Polaron Excitations in Fullerenes: Theory as $\pi$-Conjugated Systems

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(Received September 24, 1992)

We review the recent theoretical treatment of fullerenes as $\pi$-conjugated systems. Polaronic properties due to the Jahn-Teller type effects are mainly discussed. (1) A Su-Schrieffer-Heeger type electron-phonon model is applied to fullerenes: $\text{C}_{60}$ and $\text{C}_{70}$, and is solved within the adiabatic approximation applied to the phonons. When the system ($\text{C}_{60}$ or $\text{C}_{70}$) is doped with one or two electrons (or holes), the additional charges accumulate at twenty carbons almost along an equatorial line of the molecule. The dimerization becomes the weakest along the same line. Two energy levels, the occupied state and the empty state, intrude largely in the gap. The intrusion is larger in $\text{C}_{70}$ than in $\text{C}_{60}$. These are “polarons” in doped fullerenes. It is also found that $\text{C}_{60}$ and $\text{C}_{70}$ are related mutually with respect to electronical structures as well as lattice geometries. (2) We apply the model to the fullerene epoxide $\text{C}_{60}O$. It has the polaron-type lattice distortion around the oxygen, and also shows the energy level intrusion in the gap. (3) Optical properties of $\text{C}_{60}$ are calculated and discussed. In the absorption of the doped molecule, a new peak structure is present owing to the polaronic distortion. In the luminescence of the neutral $\text{C}_{60}$, the spacing between $9\hbar$-phonon side-band peaks and the relative intensities agree well with experiments. In the dispersion of the third harmonic generation, the magnitudes of $|\chi^{(3)}|$ agree with those of experiments at the resonance of the lowest allowed transition as well as in the region away from the resonance.

§ 1. Introduction

Recently, the “fullerenes” $\text{C}_N$ which have the hollow cage structures of carbons have been intensively investigated. There are several experimental indications that the doped fullerenes show polaronic properties due to the Jahn-Teller distortion, for example: (1) The electron spin resonance study$^1$ on the radical anion of $\text{C}_{60}$ has revealed the small $g$-factor, $g=1.9991$, and this is associated with the residual orbital angular momentum due to the Jahn-Teller distortion. (2) Photoemission studies$^2$ of $\text{C}_{60}$ and $\text{C}_{70}$ doped with alkali metals have shown peak structures, which cannot be described by a simple band-filling picture. (3) When poly (3-alkylthiophene) is doped with $\text{C}_{60}$,$^3$ interband absorption of the polymer is remarkably suppressed and a new absorption peak evolves in the low energy range. The Jahn-Teller splitting of LUMO in $\text{C}_{60}$ state and/or the Coulomb attraction of positively charged polaron to $\text{C}_{60}$ might occur. (4) The luminescence of neutral $\text{C}_{60}$ has been measured.$^4$ There are two peaks around 1.5 and 1.7 eV below the gap energy 1.9 eV, interpreted by the effect of the polaron exciton. In addition, the experiments on the dynamics of photoexcited states have shown the interesting roles of polarons.$^5$
In this article, we first review the recent investigation of polaronic excitations in the C\textsubscript{60} and C\textsubscript{70} molecules, and discuss lattice distortion and changes of electronic levels upon doping. We have described C\textsubscript{60} and C\textsubscript{70} as an electron-phonon system and have extended the Su-Schrieffer-Heeger (SSH) model\textsuperscript{6} of conjugated polymers. We have calculated for systems where one or two electrons are added or removed. We shall discuss properties of “polarons” in fullerenes, which have been reported in detail in Refs. 7)~9).

We have found that sites, where additional charges are prone to accumulate, are common to C\textsubscript{60} and C\textsubscript{70}. They are along the equatorial line in C\textsubscript{60}. Then more carbons are inserted between these sites in C\textsubscript{70}. In this regard, we should bear in mind that C\textsubscript{70} is made from C\textsubscript{60}, by division into two parts and adding ten carbons. Thus, there are relations of electronical properties as well as the structural relation between (doped as well as undoped) C\textsubscript{60} and C\textsubscript{70}.

Next, we review the application of the extended SSH model to the fullerene epoxide C\textsubscript{60}O\textsubscript{10}. The dimerization has been found to become weaker around the sites near the oxygen. Two energy levels make a sizable intrusion into the gap. These polaronic features are certainly the effects of the external potential given by the additional oxygen.

Finally, we look at optical properties of C\textsubscript{60}. We have considered optical absorption spectra of the doped molecules,\textsuperscript{9} luminescence from the photo-excited neutral C\textsubscript{60},\textsuperscript{11} and the dispersion of the third harmonic generation (THG).\textsuperscript{12} In the absorption of the doped C\textsubscript{60}, a new peak structure is present owing to the polaronic distortion. In the luminescence, the spacing between \(H\textsubscript{\sigma}(8)\)-phonon side-band peaks and the relative intensities agree well with experiments. In the dispersion of the THG, the magnitudes of \(|\chi^{(3)}|\) agree with those of experiments at the resonance of the lowest allowed transition as well as in the region away from the resonance.

This article is organized as follows. In §2, the model is presented. Polarons in C\textsubscript{60} and C\textsubscript{70} are discussed in the following two sections. In §5, the extended SSH system is applied to the fullerene epoxide. In §6, we show the optical properties. We close this article with brief remarks in §7.

§ 2. Model

We use the extended SSH hamiltonian for the topological geometries of fullerenes: C\textsubscript{60} and C\textsubscript{70}. The model is:

\[
H = \sum_{(i,j)} (-t_0 + \alpha y_{i,j})(c_{i,\sigma} c_{j,\sigma} + \text{h.c.}) + \frac{K}{2} \sum_{(i,j)} y_{i,j}^2, \tag{1}
\]

where \(c_{i,\sigma}\) is an annihilation operator of a \(\pi\)-electron; the quantity \(t_0\) is the hopping integral of the ideal undimerized system; \(\alpha\) is the electron-phonon coupling; \(y_{i,j}\) indicates the bond variable which measures the length change of the bond between the \(i\)- and \(j\)-th sites from that of the undimerized system; the sum is taken over nearest neighbor pairs \(<ij>\); the second term is the elastic energy of the lattice; and the quantity \(K\) is the spring constant. This model is solved with the assumption of the adiabatic approximation and by an iteration method.
§ 3. Polarons in C_{60}

We have taken $t_0 = 2.5$ eV which has been used in the two-dimensional graphite plane\textsuperscript{13} and polyacetylene.\textsuperscript{6} Two quantities, $\alpha = 6.31$ eV/Å and $K = 49.7$ eV/Å\textsuperscript{2}, have been determined so that the length difference between the short and long bonds in C\textsubscript{60} is the experimentally observed value: 0.05 Å.\textsuperscript{14} Here, the dimensionless electron phonon coupling $\lambda = 2\alpha^2 / \pi K t_0$ has been taken as 0.2 as in polyacetylene.\textsuperscript{6} The number of electrons $N_{e\text{el}}$ has been varied within $-2 \leq N_e \leq 2$, where $N_e = N_{e\text{el}} - N$, and $N$ is the number of carbon atoms.

First, we discuss lattice and electronic structures of C\textsubscript{60}.\textsuperscript{7,9} The lattice configurations of the doped systems are shown in Figs. 1(a) and (b). We show three kinds of the shorter bonds. The shortest bonds, $d$, are represented by the thick lines. The second shortest ones, $b$, are shown by the usual double lines. The dashed lines indicate the third shortest bonds. They are the bonds $f$ in Fig. 1(a) and bonds $g$ in (b).

![Lattice structures of doped C\textsubscript{60}](https://example.com/lattice.png)

Fig. 1. Lattice structures of doped C\textsubscript{60} [(a) $|N_e| = 1$ and (b) $|N_e| = 2$], (c) neutral C\textsubscript{60} and (d) fullerene epoxide C\textsubscript{60}O.
Other longer bonds are not shown. The figures are the same for the electron and hole dopings. When the change in the number of electrons is one, the change in the electron density is the largest at the sites at the ends of dashed lines, namely, points D. The dashed lines are mostly located along an equatorial line of C\textsubscript{60}. The absolute value of the length of the bonds g is the smallest of the four kinds of bonds with negative bond variables. The dimerization becomes the weakest along this equatorial line. The distortion of the lattice is similar to that of a polaron\textsuperscript{15} in conjugated polymers. When the change in the electron number is two, configurations of dashed lines along the equatorial line change, as shown in Fig. 1(b). The ordering of bonds, f and g, with respect to the bond variable is reversed. Other configurations are the same. The change in the electron density is also the largest at points D. Therefore, polaronic distortion persists when the doping proceeds from one to two electrons (or holes).

Next, we look at changes in the electronic level structures. They are shown in Fig. 2. When the system is doped, the degeneracy decreases due to the reduced symmetry. This reduction comes from the deformation of the lattice. This is one of the Jahn-Teller distortions. The removal of the degeneracies of energy levels is due to the $H_6$ distortion.\textsuperscript{16} When $|N_{c}|=1$ and 2, the highest level, which splits from the highest occupied molecular orbital (HOMO) of the neutral system, is nondegenerate. Its energy shifts upward. In contrast, the other two levels shift only slightly. Similarly, the lowest unoccupied molecular orbital (LUMO) of the neutral system splits into two levels. The energy of the nondegenerate level shifts downward, while change of the energy of the doubly degenerate level is small. This change in the level structures is common to the two cases of the electron and hole dopings. The change is similar to that in the polaron formation\textsuperscript{15} in conjugated polymers.

§ 4. Polarons in C\textsubscript{70}

We describe changes in lattice structures and electron distributions of the doped C\textsubscript{70}.\textsuperscript{8,9} The dimerization strengths change their values mostly along the ring-like part shown in Fig. 1(c), while the patterns with the mirror reflection symmetry persist. Change in electron density at sites E is very small. This is a consequence of the fact
that dimerization almost disappears along bonds f and g. The property of the part along the equatorial line is similar to that of the graphite plane. The strengths of the dimerization change largely along bonds, from a to e, upon doping. The additional charges tend to accumulate near these bonds. The positions D, where the additional charges accumulate most densely, correspond to the sites D of C_{60}. When we make C_{70} from C_{60}, sites E are added in the interval, but the property, that additional charges tend to accumulate at sites D, persists for C_{70}. This finding is quite interesting.

We discuss structures of electronic energy levels. We show the changes in electronic structures in Fig. 3. Two levels have already intruded in the gap in the neutral C_{70}. This is due to the structural elongation from C_{60} to C_{70}. When the system is doped with up to two electrons or holes, the HOMO and LUMO of the neutral system largely extend into the gap. The positions of the other levels change only slightly. The magnitude of level intrusion is larger than that in C_{60} due to nondegenerate levels near the gap at N_e=0. The HOMO and LUMO of the neutral system have large amplitude at sites, from A to D. The amplitude at D is the largest. The amplitude at E is very small. Therefore, the additional charge is prone to accumulate most at sites D.

§ 5. Fullerene epoxide

The fullerene epoxide C_{60}O shown in Fig. 1(d) has been produced in macroscopic quantities.\(^\text{17}\) In this section, we look at the dimerization and energy level structures. Details are discussed in Ref. 10). The oxygen atom is treated by an impurity model with one effective atomic level. The following term is added to the extended SSH model:

\[
H_0 = E_0 \sum_\sigma d_\sigma^\dagger d_\sigma - t_0 \sum_\sigma [d_\sigma^\dagger (c_{1,\sigma} + c_{2,\sigma}) + \text{h.c.}].
\] (2)

The carbons bonding to the oxygen are numbered as 1 and 2.

We find the following properties: The dimerization becomes weaker around the oxygen as shown in Fig. 1(d). Two localized states appear deep in the gap. Figure 4 shows the data for \(t_0 = 0.5t_0\). The HOMO and LUMO are shown by full and open
circles, respectively. The next HOMO (NHOMO) and next LUMO (NLUMO) are represented by the small squares which are connected by curves. Other energy levels are not shown. All the levels are nondegenerate. When $E_0$ is varied, the energies of NHOMO and NLUMO do not change so much as those of HOMO and LUMO. This is the consequence of the fact that the wave functions of NHOMO and NLUMO spread almost over the $C_{60}$ while those of HOMO and LUMO are localized around the defect. Thus, we can regard the HOMO and LUMO as impurity states which are well known in bulk semiconductors. Therefore, we conclude that the energy gap of $C_{60}$ itself is less affected by the defect while two new localized states are emitted into the gap due to the defect potential. This property is like that of polarons but mainly due to the external potential from the oxygen. We note that optical transition between them is allowed. This accords with the recent optical absorption data.\footnote{18}

§ 6. **Optical properties of $C_{60}$**

For optical properties, we consider optical absorption spectra of the doped molecules (Ref. 9)), luminescence from the photoexcited neutral $C_{60}$ (Ref. 11)), and the dispersion of the THG (Ref. 12)).

We show how the “polarons” in $C_{60}$ would be observed in optical absorption.\footnote{9} Figure 5 shows the results of undoped and electron-doped systems with $0 \leq N_c \leq 2$. We only show data of the electron-doped cases. Figure 5(a) is the data of the

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig5.png}
\caption{Optical absorption of $C_{60}$ for (a) $N_c=0$, (b) $N_c=1$ and (c) $N_c=2$.}
\end{figure}
undoped system. There are two peaks in the figure. The peak at 2.9 eV is the transition between the HOMO and the NLUMO. The other peak at 3.1 eV is the transition between the NHOMO and the LUMO. The transition between the HOMO and the LUMO is forbidden and does not appear in the figure. Figures 5(b) and (c) show the data of the systems with \( N_c = 1 \) and 2, respectively. The two large peaks in Fig. 5(a) now have small substructures due to the level splittings. In addition, there appears a new peak at low energy (\( \sim 0.7 \) eV). This peak corresponds to the transition between the singly occupied molecular orbital and the NLUMO, etc., when \( N_c = 1 \). It corresponds to the transition between the LUMO and the NLUMO, etc., when \( N_c = 2 \). Therefore, the new peak at low energy is due to the splitting of the LUMO.

Next, we consider quantum lattice fluctuations and discuss the phonon side bands in the luminescence spectrum. To calculate the luminescence, we use a collective coordinate method which resembles the displacement of the carbon atoms of the \( H_g(8) \) phonon mode and extrapolates between the ground state “dimerization” and the exciton polaron. Wave functions of the singly occupied molecular orbitals of the exciton polaron have large amplitudes at twenty sites along the equatorial line. The coordinate describing the weakening of the dimerization along the equator is assigned to the twenty carbons. The collective coordinate Schrödinger equation is solved and the luminescence is calculated by the formula used by Friedman and Su. It is assumed that disorders and/or solid state effects make the dipole-forbidden transition allowed partially. The result is shown by plots in Fig. 6. The curves are the envelopes of the experimental data. There is good agreement for the existing luminescence peak spacing. This indicates that the \( H_g(8) \) mode frequency 1575 cm\(^{-1}\) is quantitatively derived by the coordinate. We also find fair agreement for the relative intensity. The difficulty in making the \( \text{C}_{60} \) thin films and different experimental conditions would be the origins of the variety of experimental data. Anyway, our success has revealed the importance of the intramolecular electron-phonon couplings.
in \( \text{C}_{60} \).

Finally, we look at spectral dispersions of the THG of the neutral \( \text{C}_{60} \). We display the absolute value in Fig. 7. In the bottom of the figure, we show the energies of the dipole allowed excitations, where three-photon resonances can appear, and also the energies of the forbidden excitations multiplied by \( \frac{3}{2} \), where two-photon resonances can appear. The peaks in the THG spectrum can be assigned as two- or three-photon resonances. We point out three properties: (1) The magnitude of \( \chi^{(3)} \) at \( \omega = 0 \) is \( 1.22 \times 10^{-12} \) esu and is similar to the magnitudes in the THG experiments: \( 4 \times 10^{-12} \) esu at \( 3\omega \approx 1.6 \text{ eV} \) (Ref. 21)) and \( 7 \times 10^{-12} \) esu at \( 3\omega \approx 3.6 \text{ eV} \) (Refs. 21 and 22)). Here, we compare the magnitudes at frequencies far from the resonances. (2) The value of the THG around the peak at 2.5 eV is of the order of \( 10^{-11} \) esu. This well explains the magnitude \( 2.7 \times 10^{-11} \) esu at the peak centered around 2.8 eV (Ref. 21)). A larger broadening in our theory would yield better agreement with the experiment. We note that several authors have pointed out the similar property that the third harmonic generation of \( \text{C}_{60} \) can be explained by the free electron theory or the calculation within the Hartree-Fock approximation. (3) The three-photon peaks, at \( 3\omega \approx 6.1 \) and 6.3 eV, have remarkably large strengths. This large enhancement would be due to the fact that there are two-photon resonances \( 3\omega \approx 6.1, 6.4 \) and 6.5 eV, meaning that double resonance enhancement occurs. Electron correlations might change this third consequence.

§ 7. Concluding remarks

We have reviewed the recent theoretical treatment of the fullerenes as the \( \pi \)-conjugated systems. Even though the extended SSH model is very simple, we have derived interesting general properties about polaronic lattice distortions and energy level intrusions. There have been several origins of the polaronic changes: the doping of additional charges to \( \text{C}_{60} \) and \( \text{C}_{70} \) (Refs. 7) and 8)), the structural elongation from \( \text{C}_{60} \) to \( \text{C}_{70} \) (Ref. 9)), and effects of the external potential in \( \text{C}_{60} \text{O} \) (Ref. 10)).

Recently, several interesting optical experiments have been reported. The properties more or less resemble those of the conjugated polymers, which have been explained by the one-dimensional models like the SSH hamiltonian.15 We have derived quantitative agreements with the luminescence and THG experiments. Thus, the theoretical model of fullerenes as the \( \pi \)-conjugated systems is a powerful method for investigating the dynamical as well as static properties.

We have neglected various effects: Coulomb interactions among \( \pi \)-electrons, thermal fluctuations of phonons, interactions between molecules, and so on. They should be taken into account when we compare the theory with various experiments11-15 consistently. These effects would be important when the excitation energy is large in the dynamical processes. They pose interesting problems for future works.

Acknowledgements

Useful discussion with Professor Y. Wada, Dr. K. Yamaji, Professor H.
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Fukuyama, Professor W. P. Su, Dr. A. Oshiyama, Dr. S. Saito, Dr. N. Hamada, Professor G. A. Gehring, Dr. M. Fujita, Dr. Y. Asai, Dr. A. Terai, Dr. T. Yanagisawa, and Dr. Y. Shimoi is acknowledged. Fruitful collaboration with Professor B. Friedman and Dr. S. Abe is also acknowledged. Numerical calculations have been performed on FACOM M-780/20 and M-1800/30 of the Research Information Processing System, Agency of Industrial Science and Technology, Japan.

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