EFFECTS OF e-e INTERACTION ON LATTICE DISTORTIONS AND ELECTRONIC STRUCTURES OF ELECTRON OR HOLE DOPED C_{60}

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ABSTRACT

The Su-Schrieffer-Heeger Hamiltonian and the Hubbard Hamiltonian within the unrestricted Hartree-Fock scheme have been used to study the effects of e-e interaction on lattice distortions and electronic structures of C_{60}^{-}, C_{60}^{2-}, C_{60}^{+}, C_{60}^{2+}. When the interaction parameter increases from 0 to 3 eV, the bond variables of the C_{60} molecules are altered slightly, but the polaron energy levels and the charge density distributions of the C_{60} molecules are modified seriously.

Keywords C_{60}, Polaron, e-e interaction

1 INTRODUCTION

The soccerball-shaped buckminsterfullerene molecule C_{60} has attracted much attention recently. Because of the conjugated character of bonds, C_{60} molecule is similar to polyacetylene in many ways. Undoped C_{60} is dimerized, the 60 bonds forming the pentagons are long and other 30 bonds are short; doped with electron or hole, the electronic structures and lattice distortions which can be analyzed with Jahn-Teller distortions[1], are similar to those of polaron in polyacetylene. Matus *et al* [2] elucidated the self-trapped polaron excitation from the luminescence of C_{60}. Harigaya[3] and Friedman[4] calculated the lattice and electronic structures of undoped and doped C_{60} molecules by using the eminent Su-Schrieffer-Heeger(SSH)[5] model, which described conducting polymer successfully. But the electron-electron interaction, which may play important role in the superconductivity of potassium-doped C_{60} crystal[6], is not considered in the calculations of the polaron levels and charge density distributions of electron and hole doped C_{60} molecules.

The Hubbard model is one of the simplest Hamiltonians for studying a strongly correlated electron system and is considered as a possible candidate to describe high-T_c superconductivity. In this paper, starting with the SSH Hamiltonian and the Hubbard Hamiltonian, we explored the effects of electron-electron interaction on the lattice distorations and electronic structures of C_{60}^{-}, C_{60}^{2-}, C_{60}^{+} and C_{60}^{2+} within unrestricted Hartree-Fock (HF) scheme.

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2 FORMULATION

The Hamiltonian used is the sum of two parts:

$$H_0 = \sum_{<i,j>,s} (-t_0 - \alpha Y_{<i,j>})(C_{i,s}^{+} C_{j,s} + H.c.) + (K/2) \sum_{<i,j>} Y_{i,j}^2 \tag{1}$$

and

$$H_{\mathrm{e-e}} = (U/2) \sum_{i,s} (C_{i,s}^{+} \cdot C_{i,s} C_{i,-s}^{+} \cdot C_{i,-s}) \tag{2}$$

Here, H_0 is the extended SSH Hamiltonian. $C_{i,s}^{+}$ and $C_{i,s}$ are the creation and annihilation operators for a π electron with spin s at i-th site, respectively. $Y_{i,j}$ is the change of the bond length between the i- and j-th atoms, t_0 the nearest-neighbor transfer integral which corresponding to undimerized C_{60}, α the electron-phonon displacement constant, and k the spring constant. The Hubbard Hamiltonian $H_{\mathrm{e-e}}$ is used to describe the on-site repulsion between electrons of C_{60} molecules doped with electron or hole. The value of U represents an effective on-site interaction strength.

The single-electron Hamiltonian is chosen as:

$$H^{HF} = \sum_{<i,j>,s} (-t_0 - \alpha Y_{i,j})(C_{i,s}^{+} C_{j,s} + H.c.) + U \sum_{i,s} (X_{i,-s} C_{i,s}^{+} C_{i,s}) \tag{3}$$

Where $X_{i,-s}$ is the self-consistent ground state average of electron which occupied at i-th site with spin -s. Let $\epsilon_{k,s}$ and $\psi_{k,s}$ be the eigenvalues and eigenfunctions of the HF Hamiltonian, and let $\psi_{k,s}(i)$ be the coefficient of the π orbital centered on the i-th atom in the linear-combination-of-atomic-orbitals(LCAO) expansion of $\psi_{k,s}$, one gets the equations for π electrons

$$\epsilon_{k,s}\psi_{k,s}(i) = \sum_{j} (-t_0 - \alpha Y_{i,j}) \psi_{k,s}(j) + U X_{i,-s} \psi_{k,s}(i) \tag{4}$$

and

$$X_{i,-s} = \sum_{k,s}^{\mathrm{Occ}} \psi_{k,-s}(i) \psi_{k,-s}(i) \tag{5}$$

The equations for different spins are performed separately. From the constraint

$$\sum_{<i,j>} Y_{i,j} = 0 \tag{6}$$

one gets the equations for lattice

$$Y_{i,j} = (2\alpha/K) \sum_{k,s}^{\mathrm{Occ}} \psi_{k,s}(i) \psi_{k,s}(j) - [2\alpha/(KN_b)] \sum_{<m,l>} \sum_{k,s}^{\mathrm{Occ}} \psi_{k,s}(m) \psi_{k,s}(l) \tag{7}$$

and the total energy in the HF ground state

$$E_i = \sum_{k,s}^{\mathrm{Occ}} \epsilon_{k,s} - (U/2)\sum_{i,s} X_{i,s}X_{i,-s} + (K/2)\sum_{<i,j>} Y_{i,j}^2 \tag{8}$$

where $N_b = 90$, is the number of π bonds in C_{60}. In the calculation, the iteration times depend on the initial values of $Y_{i,j}$ and the value of U seriously. For an arbitrary U and a given set $Y_{i,j}$, we are performing the calculation till the (n+1)-th iteration of the self-consistent average of electron occupancy at each site of 60 carbon atoms satisfies $|(X_{i,s})_{n+1} - (X_{i,s})_n| < 10^{-10}$, then we get next set $Y_{i,j}$ from the left-hand side of Eq.(7). The iteration is repeated at least 300 times, till the sum of $\sum[(Y_{i,j})_{n+1} - (Y_{i,j})_n]^2$ becomes negligibly small. The total energy of the C_{60} molecule will be a minimum if the electronic energy levels and lattice structures of the system are the solutions of the above self-consistent equations.

3 RESULTS AND DISCUSSION

We use the parameter values t_0 =2.5 eV, α = 63.1 eV/nm and K = 4970 eV/nm^2. These values are given by Harigaya[3], and consistent with the observed experimentally length difference between the short and long bonds[7]. The value of the interaction parameter of Hubbard repulsion U is uncertain[8]. In the calculation, U is chosen as 1,2 and 3 eV, respectively. If U is large enough, the numerical solution of the iteration equations will be very complicated. However, when electron-electron interaction is dominant and the electron-phonon interaction in the SSH Hamiltonian can be ignored, it will not difficult to get the solution.

First, the effects of e-e interaction on the electronic energy levels is studied. Undoped C_{60} is dimerized, the energy levels are obtained from the SSH model irrespective of e-e interaction. The energy gap between the fivefold-degenerate highest occupied molecular orbital (HOMO) and the threefold-degenerate lowest unoccupied molecular orbital (LUMO) is 2.25526 eV. Doped with electron or hole, ϵ_{30} and ϵ_{31} will decoulpe from the HOMO and LUMO respectively, and form the polaron energy levels. The e-e interaction will change the electronic level structures, especially for the polaron levels. Because the energy levels around the Fermi surface of C_{60} depend on the strength of the electron-phonon interaction severely, thus, in this paper, we pay more attention to the energy levels around the polaron levels. The gaps of the energy levels around the polaron levels for C_{60}^-, C_{60}^{2-}, C_{60}^+ and C_{60}^{2+} are given in Table 1. For one electron with spin up doped C_{60}, the electron will add to $\psi_{31,\uparrow}$ and the polaron carrys one negative charge with spin up. If $U = 0$, all the energy levels of C_{60}^- are degenerate with spin; if $U \not\equiv 0$, the spin-up and spin-down energy levels are nondegenerate. It can be seen that the gaps of the energy levels with spin up and down split rapidly, nearly in proportion as U. The value of $\epsilon_{31,\uparrow}$ -$\epsilon_{31,\downarrow}$ increases from 0 to 0.1 eV when U increases from 0 to 3 eV, while the gaps between $\epsilon_{32,\uparrow}$ and $\epsilon_{31,\uparrow}$, $\epsilon_{31,\uparrow}$ and $\epsilon_{30,\uparrow}$, $\epsilon_{30,\uparrow}$ and $\epsilon_{29,\uparrow}$ are modified smoothly. If the effect of electron-phonon interaction is neglected, the split values of the energy levels with spin up and down will be equal and proportional to U. Added another electron with spin down to the C_{60}^- molecule, we will get a negative bipolaron which carries two negative charges without spin. Although the e-e repulsion does not affect the degeneracy of spin, the gaps for different energy levels are modified when U varies. For one hole with spin up doped pristine C_{60}, the electron in $\epsilon_{30,\downarrow}$ will be removed, and the polaron take one positive charge with spin up. As in C_{60}^-, the polaron levels of C_{60}^+ with spin-up and spin down split seriously when U varies. Taking another electron from $\epsilon_{30,\uparrow}$, we will get a polaron with two positive charges. As in C_{60}^+, the energy level of C_{60}^{2+} between ϵ_{30} and ϵ_{29} decrease when U increases. From the above calculation, it is not difficult to find that the e-e interaction modifies the polaron levels of single electron or hole doped C_{60} severely. Since the C_{60}^+ ions have been largely produced in accelerators, we suggest that the value U may be obtained from the optical absorption of these pure C_{60}^+ ions.

Table 1

The gaps of the energy levels around the polaron levels for C_{60}^-, C_{60}^{2-}, C_{60}^+ and C_{60}^{2+} eV

	U/ev	0	1	2	3
C_{60}^-	$\epsilon_{32,\uparrow}-\epsilon_{31,\uparrow}$	0.11665	0.11794	0.12143	0.12731
	$\epsilon_{31,\uparrow}-\epsilon_{30,\uparrow}$	1.99877	1.99811	1.99678	1.99470
	$\epsilon_{30,\uparrow}-\epsilon_{29,\uparrow}$	0.13829	0.13763	0.13499	0.13020
	$\epsilon_{32,\uparrow}-\epsilon_{32,\downarrow}$	0	-0.00957	-0.01822	-0.02573
	$\epsilon_{31,\uparrow}-\epsilon_{31,\downarrow}$	0	-0.03087	-0.06351	-0.09838
	$\epsilon_{30,\uparrow}-\epsilon_{30,\downarrow}$	0	-0.02710	-0.05497	-0.08376
	$\epsilon_{29,\uparrow}-\epsilon_{29,\downarrow}$	0	-0.01499	-0.03338	-0.05100
C_{60}^{2-}	$\epsilon_{32}-\epsilon_{31}$	0.24146	0.22251	0.20522	0.18938
	$\epsilon_{31}-\epsilon_{30}$	1.73122	1.73406	1.73657	1.73880
	$\epsilon_{30}-\epsilon_{29}$	0.28371	0.30139	0.30826	0.31476
C_{60}^+	$\epsilon_{31,\uparrow}-\epsilon_{30,\uparrow}$	1.95448	1.95883	1.96319	1.96760
	$\epsilon_{30,\uparrow}-\epsilon_{29,\uparrow}$	0.20220	0.18298	0.16349	0.14357
	$\epsilon_{31,\uparrow}-\epsilon_{31,\downarrow}$	0	-0.02759	-0.05612	-0.08572
	$\epsilon_{30,\uparrow}-\epsilon_{30,\downarrow}$	0	-0.03231	-0.06573	-0.10038
	$\epsilon_{29,\uparrow}-\epsilon_{29,\downarrow}$	0	-0.01244	-0.02436	-0.03568
C_{60}^{2+}	$\epsilon_{31}-\epsilon_{30}$	1.64698	1.64934	1.65164	1.65386
	$\epsilon_{30}-\epsilon_{29}$	0.40750	0.38928	0.37202	0.35567

Second we explored the effects of e-e interaction on the lattice distortions of doped C_{60} molecules. For the pristine C_{60} molecule, the sixty sites of carbon atoms are equivalent, the average of electron which occupied at each site with spin up or down is 0.5. If electron or hole is added, the lattice will deform and the 60 vertexs will be divided into 4 groups, labelled as A, B, C and D, the sites in each groups are still equivalent. In group A, there are ten sites which belong to the two pentagons at top and bottom of C_{60}; In group B, there are other 10 sites which are the nearest-neighbor of sites in group A; In group C, there are 20 sites which are the nearest-neighbor of sites in group B (the other 10 nearest-neighbor sites have been included in group A); The left 20 sites are indicated as group D. The 90 bonds which connected the sites from A to D can be divided into 7 groups, labelled as *a* to *g* respectively. It can be seen from Table 2 that the electron-electron interaction has little effect on the bond variable. However, the charge density distribution is altered severely when U increases from 0 to 3 eV. The excess electron density per site of C_{60}^{-}, C_{60}^{2-}, C_{60}^{+} and C_{60}^{2+} are given in Table 3, where the excess electron density at i-th site is calculated through $[X_{i,\uparrow} + X_{i,\downarrow} - 1]$. It can be seen that the charge density distribution tends to be equal. For C_{60}^{-}, the excess electron density of sites in group A and C increase seriously, while sites in group B and D decrease step by step; for C_{60}^{+}, the excess electron density of sites in group D increase, while sites in group A, B and C decrease; for C_{60}^{2-} and C_{60}^{2+}, the excess electron densities at each group are nearly twice as much as those in C_{60}^{-} and C_{60}^{+}, respectively. The result that the charge density distribution tends to be same is due to the simple reason that the increase of e-e interaction cancel the effect of electron-phonon interaction on charge distributions, and

Table 2

The bond variables for C_{60}^{-} nm

U/eV	0	1	2	3
a[10]	-0.001444	-0.001440	-0.001437	-0.001434
b[10]	0.002948	0.002946	0.002943	0.002940
c[20]	-0.001499	-0.001498	-0.001497	-0.001496
d[10]	0.003275	0.003275	0.003275	0.003274
e[20]	-0.001744	-0.001747	-0.001749	-0.001752
f[10]	0.002034	0.002036	0.002038	0.002040
g[10]	-0.000328	-0.000327	-0.000326	-0.000326

The values in the square brackets denote the number of bonds in each group

Table 3

The excess electron density per site for each group of C_{60}^{-}, ${}_{60}^{2-}$, C_{60}^{+} and C_{60}^{2+}

U/ev		0	1	2	3
C_{60}^{-}	A	0.00475	0.00547	0.00610	0.00664
	B	0.02226	0.02139	0.02066	0.02006
	C	0.00145	0.00229	0.00305	0.00373
	D	0.03504	0.03427	0.03357	0.03292
C_{60}^{2-}	A	0.00923	0.01056	0.01172	0.01273
	B	0.04248	0.04097	0.03973	0.03870
	C	0.00335	0.00498	0.00641	0.00776
	D	0.07080	0.06926	0.06783	0.06653
C_{60}^{+}	A	-0.00108	-0.00160	-0.00209	-0.00254
	B	-0.00059	-0.00092	-0.00125	-0.00158
	C	-0.01099	-0.01128	-0.01154	-0.01178
	D	-0.03817	-0.03746	-0.03679	-0.03616
C_{60}^{2+}	A	-0.00214	-0.00320	-0.00418	-0.00507
	B	-0.00122	-0.00187	-0.00252	-0.00316
	C	-0.02267	-0.02304	-0.02339	-0.02371
	D	-0.07565	-0.07442	-0.07326	-0.07217

when the electron-electron interaction is once dominant, the excess electron density at each sites is same, even though the 60 sites are not equivalent.

In conclusion, the on-site electron-electron interaction plays important role in electron and hole doped C_{60}, it alters the length of the bonds slightly, while modifies the polaron levels and charge density distributions seriously.

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