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Structural and electronic properties of C_{59}X (X=B,N):
The extended Su-Schrieffer-Heeger model

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The molecules C_{59}X (X=B,N) are investigated by the extended Su-Schrieffer-Heeger model. The obtained results for the energy levels and molecular structures are compared with those from a self-consistent-field molecular-orbital (SCF-MO) method. We have found that by choosing suitable empirical parameters, most of the features included in the results of the SCF-MO method can be well reproduced. Other structural and electronic properties such as the excess electron density and the amplitude of the midgap states have also been studied.

Recently, the doped C_{60} has stimulated a great interest of researchers in physics and chemistry to investigate its structural, electronic, optical, and other properties. This is because it not only exhibits rather strong nonlinear optical properties but also because alkali ion doped C_{60} crystals become superconducting at a critical temperature T_c = 18 K for K_3C_{60} (Ref. 8) and 28 K for Rb_3C_{60}, which leads to a great effort to dope different kinds of atoms into the C_{60}, in efforts to find C_{60} samples with higher T_c superconductors. Experimental observations indicate that the lattice and electronic structures of C_{60} change with doping. Besides the alkali metal doping, there is also another type of doping, i.e., substituting one or more carbon atoms of the C_{60} molecule by other atoms. For example, boron and nitrogen atoms have been successfully used to replace carbon atoms of the C_{60} molecule, which led to synthesis of many kinds of modified C_{60} molecules: C_{60-n}\_m\_X_m\_Y_n, where X, Y represent the B, N, or other possible substitute atoms and n, m range from zero to a possible maximum value (≤ 3). Although this new type of substituted fullerenes may not be a kind of superconductor with higher T_c, since their band gaps and electronic polarizations can vary much with different substitute dopings, they might attain a potential application as semiconductor components and possible building materials for nanometer electronics. Therefore, it is interesting and useful to investigate experimentally and theoretically their structural and electronic properties from the viewpoint of practical applications.

Theoretically, quantum molecular dynamics has been used to study stable structure of C_{59}B and C_{59}N, and also the molecular cluster calculations has been made for C_{58}B_2 and C_{58}N_2. More recently, Kurita et al., used the molecular-orbital method with Harris-functional and spin-restricted approximations to calculate molecular structures and electronic properties of C_{59}X (X=B, N, and S), as well as C_{58}B_2 and C_{58}N_2. Their results show that the substitute dopings of the C_{60} with B and N change significantly their energy levels near the Fermi level and the corresponding band gaps between the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO), although their structure and binding energies are almost unchanged. On the other hand, it is well known that the Su-Schrieffer-Heeger (SSH) model proposed originally for the polyacetylene was applied successfully in the study of conducting polymer in the past decade and has also been extended to describe the pure and non-substitute doped C_{60} systems satisfactorily. Thus, it is natural to ask if the extended SSH model can be employed to study the substituted fullerenes C_{60-n}\_X_n and to get a reasonable result which is consistent with, or at least compatible with, those obtained by the self-consistent-field molecular-orbital (SCF-MO) method. If it is the case, the advantage is obvious because the extended SSH model is simple and contains only three adjustable empirical parameters, which will significantly reduce complexity and computing time needed in the numerical calculation. In this paper we will perform a numerical calculation on the single substituted molecules C_{59}X by using the extended SSH model and justify such simple model is indeed suitable for that.

The extended SSH model for C_{60} molecule can be written as

\[ H = \sum_{ij} [-t_0 - \alpha_0 Y_{ij}] (c_{ij}^\dagger c_{ij} + H.c.) + \frac{K_0}{2} \sum_{ij} y_{ij}^2, \]  

where \( c_{ij}^\dagger \) and \( c_{ij} \) are, respectively, the usual creation and annihilation operators of a \( \pi \) electron at the \( ij \)th carbon atom with spin \( s \); \( t_0 \) is the hopping integral of the undimerized system; \( \alpha_0 \) is the coupling constant between electron and phonon, and \( y_{ij} \) is the change of the bond length between the \( i \)th and \( j \)th atoms. The sum over \( \langle ij \rangle \) is taken over nearest-neighbor pair sites \( \langle ij \rangle \). The last term is the elastic energy of the phonon system with the \( K_0 \) as the spring constant. Notice that Eq. (1) is applied only to the pure C_{60} system. In fact, it should be modified to include the effect of the dopant ions in the...
TABLE I. The energy gaps between LUMO and HOMO and the maximum atomic distortions from the C_{60} calculated with SCF-MO method and SSH model.

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<th>SCF-MO</th>
<th>SSH</th>
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<td></td>
<td>C_{59}B</td>
<td>C_{59}N</td>
</tr>
<tr>
<td>HOMO-LUMO gaps (eV)</td>
<td>1.06</td>
<td>0.30</td>
</tr>
<tr>
<td>The maximum atomic distortion from the C_{60} (Å)</td>
<td>0.07</td>
<td>0.06</td>
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Here \( N (= 90) \) is the number of \( \pi \) bonds. The coupled equations (3) and (5) can be solved iteratively, and final result should be independent of choosing the different initial values of the set \( y_{ij} \).

In the numerical calculation, we take \( t_1 = 1.025 \) eV, \( \alpha_1 = 5.8 \) eV/Å, and \( K_1 = 49 \) eV/Å² for C_{59}B and \( t_1 = 0.95 \) eV, \( \alpha_1 = 6.0 \) eV/Å, and \( K_1 = 48 \) eV/Å² for C_{59}N. The numerical results for the band gaps between LUMO and HOMO, and the maximum atomic distortions from the C_{60} structure are presented in Table I and compared with those obtained by the SCF-MO method.\(^{12,15}\) We can see from Table I that the extended SSH model with appropriately chosen parameters for the substitute impurity atoms is able to accurately reproduce the results calculated with the SCF-MO method.\(^{12,15}\)

The total energies of the molecules and the excess electron densities at and around the positions of substitute impurity atoms (B or N) are listed in Table II. It is found that both C_{59}B and C_{59}N have nearly the same total energy, which means that they are equally stable. The excess electron density of the B atom is \(-0.564\) but that of N is 0.27, which implies that electron deficiency is produced at the doped B atom site and the B atom gives up its electronic charge to its neighbors and exists as a donor. Obviously, electronic charge accumulates on the doped N site and the N atom exists as an acceptor. The signs of excess electron density for the B and N atoms are different, which makes C_{59}B and C_{59}N have opposite electronic polarization. This conclusion is well consistent with the SCF-MO calculation\(^{12,15}\) as well as the experimental observation.\(^{11}\)

The energy levels near the Fermi level for C_{59}B and C_{59}N are shown in Fig. 1. They are quite different as expected because in C_{59}B one hole is doped in the HOMO of C_{60}, while in C_{59}N one electron is doped into the LUMO of C_{60}. Obviously, these substitute dopings destroy the special icosahedral symmetry of the C_{60} molecule and make the energy degeneracy much reduced. For example, the highest occupied level in C_{59}B splits

\[\varepsilon_k Z_{ks}(i) = \sum_{n=0,1} \sum_{(ij)}^{(n)} (-t_n - \alpha_n y_{ij}) Z_{ks}(j), \quad (3)\]

where \( \varepsilon_k \) is the eigenvalue of the \( k \)th eigenstate and the \( Z_{ks} \) is the electronic wave function. The total energy of the molecule C_{59}X is a functional of the set of \( y_{ij} \).

\[E_T(y_{ij}) = \sum_k \varepsilon_k + \sum_{n=0,1} \sum_{(ij)}^{(n)} (K_n/2)y_{ij}^2, \quad (4)\]

where the first sum with a prime runs over only the occupied states. Minimizing the total energy \( E_T \) over \( y_{ij} \) and using the constraint condition \( \sum_{n=0,1} \sum_{(ij)} y_{ij} = 0 \), we are able to obtain the self-consistency equations for \( y_{ij} \)

\[y_{ij}^{(n)} = \frac{2\alpha_n}{K_n} \sum_{k,s} Z_{ks}(i) Z_{ks}(j) - \Delta y, \quad (5)\]

with \( n = 0 \) for C-C bonds and \( n = 1 \) for X-C bonds, where

\[\Delta y = \frac{1}{N} \sum_{n=0,1} \sum_{(ij)}^{(n)} \left( \frac{2\alpha_n}{K_n} \right) \sum_{k,s} Z_{ks}(i) Z_{ks}(j). \quad (6)\]
from other HOMO of C$_{60}$ and becomes nondegenerate. Its energy shifts upward about 0.9 eV. Similarly, in C$_{59}$N the original threefold degenerate LUMO of C$_{60}$ splits into one singlet and a twofold degenerate levels with the singlet being half-occupied and shifting downward from the twofold degenerate levels about 0.30 eV. Therefore, the band gaps between the half-filled levels and the LUMO levels of C$_{59}$X will be able to vary greatly with different substituted impurity atoms (here, the gaps for X=B, N are equal to 1.06 eV and 0.30 eV, respectively). Thus, there exists a possibility to produce the semiconductor components using the C$_{60-n}$X$_n$ (X=B, N, or others) with various band gaps. We should emphasize here that by adjusting two parameters $t_1$ and $\alpha_1$ (among them the effect of $t_1$ is stronger) the calculated band gaps in the framework of the extended SSH model are well consistent with the results of the SCF-MO method.\cite{12,16} However, there are some differences. For example, in our calculation, the energy difference between the half-filled level and the other four degenerate HOMO levels for C$_{59}$B is about 0.9 eV, in contrast with the value $\sim$ 0.4 eV calculated by the SCF-MO method.\cite{12,15} Of course, we are

**FIG. 1.** Energy level structures of the molecules (a) C$_{59}$N and (b) C$_{59}$B. The energy levels with differences between each other being less than 0.02 eV are regarded as degenerated.

**FIG. 2.** The distribution function $D(y_{ij})$ of the bond variables for (a) C$_{59}$N and (b) C$_{59}$B.

**FIG. 3.** The site-occupying probability of the HOMO state for molecules (a) C$_{59}$N and (b) C$_{59}$B.
able to make the value become smaller and closer to that
obtained by the SCF-MO method, but in the meantime
the difference between the band gaps obtained respec-
tively by the two methods will become bigger. Therefore,
which one is better could not be determined up to this
step, and the question is left to be answered by future
experiments, e.g., spectroscopy observations.

In C$_{59}$X, the difference between the lengths of short
and long bonds becomes the smallest along an equa-
torial line of C$_{60}$, which is the same as that in the
usual doped C$_{60}$ system (e.g., C$_{60}^{-}$). The lattice structure
of C$_{59}$X is different from that of pure C$_{60}$ due to effects
of the dopant ion, but the deformations of the substi-
tuted fullerene cage for the C$_{59}$X are mainly limited in
the vicinity of the dopant ions. The distribution func-
tions $D(y_{ij})$ of the bond variables are shown in Fig. 2,
in which a two-peak structure indicates the presence of
the dimerization. The narrow peaks in the negative $y_{ij}$
region correspond to the distortion part around the im-
purity ions. The area of the extended portion for C$_{59}$B
is greater than that for C$_{59}$N, which indicates that the
doped B atom will produce stronger distortions around
it than that in the N atom. Moreover, the site-occupying
probabilities of the HOMO states for C$_{59}$X are plotted
in Fig. 3. There are two large peaks at point 1 (position
of the impurity atom in C$_{59}$B molecule) and point 9 for
both C$_{59}$B and C$_{59}$N. The fact that the peak at point 1
in C$_{59}$B is higher than that in C$_{59}$N represents that the
localization effect coming from the N impurity atom is
stronger than that from the B atom. The bond connect-
ning points 1 and 9 is the shortest X-C bond among three
X-C bonds and is represented by a thick line in Fig. 4.
These structures in Fig. 3 mean that the HOMO states
are strongly localized on the X-C double bond. Such
electronic behavior looks more like that produced by
the deep impurities in the usual semiconductors.

In conclusion, the calculated results based upon
the extended SSH model for the substituted fullerene
C$_{59}$X are well consistent with those from the SCF-MO
method.\textsuperscript{12,15} It has been found that the lattice struc-
tures change due to doping, in particular significantly in
the vicinity of the dopant ions. The HOMO-LUMO en-
ergy gaps for the molecules C$_{59}$B and C$_{59}$N are shown
to be smaller than that for C$_{60}$. The HOMO states are
mainly localized on the X-C double bonds and the excess
electron densities are concentrated on the impurity sites.
From our results, it seems that the general substituted
fullerene C$_{60-m-n}$X$_m$Y$_n$ can also well be described by
the extended SSH model.

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\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{figure4.png}
\caption{The plane projective figure of the C$_{60}$ molecule.
The black ball corresponds to the substituted impurity atom
(B or N). The double line represents the shortest X-C bond.}
\end{figure}

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\bibitem{19} When $y_{ij}$ is positive, the hopping integral is larger than $t_0$,
and so the sign before $a$ is negative.
\bibitem{20} Usually it is less than or equal to 6, but it is set to be 1 in
this paper.
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