

## Ring-bipolaron exciton in neutral fullerene C<sub>60</sub>

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Neutral fullerene C<sub>60</sub> is studied by the electron-lattice-coupling tight-binding model. When one or two electrons are excited from the highest occupied molecular orbital to the lowest unoccupied molecular orbital of a C<sub>60</sub> molecule, the lattice relaxes and the lowest-energy state of C<sub>60</sub> is discovered to be a ring-bipolaron exciton which is qualitatively consistent with the self-trapped polaron exciton observed in the luminescence experiment of neutral C<sub>60</sub>. The symmetry of optical excitation C<sub>60</sub> is reduced from *I<sub>h</sub>* to *D<sub>5d</sub>* and it is proposed that four NMR lines would be observed in this material.

Much attention has been focused on C<sub>60</sub> since Kroto *et al.*<sup>1</sup> conjectured the structure of a C<sub>60</sub> molecule, especially since Krätschmer *et al.*<sup>2</sup> found a method to produce large quantities of pure C<sub>60</sub>. Since then, many interesting characteristics of C<sub>60</sub> have been discovered. One of its most fascinating features is that C<sub>60</sub> becomes superconducting<sup>3</sup> when it is doped with alkali metals. From this discovery we get the enlightenment: What behavior C<sub>60</sub> will exhibit if it is excited by light. Based on this consideration, we study the effect of light excitation on neutral fullerene C<sub>60</sub>. Recently, Harigaya<sup>4</sup> calculated the optical-absorption coefficient for doped C<sub>60</sub>. This work explores the bond distortion and the nonlinear excited states of optical-excitation neutral C<sub>60</sub>.

Experiments show that the excitation stays on the C<sub>60</sub> molecule<sup>5</sup> at *T* > 100 K since the C<sub>60</sub> molecules rotate so rapidly that the overlap between  $\pi$  orbitals from neighboring molecules does not last long enough to transfer mechanical distortion, and the electron-lattice coupling is the main interaction of the C<sub>60</sub> molecule since there exists the dimerized structure<sup>6</sup> of long and short bonds for the ground state of the pristine C<sub>60</sub> molecule. Thus, we only consider the single C<sub>60</sub> molecule, and use the tight-binding model of electron-lattice coupling<sup>7</sup> to study our problem.

We only take into account the electron's hopping between adjacent atoms and neglect other hopping processes. The electronic Hamiltonian of a tight-binding model reads

$$H = - \sum_{i,j,s} t_{i,j}(|\mathbf{r}_i - \mathbf{r}_j|)(a_{i,s}^\dagger a_{j,s} + \text{H.c.}), \quad (1)$$

where *i* is the atomic indices *i* = 1, ..., 60, *j* is the nearest-neighbor atomic indices for the *i*th atom,  $a_{i,s}^\dagger$  and  $a_{i,s}$  are the creation and annihilation operators of an electron on site *i* with spin *s*,  $t_{i,j}(|\mathbf{r}_i - \mathbf{r}_j|)$  is the hopping probability. Since the difference between the long and short bond lengths is 0.04 Å, which is much smaller than bond length, we can expand  $t_{i,j}(|\mathbf{r}_i - \mathbf{r}_j|)$  with respect to distance and take only the linear term. Thus, the matrix elements in the electronic Hamiltonian are

$$t_{ij} = \begin{cases} t_0 - \alpha(|\mathbf{r}_i - \mathbf{r}_j| - d_0) & \text{nearest neighbor} \\ 0 & \text{otherwise,} \end{cases} \quad (2)$$

where  $\alpha$  is the electron-lattice-coupling constant.

The energy spectra  $\epsilon_\mu(\{\mathbf{r}_i\})$  and the wave function  $Z_{\mu,i}$  of the electrons are determined by the eigenequation of the electronic Hamiltonian (1),

$$- \sum_j [t_0 - \alpha(|\mathbf{r}_i - \mathbf{r}_j| - d_0)] Z_{\mu,j} = \epsilon_\mu Z_{\mu,i}. \quad (3)$$

Besides the electronic part,  $\frac{1}{2}K\frac{1}{2}\sum_{i,j}(|\mathbf{r}_i - \mathbf{r}_j|)^2$  (the lattice elastic energy) should also be taken into account. Hence, the total energy of the system is

$$E(\{\mathbf{r}_i\}) = \sum_{\mu}^{\text{occ}} \epsilon_\mu(\{\mathbf{r}_i\}) + \frac{1}{4}K \sum_{i,j} (|\mathbf{r}_i - \mathbf{r}_j| - d_0)^2. \quad (4)$$

We determine the lowest energy state by use of variational theorem:

$$\delta E(\{\mathbf{r}_i\}) / \delta \mathbf{r}_i = 0. \quad (5)$$

Solving these combined equations (3)–(5), we obtain self-consistently the electronic levels, atomic configuration, bond lengths, wave function, and total energy of a C<sub>60</sub> molecule at its lowest energy state which is procured after more than 10 000 iterations.

For the ground state of C<sub>60</sub>, with the parameters  $t_0 = 1.8$  eV,  $\alpha = 3.5$  eV/Å,  $K = 30.0$  eV/Å<sup>2</sup>, the length of a long bond is 1.432 Å, and that of a short bond is 1.395 Å; the separation between LUMO (the lowest unoccupied molecule orbit) level and HOMO (the highest occupied molecule orbit) is 1.83 eV. The x-ray experiments show that the long-bond and short-bond lengths for the C<sub>60</sub> molecule are 1.433 and 1.389 Å, respectively,<sup>6</sup> and the gap between LUMO and HOMO for the C<sub>60</sub> molecule is 1.9 eV.<sup>8</sup> Since the theoretical values are very close to the available experimental data, the above-state parameters are used in this work.

For optical excitation C<sub>60</sub>, our results show the following four characteristics.

(1) The lowest-energy state of C<sub>60</sub> is not the dimerized state after adding one or two electrons and holes. The total energy for the lowest-energy state (it is named the ex-

cited state in the following passage) of the system adding an electron and a hole into the ground state is 101 meV less than that of the rigid dimerized lattice adding an electron and a hole. If we add two electrons to the LUMO level and two holes to the HOMO level, the total energy of the new excited state is 400 meV less than that of the rigid dimerized state adding two electrons and holes.

(2) The variation of bond length is a ringlike polaron. The  $C_{60}$  molecule is a truncated icosahedron. When  $C_{60}$  is at the ground state, there exists only two different kinds of bonds: the five sides of its pentagon are long bonds, the bonds joined by two hexagons are short ones. The lengths of the long and short bond are 1.4316 and 1.3947 Å, respectively.

After adding an electron and a hole to  $C_{60}$ , the lattice relaxes due to the interaction of electron and lattice. After relaxation, there will exist seven different kinds of bond lengths; four of them are evolved from the original long bond and they are 1.4385, 1.4304, 1.4301, and 1.4107 Å, respectively. The other three bond lengths are evolved from the original short bond and they are 1.4148, 1.3977, and 1.3912 Å, respectively. The arrangement of these bond lengths is shockingly regular: If we take the opposite pentagons as north and south poles and name this direction as meridian, then the equator is perpendicular to the meridian. We can see that the same-length bonds are ring-arranged parallel to the equator in a different posture, whereas, along the meridian, these seven different bond lengths form 13 layers. The basic situation of adding two electrons and holes to  $C_{60}$  is similar to that of adding one electron and hole except for the larger variation of bond length.

We project  $C_{60}$  on a plane. The distribution of its bond length is shown in Fig. 1. The straight lines at the top and bottom in Fig. 1 represents the sides of the pentagon. The carbon atoms are on the vertex of the pentagon and the hexagon. From Fig. 1 we can see the bond structure is

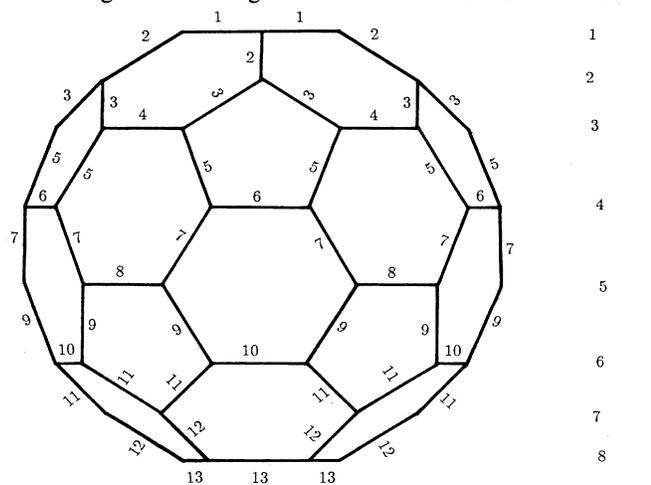


FIG. 1. The bond structure of  $C_{60}$  is projected on a flat surface. (The numbers in the figure denote the layer series of bonds along the meridian of  $C_{60}$ . Number seven layer is the equator. The same number corresponds to the bonds with the same length. The numbers to the right of the figure denote the layer series of carbon atoms.)

a laminar one with seven different bond lengths: the bonds of equal length are ring-arranged in the direction parallel to the equator, whereas, in the meridian direction, a long bond alternates with a short one and the distribution of bond length is in up-down symmetry with respect to the equator.

The physical reason for the variation of bond length is the instability of the low dimensional lattice. The lattice of the  $C_{60}$  molecule will be deformed by the action of the extra electron and hole because it has a two-dimensional spherical structure. The lattice deformation makes the original bond length contract or argument. Thus, the distribution of the bond length will differ from that at the ground state. Figure 2 shows the variation of the bond length for the excited state, compared with that of the ground state and in the meridian direction. From Figs. 1 and 2 we can see that the variation of the bond length has the characteristic of a definite even-parity polaron: being the largest in the equator area, nearly unchanged at the poles, and symmetric with respect to the equator. The bold line represents the result of adding an electron and a hole, the slender line is that of adding two electrons and holes. The bond-length variation of the latter is twice that of the former.

From the atomic positions of the excited state we have calculated, the symmetry of optical excitation  $C_{60}$  is a  $D_{5d}$  group. The ground state of  $C_{60}$  belongs to an  $I_h$  group. The symmetry reduction of optical excitation  $C_{60}$  is consistent with the result<sup>9</sup> of group theory analysis.

(3) The energy spectra have the characteristics of a polaron. The calculated energy levels and the representation of the groups  $I_h$  and  $D_{5d}$  are listed in Table I, where  $E_k^0$ ,  $E_k^1$ , and  $E_k^2$  are the energy levels of pristine  $C_{60}$  and  $C_{60}$  with one or two electron-hole pairs, respectively;  $k$  is the representation of the molecule orbit of the  $\pi$  electron;  $g_k$  is the degeneracy.

From Table I, we can see the following. (1) The original degenerate-energy levels split. The original fivefold-degenerate HOMO level splits into three separate levels,

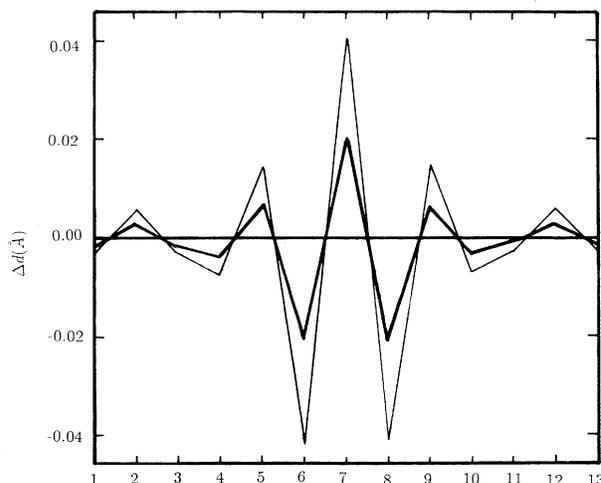


FIG. 2. The variation of bond length of the new excited states compared with the dimerized ground state. (The bold line represents the result of adding an electron and a hole, the slender line is that of adding two electrons and holes.)

and two of them are twofold degenerate and close to the original HOMO level; another nondegenerate level distinctly enters into the gap of the original ground state and we call this level  $E_A$ . The original triply degenerate LUMO level splits into two separate levels, and one of them is twofold degenerate and close to the original LUMO level; the other nondegenerate level distinctly enters into the gap of the original ground state and we call this level  $E_D$ . (2) When one electron-hole pair is added to the ground state,  $E_A$  is pulled up 0.148 eV, and there is a hole in this level;  $E_D$  is pulled down 0.123 eV, and there is an electron in this level. (3) When two electron-hole pairs are added to the ground state,  $E_A$  is pulled up 0.299 eV, and there are two holes with up and down spin in this level;  $E_D$  is pulled down 0.252 eV, and there are two electrons with up and down spins in this level. (4) Except for  $E_A$  and  $E_D$ , other energy levels are

TABLE I. The energy levels of  $C_{60}$  before and after it is excited by light.

$I_h$ (pristine $C_{60}$ )			$D_{5d}$ (after $C_{60}$ is excited by light)			
$e, 12C_5, 12C_5^2, 20C_3, 15C_2$			$e, 2C_5, 2C_5^2, 5C_2$			
$i, 12S_{10}, 12S_{10}^3, 10S_3, 15\sigma$			$i, 2S_{10}^3, 2S_{10}, 5\sigma_d$			
$E_k^0$ (eV)	$k$	$g_k$	$E_k^1$ (eV)	$E_k^2$ (eV)	$k$	$g_k$
-6.668	$A_g$	1	-6.657	-6.647	$A_{1g}$	1
-6.125	$T_{1u}$	3	-6.129	-6.134	$A_{2u}$	1
			-6.109	-6.093	$E_{1u}$	2
-5.111	$H_g$	5	-5.119	-5.128	$E_{1g}$	2
			-5.110	-5.108	$A_{1g}$	1
			-5.088	-5.064	$E_{2g}$	2
-3.985	$T_{2u}$	3	-4.003	-4.021	$A_{2u}$	1
			-3.998	-3.993	$E_{2u}$	2
-3.529	$G_u$	4	-3.532	-3.536	$E_{1u}$	2
			-3.489	-3.448	$E_{2u}$	2
-2.267	$G_g$	4	-2.295	-2.326	$E_{1g}$	2
			-2.256	-2.285	$E_{2g}$	2
-2.224	$H_g$	5	-2.253	-2.268	$A_{1g}$	1
			-2.212	-2.198	$E_{1g}$	2
			-2.169	-2.095	$E_{2g}$	2
-1.407	$H_u$	5	-1.430	-1.454	$E_{1u}$	2
(HOMO)			-1.425	-1.443	$E_{2u}$	2
			-1.227( $E_A$ )	-1.144( $E_A$ )	$A_{1u}$	1
0.419	$T_{1u}$	3	0.311( $E_D$ )	0.199( $E_D$ )	$A_{2u}$	1
(LUMO)			0.434	0.451	$E_{1u}$	2
0.962	$T_{1g}$	3	0.906	0.852	$E_{1g}$	2
			0.993	1.027	$A_{2g}$	1
2.847	$H_g$	5	2.839	2.832	$A_{1g}$	1
			2.845	2.844	$E_{1g}$	2
			2.869	2.892	$E_{2g}$	2
3.152	$T_{2u}$	3	3.117	3.084	$A_{2u}$	1
			3.178	3.204	$E_{2u}$	2
3.587	$H_u$	5	3.561	3.536	$E_{1u}$	2
			3.592	3.597	$E_{2u}$	2
			3.612	3.637	$A_{1u}$	1
4.446	$G_g$	4	4.436	4.425	$E_{1g}$	2
			4.443	4.442	$E_{2g}$	2
5.708	$G_u$	4	5.690	5.670	$E_{1u}$	2
			5.703	5.698	$E_{2u}$	2
5.835	$T_{2g}$	3	5.819	5.800	$A_{2g}$	1
			5.825	5.815	$E_{2g}$	2

very close to the corresponding levels for the ground state.

$\psi_A$  and  $\psi_D$ , as shown in Figs. 3 and 4, are the wave functions corresponding to  $E_A$  and  $E_D$ . In these figures, the numerical values of the amplitude for the wave function are given on every lattice point. Comparing with the wave functions corresponding to the other levels, we can see that  $\psi_A$  and  $\psi_D$  have the following features. (1) These two states are localized near the equator area. The maximum values of  $\psi_A$  and  $\psi_D$  are near the equator area. This represents that the electrons and holes bound on  $E_A$  and  $E_D$  levels appear mainly near the equator area since the square of the wave-function amplitude is directly proportional to the probability of particles. (2) Wave functions  $\psi_A$  and  $\psi_D$  have the same laminar distribution as bonds do.

$\psi_A$  and  $\psi_D$  are not present at the ground state. From the ground state to the excited state, the lattice deforms. The distorted lattice makes the bond structure vary from a dimerized structure to a laminar one, and two localized states appear in the gap. Furthermore, these two states have laminar structures too. These facts vigorously indicate these two localized states are the self-trapping bound states induced from laminar-bond deformation.

This is similar to the self-trapping bound states induced by an electron in ionic crystals. When electrons move in an ionic crystal, electrons attract positive ions and exclude anions, thus polarization occurs.<sup>10</sup> As a result, the lattice near the electron deforms. The distorted lattice will induce a localized deformation potential. Meanwhile, the electrons in this localized strain field form a localized electron bound state. The electron in this bound state and its polarized strain field form a combined particle, known as a polaron. In brief, it is the electron's "self-trapping bound state," i.e., the electron-induced ion-lattice deformation, which in turn traps this electron.

The situation for  $C_{60}$  excited by light is very similar to

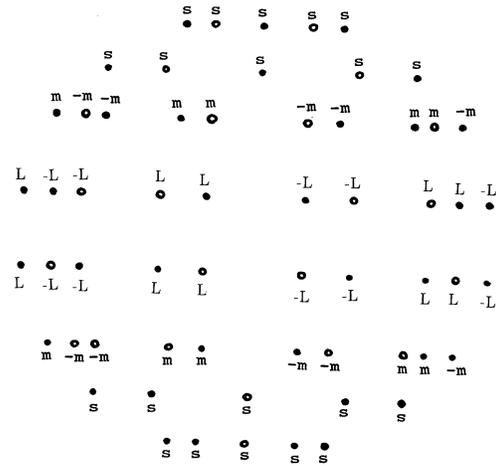


FIG. 3. The wave function  $\psi_A$  corresponding to the  $E_A$  energy level. (The dots denote the atoms on the front side of the ball, the circles denote the atoms on the back side of the ball. Adding an electron-hole pair:  $L=0.1918$ ,  $m=0.1149$ ,  $s=0$ ; adding two electron-hole pairs:  $L=0.1907$ ,  $m=0.1167$ ,  $s=0$ .)

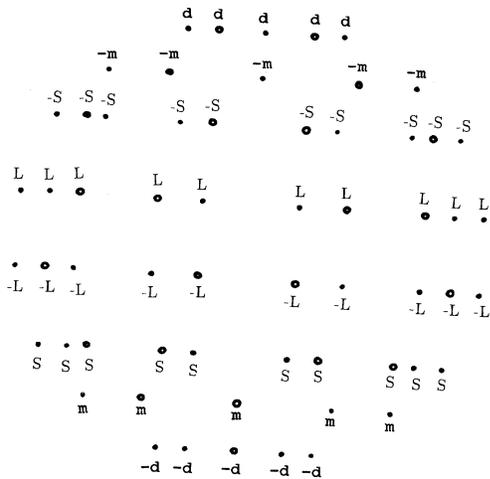


FIG. 4. The wave function  $\psi_D$  corresponding to the  $E_D$  energy level. (The dots denote the atoms on the front side of the ball, the circles denote the atoms on the back side of the ball. Adding an electron-hole pair:  $L=0.1873$ ,  $m=0.1508$ ,  $s=0.0741$ ,  $d=0.0282$ ; adding two electron-hole pairs:  $L=0.1885$ ,  $m=0.1467$ ,  $s=0.0733$ ,  $d=0.0317$ .)

the polaron stated above. The interaction among electrons, holes, and ions in lattice points makes the dimerized lattice deform in the local part. An electron hole forms the localized self-trapping bound state in this local-deformed potential. Hence, two localized levels appear in the gap. This physical process is very similar to the formation of a polaron in an ionic crystal.

(4) The new excited state is a ring-bipolaron exciton. The polaron in an ionic crystal is a single-charge polaron, which in  $C_{60}$  excited by light is an electron-hole polaron, which is the quasiparticle of electron + hole + lattice deformation. It is named a bipolaron.<sup>11</sup> In ionic crystals or conducting polymers,<sup>11</sup> the polaron or the self-trapping bound state is localized around a point, whereas the self-trapping bound states of a bipolaron in  $C_{60}$  are localized on the equator area (not a point). In addition, both the electron and hole located in these two bound states are situated on the same area of real space and close to each other, they can form the bound-state exciton; thus the energy of the system can be lowered further. This kind of exciton is a nonlinear exciton because the atom positions are changed during the process of its formation. Besides, the distribution of the bond length for the new excited state of  $C_{60}$  has a ringlike laminar structure: The same-

length bonds are arranged in the same layer parallel to the equator, and in the meridian direction, the bond-length distribution is polaronlike. To indicate the above-stated characteristics of the new excited state of  $C_{60}$ , we name the new excited state of  $C_{60}$  ring-bipolaron exciton.

The present calculation is in agreement with the photoluminescence measurement,<sup>5</sup> which indicates that a self-trapped polaron exciton is an appealing structure to describe the luminescence behavior of neutral fullerene  $C_{60}$  excited with light in a satisfying way. Furthermore, we suggest that the ring-bipolaron exciton with an electron-hole pair might correspond to the main peak in Ref. 5, and that with two electron-hole pairs might correspond to the low-energy sideband.

We also suggest there exists the other observable effect in a ring-bipolaron exciton. At the ground state of pristine  $C_{60}$ , all the 60 carbon atoms are equivalent, and the NMR spectrum has only one line.<sup>12</sup> From Fig. 1 we can see that 60 carbon atoms in a ring-bipolaron exciton are divided into eight layers. They are symmetric with respect to the equator. The atoms in the first and eighth layers are equivalent, there are ten atoms. Similarly, the atoms in the second and seventh, the third and sixth, the fourth and fifth layers are equivalent, respectively, and there are 10, 20, and 20 atoms, respectively. The symmetry determines that the atoms in the same group are equivalent, and those in different groups are nonequivalent. Thus, there will exist four different kinds of carbon atoms and the original one NMR line will split into four sublines. The strength ratio of them is 1:1:2:2, which is determined by the atom number of each group. Hence, this suggests that the ring-bipolaron exciton in  $C_{60}$  excited by light can be observed in the NMR spectrum.

The major results of this calculation can be summarized as follows: The configuration of carbon atoms, the bond structure, electronic spectra, and total energy of optical-excitation  $C_{60}$  are studied within the electron-lattice-coupling tight-binding approach. The lowest energy state of optical-excitation  $C_{60}$  is discovered to be a ring-bipolaron exciton and its symmetry is reduced from  $I_h$  to  $D_{5d}$ . This finding is qualitatively consistent with the luminescence experiment of neutral  $C_{60}$ . It can also be observed in the NMR spectrum; the validity of this prediction remains to be justified by experiments.

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