Charge transfer excitons in $C_{60}$-dimers and polymers

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ABSTRACT
Charge-transfer (CT) exciton effects are investigated for the optical absorption spectra of crosslinked $C_{60}$ systems by using the intermediate exciton theory. We consider the $C_{60}$-dimers, and the two (and three) molecule systems of the $C_{60}$-polymers. We use a tight-binding model with long-range Coulomb interactions among electrons, and the model is treated by the Hartree-Fock approximation followed by the single-excitation configuration interaction method. We discuss the variations in the optical spectra by changing the conjugation parameter between molecules. We find that the total CT-component increases in smaller conjugations, and saturates at the intermediate conjugations. It decreases in the large conjugations. We also find that the CT-components of the doped systems are smaller than those of the neutral systems, indicating that the electron-hole distance becomes shorter in the doped $C_{60}$-polymers.

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1. INTRODUCTION

Recently, it has been revealed that the C\textsubscript{60} molecules polymerize under UV irradiation [1], and also by applying high pressures [2-4]. In these polymerized forms of C\textsubscript{60}, the number of electrons does not change from that of C\textsubscript{60} molecules, and the systems are kept neutral. And further, the linear (one-dimensional) C\textsubscript{60}-polymers have been synthesized in alkali-metal doped C\textsubscript{60} crystals: AC\textsubscript{60} (A =K, Rb, Cs) [5-8]. One electron per one C\textsubscript{60} is donated in the polymer chain in these compounds. The lattice structures are shown in Fig. 1. The C\textsubscript{60} molecules are arrayed in a linear chain. Between the neighboring C\textsubscript{60} molecules, there are four membered rings which are formed by the [2+2] cycloaddition.

In the previous papers [9-10], we have studied the electronic structures of one dimensional C\textsubscript{60}-polymers by using an interacting electron-phonon model. We have introduced a phenomenological parameter which represents the strength of conjugations of electrons in the polymer chain direction. When the conjugations are stronger, the hopping integrals between C\textsubscript{60} molecules become larger. We have found that the level crossing between the highest occupied state and the lowest unoccupied state occurs when the conjugations increase in the neutral polymer [9]. We have discussed that this fact might give rise to a reentrant transition between insulators and a metal while a high pressure is applied in order to change conjugations between molecules. The electron doping effects have been further studied [10]. We have found that the C\textsubscript{60}-polymer doped with one electron per one molecule is always a metal, and the polymer doped with two electrons per one C\textsubscript{60} changes from an indirect-gap insulator to the direct-gap insulator, as the conjugations become stronger.
A lot of optical experiments on the neutral C\textsubscript{60} thin films and the alkali-metal doped crystals have been performed (see reviews, refs. [11] and [12], for example). Along with the experimental develops, we have theoretically analyzed the optical spectra of C\textsubscript{60} and C\textsubscript{70} molecules [13] and solids [14,15]. The C\textsubscript{60} and C\textsubscript{70} systems maximally doped with alkali metals have been also studied [16]. We have searched for parameter sets in order to explain the photoexcitation energies, and relative oscillator strengths, which have been measured in experiments of C\textsubscript{60} and C\textsubscript{70} systems. We now expect that our experiences on exciton effects in fullerene systems can be well applied to the C\textsubscript{60}-polymers, too.

In this paper, we shall study optical excitation properties of the polymerized C\textsubscript{60} systems by using the intermediate exciton theory used in the above literatures. We consider the C\textsubscript{60}-dimers and the two-molecule system of the C\textsubscript{60}-polymers (and three-molecule system in the Appendix), as the examples of the crosslinked C\textsubscript{60}. We use a tight-binding Hamiltonian with long-range Coulomb interactions among electrons. The model has been used in the discussion of the antiferromagnetism in the previous paper [17]. We shall perform Hartree-Fock approximation and take into account of electron-hole excitations by the single-excitation configuration interaction method. This is a sufficient method when we discuss linear excitation properties. An interesting problem, special to the polymerized systems, is the possibility of the crossover among the Frenkel (molecular) excitons and Wannier [charge-transfer (CT)] excitons. If interactions are not present between molecules, the exciton is localized on a molecule. As the interactions turn on, some of the optical excitations might have amplitudes over several molecules, and thus the excitations become like...
CT-excitons. The main purpose of this paper is to look at the development of CT-exciton features in the optical absorption spectra of C$_{60}$-dimers and polymers, when the electronic system is neutral and is doped with one electron per one C$_{60}$.

Our main conclusions are: (1) The CT-exciton component first increases in smaller conjugations, i.e., in weak intermolecular interactions, and saturates at the intermediate conjugations. The component begins to decrease in the large conjugations. This fact is commonly seen in the C$_{60}$-dimers and polymers. (2) The CT-components of the one-electron doped systems per C$_{60}$ are smaller than those of the neutral systems. The electron-hole separations become shorter upon doping in polymerized C$_{60}$ systems.

This paper is organized as follows. In the next section, we present our model and describe procedures of calculations. Section 3 is devoted to the results of C$_{60}$-dimers, and sec. 4 is for the results of C$_{60}$-polymers. We summarize the paper in sec. 5. The three-molecule system is compared with the two-molecule system in the Appendix.

2. MODEL

We use the following tight-binding model with Coulomb interactions among electrons.

\[ H = H_{\text{pol}} + H_{\text{int}}, \]  
\[ H_{\text{pol}} = -at \sum_{l,\sigma} \sum_{\langle i,j \rangle = (1,3), (2,4)} (c_{l,i,\sigma}^{\dagger} c_{l+j,\sigma} + \text{h.c.}) - (1 - a)t \sum_{l,\sigma} \sum_{\langle i,j \rangle = (1,2), (3,4)} (c_{l,i,\sigma}^{\dagger} c_{l,j,\sigma} + \text{h.c.}) \]
\[ - t \sum_{l,\sigma} \sum_{\langle i,j \rangle=\text{others}} (c_{l,i,\sigma}^{\dagger}c_{l,j,\sigma} + \text{h.c.}), \quad (2) \]

\[ H_{\text{int}} = U \sum_{l,i} (c_{l,i,\uparrow}^{\dagger}c_{l,i,\uparrow} - \frac{n_{\text{el}}}{2})(c_{l,i,\downarrow}^{\dagger}c_{l,i,\downarrow} - \frac{n_{\text{el}}}{2}) \]
\[ + \sum_{l,l',i,j} W(r_{l,l',i,j})(\sum_{\sigma} c_{l,i,\sigma}^{\dagger}c_{l,i,\sigma} - n_{\text{el}})(\sum_{\tau} c_{l',j,\tau}^{\dagger}c_{l',j,\tau} - n_{\text{el}}). \quad (3) \]

In eq. (1), the first term is the tight binding part of the C\textsubscript{60}-polymer backbone, and the second term is the Coulomb interaction potential among electrons. In eq. (2), \(t\) is the hopping integral between the nearest neighbor carbon atoms; \(l\) means the \(l\)th C\textsubscript{60} molecule, and \(\langle i,j \rangle\) indicates the pair of the neighboring \(i\)th and \(j\)th atoms; the atoms with \(i = 1 - 4\) of the four-membered ring are shown by numbers in Fig. 1, 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 \(\sigma\); and the sum is taken over the pairs of neighboring atoms. Equation (3) is the Coulomb interactions among electrons. Here, \(n_{\text{el}}\) is the number of electrons per site; \(r_{l,l',i,j}\) is the distance between the \(i\)th site of the \(l\)th C\textsubscript{60} and \(j\)th site of the \(l'\)th C\textsubscript{60}; and

\[ W(r) = \frac{1}{\sqrt{(1/U)^2 + (r/r_0 V)^2}} \quad (4) \]

is the Ohno potential used in ref. [17]. The quantity \(W(0) = U\) is the strength of the onsite interaction; \(V\) means the strength of the long range part; and \(r_0 = 1.433\text{Å}\) is the mean bond length of the single C\textsubscript{60} molecule. We use the long-range interaction because the excited electron and hole spread over a fairly large region of the system considered.

The parameter \(a\) controls the strength of conjugations between neighboring molecules. This parameter has been introduced in the previous papers [9,10]. When \(a = 1\), the \(\sigma\)-bondings between atoms, 1 and 2, 3 and 4, in Fig. 1 are completely broken and the orbitals would become like \(\pi\)-orbitals. The bonds
between the atoms, 1 and 3, 2 and 4, become double bonds. As \( a \) becomes smaller, the conjugation between the neighboring molecules decreases, and the \( C_{60} \) molecules become mutually independent. In other words, the interactions between molecules become smaller in the intermediate \( a \) region. In this case, the operator \( c_{l,i,\sigma} \) at the lattice sites of the four-membered rings represents a molecular orbital, in other words, one of the relevant linear combinations of the \( sp^3 \) orbitals.

In the next two sections, we use the system with two \( C_{60} \) molecules in order to see CT-exciton components. The three-molecule system is considered in the Appendix. It is of course that the much larger systems will be more favorable, but the calculations are consumptive of CPU times and huge computer memories. The two molecular system is a minimum system in order to see how the CT-components are different between the \( C_{60} \)-dimers and polymers.

We consider the neutral case and the doped case with one electron per \( C_{60} \). The neutral case corresponds to the dimers formed upon UV irradiation and to \( C_{60} \)-polymers produced under high pressures. We perform the unrestricted Hartree-Fock approximation for operators of electrons, and the electron-hole excitation energies are determined by the single-excitation configuration interaction method. We will change the parameter, \( a \), within \( 0 \leq a \leq 1.0 \). For Coulomb parameters, we use \( U = 4t \) and \( V = 2t \) from our experiences of the calculations on optical excitations in \( C_{60} \) and \( C_{70} \) [13]. The same values have been used in the calculations of the \( C_{60} \) clusters with neutral charge [14,15]. The energy scale of the optical excitations is shown in units of eV by using \( t = 1.8eV \) [13].
Figure 1 shows two molecules from the C$_{60}$-polymer with the bond lengths used for the calculations of the polymers. The length 9.138 Å between the centers of C$_{60}$ and bond lengths, 1.44 Å, 1.90 Å, and 1.51 Å, around the four-membered ring are taken from the crystal structure data [6]. The other bond lengths, 1.40 Å (for the short bonds) and 1.45 Å (for the long bonds), are the same as used in the previous paper [17]. In the calculations of the dimers, the bond lengths around the four-membered ring between the molecules are the same as in Fig. 1, and the other bond lengths are 1.40 Å and 1.45 Å.

The optical spectra of C$_{60}$ are isotropic with respect to the direction of the electric field, but they become anisotropic in C$_{70}$ due to the reduced symmetry [13]. The similar thing occurs in the present calculations. In order to simplify calculated data and discussion of this paper, we would like to average over the anisotropy. Now we have in mind of the fact that the real C$_{60}$-dimers and polymers are systems where very large orientational disorder is present, and we expect that anisotropic effects in the optical spectra are not easy to be observed experimentally. The optical absorption is calculated by the formula:

$$\sum_{\kappa} \rho(\omega - E_\kappa)(f_{\kappa,x} + f_{\kappa,y} + f_{\kappa,z}),$$

(5)

where $\rho(\omega) = \gamma / [\pi(\omega^2 + \gamma^2)]$ is the Lorentzian distribution of the width $\gamma$, $E_\kappa$ is the energy of the $\kappa$th optical excitation, and $f_{\kappa,x}$ is the oscillator strength between the ground state and the $\kappa$th excited state where the electric field is parallel to the $x$-axis.
3. CT-EXCITONS IN C$_{60}$-DIMERS

Figures 2(a) and (b) show the optical absorption spectra of the neutral systems, and Figs. 2(c) and (d) show the absorption of the systems doped with one electron per C$_{60}$. There are three main peak structures which are typical to a single molecule in Figs. 2(a) and (b) [13]. In Figs. 2(c) and (d), a small feature appears around 0.4-0.6eV. This is owing to the filling of electrons in the $t_{1u}$ orbitals derived from the C$_{60}$ molecule. The optical transition from the $t_{1u}$ to the $t_{1g}$ orbitals is dipole allowed, and this gives rise to the new peak at the low energies. The similar fact has been recently reported in the optical spectra by the quantum chemical calculations [18].

In order to characterize the CT-excitons, we calculate the probability that the excited electron and hole exist on the different molecules. If the probability is larger than 0.5, we regard the excitation as CT-like. If it is smaller than 0.5, the excitation tends to localize on a single molecule and is Frenkel-like. We calculate contributions from the CT-excitons to the optical absorption, by retaining only the CT-like excitations in eq. (5). The results are shown by the thin lines in Fig. 2.

Even though the molecular exciton character is dominant, small CT-like components develop in the optical spectra. In Figs. 2(a) and (b), there are relatively larger oscillator strengths of the CT-excitons at the higher energy sides of the main three features which are centered around 3.2eV, 4.8eV, and 6.0eV. In the doped case of Figs. 2(c) and (d), the absorption of the CT-excitons become somewhat broader, but a certain amount of CT-like oscillator strengths exist. We also find that the small features around 0.4-0.6eV, which appear upon doping, are mainly Frenkel-like.
Now, we summarize the developments of the CT-components as increasing the conjugation parameter. The ratio of the sum of the oscillator strengths of the CT-excitons with respect to the total absorption is calculated and is shown as a function of the conjugation parameter in Fig. 3. In other words, we have calculated the ratio of the area below the thin line to the area below the bold line in Fig. 2. The filled and open squares are the data of the neutral and doped systems, respectively. We find that the CT-components first increase as the intermolecular interactions switch on, and saturate at about $a = 0.3$ or so. It is of some surprise that the CT-components gradually decrease at the larger $a$ than about 0.5, i.e., in the large conjugation region. Without calculations, one may expect that the value will continue increasing as the intermolecular interactions become stronger. We also find that the CT-component of the doped system is smaller than that of the neutral system. Thus, the doping effects slightly suppress the separations between the excited electron and the hole.

4. CT-EXCITONS IN $C_{60}$-POLYMERS

The calculations are extended to the $C_{60}$-polymers. The two molecule system is considered. The characterization of the CT-excitons have been done similarly as in the previous section. Figures 4(a) and (b) show the optical absorption spectra of the neutral system for the two conjugation parameters. The thin line represents the optical spectra due to the CT-excitons. The CT-excitons exist at the higher energy side of each of the three main features. This property is clearly seen for the stronger conjugations, $a = 0.5$, in Fig. 4(b).
The broadening of the main three features is larger when the intermolecular interactions are stronger. A small shoulder appears in the lower energy region than 2.8eV in Fig. 4(b). There are dipole-forbidden transitions in these energy region for the single molecule. They become partially allowed when there are intermolecular interactions. This is the origin of the broad low energy structure. Such broad structures have been measured in the optical absorption of C$_{60}$-polymers synthesized under high pressures [12], and have been ascribed as the symmetry lowering effects.

Next, we look at the optical spectra of the doped system with one electron per C$_{60}$. The total absorptions and the CT-like components are shown for $a = 0.2$ and 0.5 in Figs. 4(c) and (d), respectively. The appearance of the small feature at 0.4-0.6eV is more distinct than in the C$_{60}$-dimers. As we are treating the two-molecule system, the small feature is a peak. But, if we can do calculations for the infinitely long polymer, the feature will develop into a Drude tail which is typical for metallic systems. In the present exciton formalism, we cannot reproduce the Drude structure. This is the limitation of the calculations on small systems. By comparing the neutral and doped systems, we find that the CT-components are suppressed upon doping.

The ratio of the oscillator strengths of the CT-excitons with respect to the total absorption is calculated, and is shown as a function of the conjugation parameter in Fig. 5. The filled and open squares are for the neutral and doped systems. We find that the CT-components first increase in smaller conjugations, and saturate at the intermediate conjugations. The dramatic decrease is seen in the large conjugations. The CT-components of the C$_{60}$-polymers are larger than those of the C$_{60}$-dimers in Fig. 3. This is due to the
enhanced intermolecular interactions in polymers. We also note that the CT-components decrease when the neutral system is doped with electrons. The same qualitative feature has been seen in the calculations of the dimers.

5. SUMMARY AND DISCUSSION

In this paper, we have studied the CT-like excitons in optical absorption of the neutral and doped \( C_{60} \)-dimers and polymers. We have looked at the variations in the optical spectra by changing the conjugation parameter. We have found that the total CT-component first increases in smaller conjugations, and this is a natural result. But, it saturates at the intermediate conjugations, and the dramatic decrease follows in the large conjugations. These qualitative features are commonly seen in the \( C_{60} \)-dimers and polymers, though the strengths of CT-like oscillator strengths are different. We have also found that the CT-components of the doped systems are smaller than those of the neutral systems, and thus the electron-hole separations are suppressed upon doping in polymerized \( C_{60} \) systems.

It is more favorable to do calculations for much larger systems. But, the present exciton formalism over all the single excitations cannot be applied to systems larger than the two molecules. Then, we have considered the CT-like features in the low energies for the three molecule system in the Appendix. The variations of the CT components with respect to the conjugation conditions are qualitatively similar as in the two molecule systems: there is a saturation of the electron-hole separations at the intermediate conjugations. Therefore, we could expect that this qualitative point might be seen in larger systems.
APPENDIX: THREE MOLECULE SYSTEM OF THE C_{60}-POLYMERS

In the computation circumstances which have been used in the present paper, it is possible to take into account of all the single electron-hole pair excitations in the two C_{60} molecule systems. When the system size becomes larger, we cannot treat all of the single excitations. Alternatively, we can discuss properties of the low energy excitations by introducing some cutoffs for the optical excitations with high energies. In this Appendix, we report about the optical spectra of the three molecule system of the C_{60}-polymer. We consider the optical spectra below the energy about 4eV by taking into account of the electron excitations from the occupied states (t_{2u}, g_u, g_g, h_g, and h_u orbitals) to the empty states (t_{1u}, t_{1g}, h_g, t_{2u}, and h_u orbitals). Here, the orbitals are in the order of the energy values by Hückel theory of the single C_{60}.

Figure 6 shows the ratio of the oscillator strengths of CT-excitons with respect to the total absorption calculated for the neutral three molecules. There is a maximum at about a = 0.4, and the CT-component decreases at larger conjugations. The maximum value is about 1.6 times as large as that of Fig. 3, and it is about 2.2 times as large as that of Fig. 5. This is due to the larger system size. However, the property that the CT-component increases at small conjugations and decreases at larger conjugations is seen in Fig. 6, too.
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FIGURE CAPTIONS

Fig. 1. The structures of two molecule system of the C\textsubscript{60}-polymer. The carbon sites which constitute the four membered rings are named with numbers. The bond lengths, used in the calculations, are also shown.

Fig. 2. The optical absorption spectra of C\textsubscript{60}-dimers for the neutral case with (a) $a = 0.2$ and (b) $a = 0.5$, and for the one-electron (per C\textsubscript{60}) doped case with (c) $a = 0.2$ and (d) $a = 0.5$. The bold line represents the total absorption, and the thin line shows the contribution from the charge-transfer excitons. The broadening $\gamma = 0.108$eV is used.

Fig. 3. The ratio of the oscillator strengths (CT-component) of the charge-transfer excitons with respect to the total oscillator strengths in the C\textsubscript{60}-dimers. The closed squares are for the neutral cases and the open squares are for the one-electron (per C\textsubscript{60}) doped cases.

Fig. 4. The optical absorption spectra of C\textsubscript{60}-polymers for the neutral case with (a) $a = 0.2$ and (b) $a = 0.5$, and for the one-electron (per C\textsubscript{60}) doped case with (c) $a = 0.2$ and (d) $a = 0.5$. The bold line represents the total absorption, and the thin line shows the contribution from the charge-transfer excitons. The broadening $\gamma = 0.108$eV is used.

Fig. 5. The ratio of the oscillator strengths (CT-component) of the charge-transfer excitons with respect to the total oscillator strengths in the C\textsubscript{60}-
polymers. The closed squares are for the neutral cases and the open squares are for the one-electron (per C$_{60}$) doped cases.

Fig. 6. The ratio of the oscillator strengths (CT-component) of the charge-transfer excitons with respect to the total oscillator strengths in the neutral three molecule system.