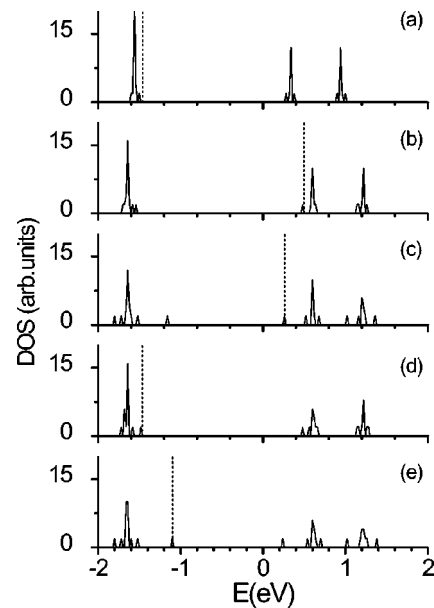


FIG. 7. Electron DOS (in arbitrary units) of the chain modeled by a system of three periodically repeated C_{60} molecules for $U=0$: (a) Neutral system, $T/t=0.1$; (b) one additional electron, $T/t=0.1$ and (c) $T/t=0.4$; (d) one additional hole, $T/t=0.1$ and (e) $T/t=0.4$. The Fermi levels are marked by the vertical dashed lines.

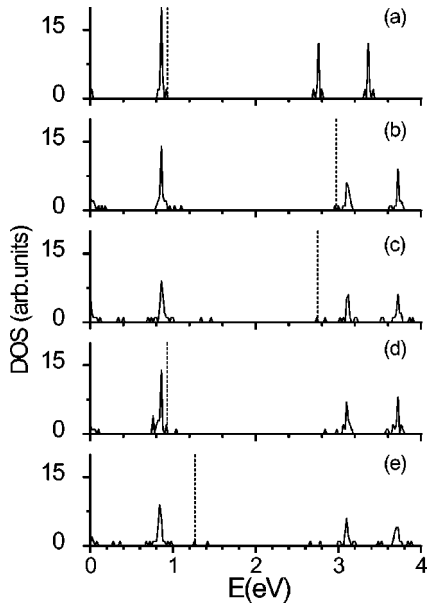


FIG. 8. Electron DOS (in arbitrary units) for the chain modeled by a system of three periodically repeated C_{60} molecules for $U = 2t$: (a) Neutral system, $T/t=0.1$; (b) one additional electron, $T/t=0.1$ and (c) $T/t=0.4$; (d) one additional hole, $T/t=0.1$ and (e) $T/t=0.4$. The Fermi levels are marked by the vertical dashed lines.

ting between the main peaks increases to 2.2 eV [Figs. 7(b, c)]. Inclusion of the Hubbard interaction gives an analogous picture of the electron density of states (DOS), but then all energy levels of the system are shifted toward higher energies. By introducing one electron (hole), the additional energy levels split into two nondegenerate levels, one of which is occupied by the extra charge (Fig. 8). All the results obtained for supercells of larger size are quite similar, with some insignificant variations.

Figure 9 shows the values of charge on the central and

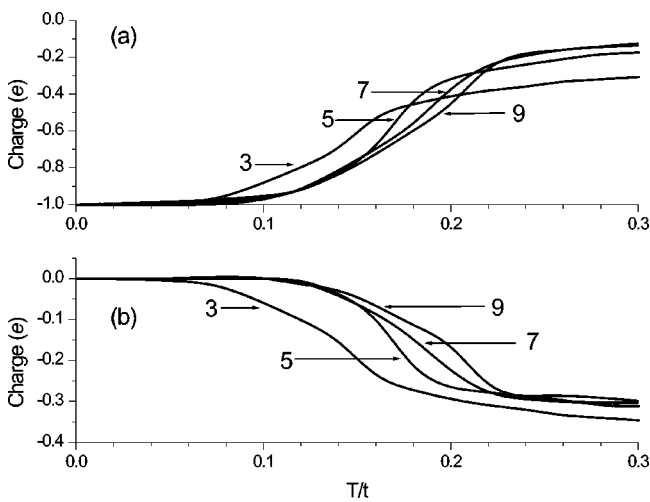


FIG. 9. Distribution of the mean value of charge on the central (a) and end molecules (b) for different supercell (supercell size is indicated by the arrows). The mean charge in the indicated range of T/t is always greater on the central and end molecules than on the other molecules in the supercell.

end molecules for supercells consisting of 3, 5, 7, and 9 fullerenes as a function of the conjugation parameter T/t for $U=0$ in the case of one added electron per supercell. One can see that for small enough values of the parameter T/t the additional charge is localized on the central molecule, and starting from the threshold value $T^*/t \approx 0.215$, redistribution on the end molecules occurs. From Fig. 9, it can be also seen that with increasing supercell size the charge distribution approaches limiting behavior for large N_c . Thus, we conclude that a polaron can also exist in the limit of an infinite supercell. Change of U within the considered limits leads to only insignificant variations in the resulting picture.

The phenomenon of polaron formation has been also studied in many models of interaction of a Fermi particle (the charge carrier) with a boson field (phonon).³⁷ Among these models are the relatively simple tight-binding Holstein³⁸ and SSH (Ref. 39) models. Using these models, the formation and self-trapping transition under changes in the relation between the electron-phonon coupling constant, the nearest-neighbor hopping integral, and the Einstein frequency have been investigated. Thus, in the one-dimensional Holstein model the line of so-called self-trapping transition separating the small polaron from the large polaron has been determined⁴⁰ and different criteria for single polaron formation have been established.⁴¹ By contrast, in our case, the formation of a polaron in a one-dimensional doped (electron or hole) C_{60} crystal has been considered. In this model, as distinct from the linear chain Holstein and SSH models, the polaron in the neutral one-dimensional C_{60} crystal is absent and forms only when an electron or hole is added.

IV. CONCLUSIONS

The electronic structure of a molecular polaron and associated Jahn-Teller distortions in a doped C_{60} chain have been studied with the use of a generalized version of the Su-Shrieffer-Heeger model for the intermolecular and intramolecular degrees of freedom. Inclusion of electron correlation effects (on-site Hubbard repulsion) has been considered.

The present numerical results for the neutral and doped single C_{60} systems agree well with the known results.^{12,13} When the molecule is doped with one electron or hole the additional charge accumulates along a nearly equatorial line in the molecule. Dimerization becomes weaker along the same line. In both cases of electron and hole doping the forms of the polaron on an isolated molecule are the same. In the case of a linear chain with one extra electron (hole), for weak π conjugation a polaron is also generated. In this case the electronic structure and distortions in the bond lengths for electron and hole doping differ significantly. These distinctions are caused by conjugation of π electrons and electron-electron interactions. For $U=0$ the electron string polaron is spread out while the hole polaron conserves its form and rotates on the surface of the molecule. Inclusion of the Hubbard interaction makes no influence on the form of the electron polaron while the structure of the hole polaron returns, with slight quantitative changes, to the form characteristic of a string polaron on an isolated molecule. Further strengthening of π electron conjugation leads to disappear-

ance of the polaron in the linear chain. In this case the doped charge is located on the nearest atoms of neighboring molecules of chain and the bond lengths between neighboring molecules change significantly. Hubbard on-site repulsion does not change the physical picture of formation and disappearance of the polaron.

Thus, as shown in this paper, single polarons existing in separate fullerene molecules can also exist in C_{60} solids for adequately strong π conjugation. Existence of such polarons is important to understand the charge transport mechanisms in fullerene and heterofullerene molecules and C_{60} solids and the reactivity of these compounds.

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