ELECTRONIC STRUCTURE OF C_{60} AND C_{70} MOLECULES: GENERATING FUNCTION APPROACH

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We study the electronic structure of C_{60} and C_{70} molecules within the tight-binding approximation. Our approach is based on recursive evaluations of the generating function, which provide the density of states of the system. Our results for C_{60} are consistent with previous calculations using very different methods, and we have also obtained results for the much-less-studied C_{70} case.

The recent discovery of a simple technique for the production in bulk quantities of fullerenes has generated tremendous interest in this new form of Carbon. Among the fullerene zoo, the soccer-ball-like C_{60} and the rugby-ball-like C_{70} are the most abundant. Due to its unique structure and the exhibition of superconductivity when doped with an electron-donor alkali-metal, C_{60} has been the most intensively studied fullerene molecule. In comparison, the electronic structure of C_{70} has received very little attention so far. In this work, we explore the electronic properties of C_{60} and C_{70} molecules using the generating function method. Several diverse approaches have been used to study the electronic properties of fullerenes (see, for instance Refs. [1-8], and references therein) and we will compare our results for C_{60} with a few of the previous calculations, including the well-known tight-binding results by Manousakis [1] and the local-density-approximation (LDA) results by the NEC group [7]. The energy spectra of these molecules are relevant to the several important experimental techniques which probe the spectroscopy of single molecules. For instance, a scanning tunneling microscope (e.g., Ref. [9]) can be used to probe the local spectroscopy of fullerenes.

The generating function is an electronic analog of the partition function used in statistical mechanics. Derivatives of the latter provide useful thermal quantities, while derivatives of the former provide information about the electronic structure. The advantage of the generating-function approach is that it provides a very efficient numerical algorithm utilizing only basic techniques of Gaussian integration and matrix algebra. More details about this elegant technique and some applications can be found in the interesting work by Lemieux and Tremblay [10].

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The generating function of the system is

$$\mathcal{G}(E) = \ln\left[\int_{-\infty}^{+\infty}\left(\prod_{i=1}^{N} du_i\right)\exp\left(-\frac{1}{2}U^T\underline{X}U\right)\right]. \quad (1)$$

Here $U = (u_1, u_2, \ldots, u_N)$ and the matrix $\underline{X}$ is defined by $\underline{X} = Z\underline{I} - \underline{H}$, in which $Z = E + i\eta$, $\underline{I}$ is the identity matrix, and $\underline{H}$ the symmetric Hamiltonian matrix. It can be derived [10] that the density of states (DOS) is given by

$$\rho(E) = \frac{2}{\pi}\lim_{\eta\to 0}\mathrm{Im}\frac{\partial\mathcal{G}}{\partial E}, \quad (2)$$

where Im denotes the imaginary part of a complex quantity.

We rewrite $\underline{X}$ as

$$\underline{X} = \begin{pmatrix} \underline{X}_1 & \underline{Y}_{12} \\ \underline{Y}_{12}^T & \underline{X}_2 \end{pmatrix},$$

where $\underline{X}_1$ is the element x_{11} and $\underline{Y}_{12}$ a row matrix $\underline{Y}_{12} = (x_{12}, x_{13}, \ldots, x_{1N})$. Performing the integration over variable u_1, one has

$$\mathcal{G}(E) = C_1 + \mathcal{G}'(E), \quad (3)$$

where $\mathcal{G}'(E)$ is the generating function associated with the renormalized matrix $\underline{X}' = \underline{X}_2 - \underline{Y}_{12}^T\underline{Y}_{12}/x_{11}$ and C_1 is given by $C_1 = \frac{1}{2}\ln(2\pi) - \frac{1}{2}\ln x_{11}$. When the above step is repeated, the generating function $\mathcal{G}$ can be evaluated recursively by

$$x_{ij}^{(k)} = x_{ij}^{(k-1)} - x_{ki}^{(k-1)}x_{kj}^{(k-1)}/x_{kk}^{(k-1)}, \quad (4.1)$$

with $1 \le k \le N-1$, $k+1 \le i \le N$, and $i \le j \le N$;

$$C_k = C_{k-1} + \frac{1}{2}\ln(2\pi) - \frac{1}{2}\ln x_{kk}^{(k-1)}, \quad (4.2)$$

with $k = 1, 2, \ldots, N$; and

$$\mathcal{G} = C_N. \quad (4.3)$$

Here the initial conditions are $C_0 = 0$ and $x_{ij}^{(0)} = x_{ij}$, $1 \leq i \leq N$, $i \leq j \leq N$.

The Hamiltonian matrix of the system is usually sparse, especially for Hamiltonians with only nearest-neighbor interactions. This makes possible a *significant reduction* of computation time. At the kth step, the renormalized matrix $\underline{X}^{(k)}$ is given by $\underline{X}^{(k)} = \underline{X}_2^{(k-1)} - [\underline{Y}_{12}^{(k-1)}]^T \underline{Y}_{12}^{(k-1)}/x_{kk}^{(k-1)}$, where $\underline{Y}_{12}^{(k-1)} = (x_{k,k+1}^{(k-1)}, x_{k,k+2}^{(k-1)}, \ldots, x_{k,N}^{(k-1)})$. Assume that the position of the last nonzero element in the row matrix $\underline{Y}_{12}^{(k-1)}$ is $k + d^{(k-1)}$. Then, in the matrix $\underline{X}^{(k)}$, only the elements $x_{ij}^{(k)}$, $k + 1 \leq i, j \leq k + d^{(k-1)}$, are renormalized, while the remaining elements are not changed. Thus, equation (4.1), with $1 \leq k \leq N - 1$, is replaced by

$$x_{ij}^{(k)} = x_{ij}^{(k-1)} - x_{ki}^{(k-1)} x_{kj}^{(k-1)}/x_{kk}^{(k-1)}, \qquad (5.1)$$

for $k + 1 \leq i \leq k + d^{(k-1)}$, $i \leq j \leq k + d^{(k-1)}$; and

$$x_{ij}^{(k)} = x_{ij}^{(k-1)}, \qquad (5.2)$$

for $k + 1 \leq i \leq k + d^{(k-1)}$, $k + d^{(k-1)} + 1 \leq j \leq N$, $k + d^{(k-1)} + 1 \leq i \leq N$, and $i \leq j \leq N$.

The C$_{60}$ molecule has twenty hexagons and twelve pentagons [see Fig. 1(a)], in which a carbon atom sits at each of the 60 sites. A carbon atom has four valence orbitals $2s$, $2p_x$, $2p_y$, and $2p_z$. In the C$_{60}$ molecule, the four atomic orbitals of each carbon atom are labelled, respectively, by $2s$, $2p_{\|(1)}$, $2p_{\|(2)}$, and $2p_\perp$, where the subscript $\|$ denotes the directions parallel to the tangential plane at the location of the carbon atom, and $\perp$ labels the direction perpendicular to the plane. The $2p_\perp$ orbitals of all the carbon atoms are mixed to form molecular orbitals, namely, π states, and they are nearly decoupled from the rest of the orbitals [1]. The tight-binding Hamiltonian for the π states is then given by

$$H_\pi = \sum_i |p_\perp(i)\rangle \, \epsilon \, \langle p_\perp(i)|$$
$$+ \sum_{i,j} |p_\perp(i)\rangle \, t_\pi(i,j) \, \langle p_\perp(j)|, \qquad (6)$$

where $|p_\perp(i)\rangle$ denotes the $2p_\perp$ atomic orbital of the carbon atom located at site i, ϵ is its energy, and $t_\pi(i,j)$ is the hopping integral between sites i and j. It has been established that the C$_{60}$ molecule has two different bond lengths, 1.46Å and 1.40Å; one is associated with the edges of the pentagons in the C$_{60}$ molecule and the other with the edges of the hexagons that are not shared by the pentagons. In the literature, these two kinds of bonds are called single and double bonds, respectively. Here, we only consider nearest-neighbor interactions in Eq. (6) and assign the hopping integrals associated with the single and double bonds to be $t_\pi^{(1)}$ and $t_\pi^{(2)}$, respectively.

The other three atomic orbitals $2s$, $2p_{\|(1)}$, and $2p_{\|(2)}$ are mixed to form σ bonding and antibonding states of the C$_{60}$ molecule. For the σ states, one can use the Hamiltonian with hopping integrals between sites, just as that for the π states, but the Hamiltonian is more com-

plex due to $ss\sigma, sp\sigma$, and $pp\sigma$ hopping integrals between the sites [2]. A simpler way to treat this is to transform the site hopping Hamiltonian to a *bond hopping model*. It is known that the three atomic orbitals $2s$, $2p_{\|(1)}$, and $2p_{\|(2)}$ involve the sp^2 hybridization. The mixture of $2s$, $2p_{\|(1)}$, and $2p_{\|(2)}$ at each site produces three sp^2 hybrid orbitals sp_a^2, sp_b^2, and sp_c^2. A given sp^2 hybrid orbital of a carbon atom can form σ bonding and anti-bonding orbitals with a sp^2 hybrid orbital of a nearest-neighbor carbon atom. The σ bonding and antibonding orbitals are distributed around the bond connecting the two carbon atoms, and correspond to two different eigenvalues. The couplings among the σ orbitals at the 90 bonds yield the σ states of the C$_{60}$ molecule. Thus, using the isolated σ bonding and antibonding orbitals at the 90 bonds as the new basis of representation, one can transform the Hamiltonian for the σ states to the bond hopping model. Since the dominant effect is due to the resonant couplings among the states of the same energy [11], the σ bonding and antibonding states will be nearly decoupled from one
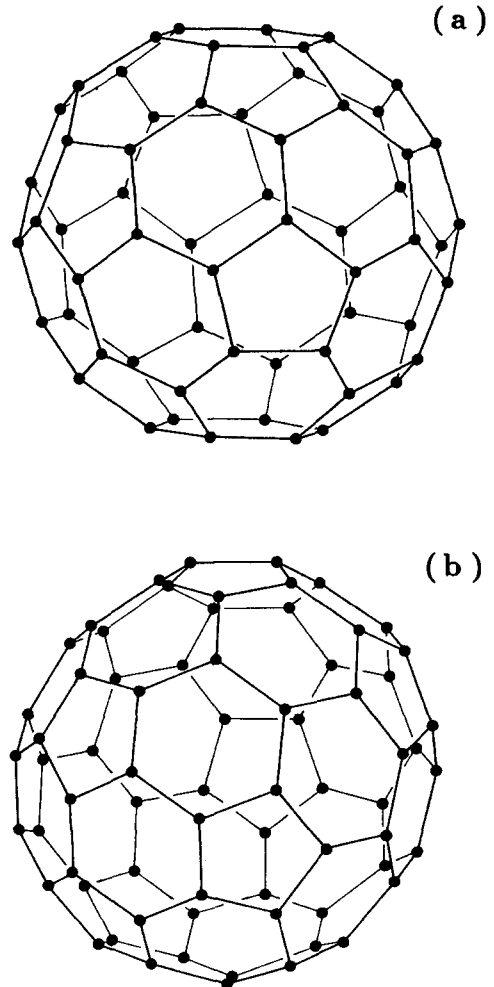
(a)

(b)

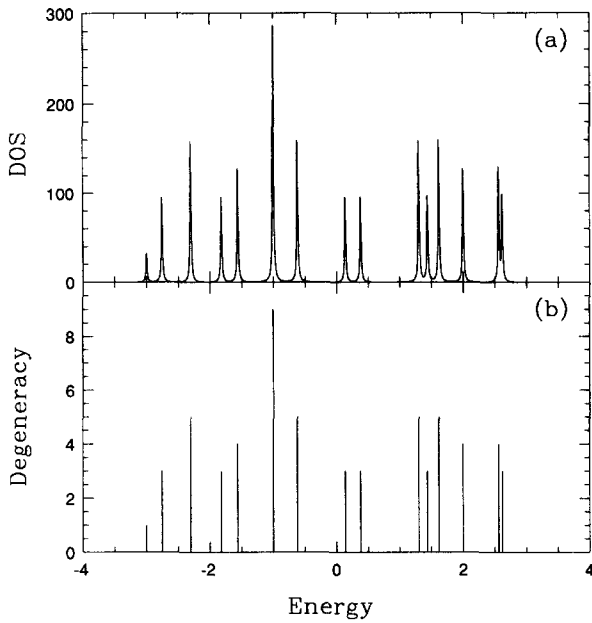Figure 1. Structures of (a) C$_{60}$ and (b) C$_{70}$ molecules.

Figure 2. Electronic structures of the π states of the undimerized C_{60} molecule. (a) DOS (arbitrary units), for which $\varepsilon = 0$ and $t = t_\pi^{(1)} = t_\pi^{(2)} = 1$ (in units of $t_\pi^{(1)}$); (b) energy levels given in Ref. [1].

another. Therefore, the Hamiltonian for the σ bonding or anti-bonding states has the following form:

$$H_\sigma = \sum_n |\sigma(n)\rangle \, \varepsilon_\sigma \, \langle \sigma(n)|$$
$$+ \sum_{n,m} |\sigma(n)\rangle \, t_\sigma(n,m) \, \langle \sigma(m)|, \qquad (7)$$

where $|\sigma(n)\rangle$ is an isolated σ bonding or anti-bonding orbital siting at bond n and ε_σ is its energy. It should be noticed that the hopping integrals now correspond to bond-to-bond hoppings. For the C_{60} molecule, there are two types of nearest-neighbor bond-to-bond configurations, namely, single-bonded to single-bonded, and double-bonded to single-bonded. Here, their corresponding bond-to-bond hopping integrals are denoted by $t_\sigma^{(1)}$ and $t_\sigma^{(2)}$, respectively.

In Fig. 2(a) we give the DOS of the π states of the undimerized C_{60} molecule, where $\varepsilon = 0$ and $t = t_\pi^{(1)} = t_\pi^{(2)} = 1$ (in units of $t_\pi^{(1)}$). It is clear that the DOS consists of fifteen peaks, in agreement with the eigenvalues obtained in Ref. [1] [see Fig. 2(b)]. The DOS for the π states and the σ bonding states of the dimerized C_{60} molecule are shown in Figs. 3(a) and 3(c), respectively. The parameters of the Hamiltonians are chosen to be $\varepsilon = 0.8$ eV, $t_\pi^{(1)} = -2.2$ eV, and $t_\pi^{(2)} = -2.5$ eV for Fig. 3(a), and $\varepsilon_\sigma = -9$ eV, $t_\sigma^{(1)} = -3$ eV, and $t_\sigma^{(2)} = -2.2$ eV for Fig. 3(c). For comparison, results obtained by using the local density approximation (LDA) (see, for instance, Ref. [7]) are given in Fig. 3(b) for the π states and Fig. 3(d) for the σ bonding states. Our
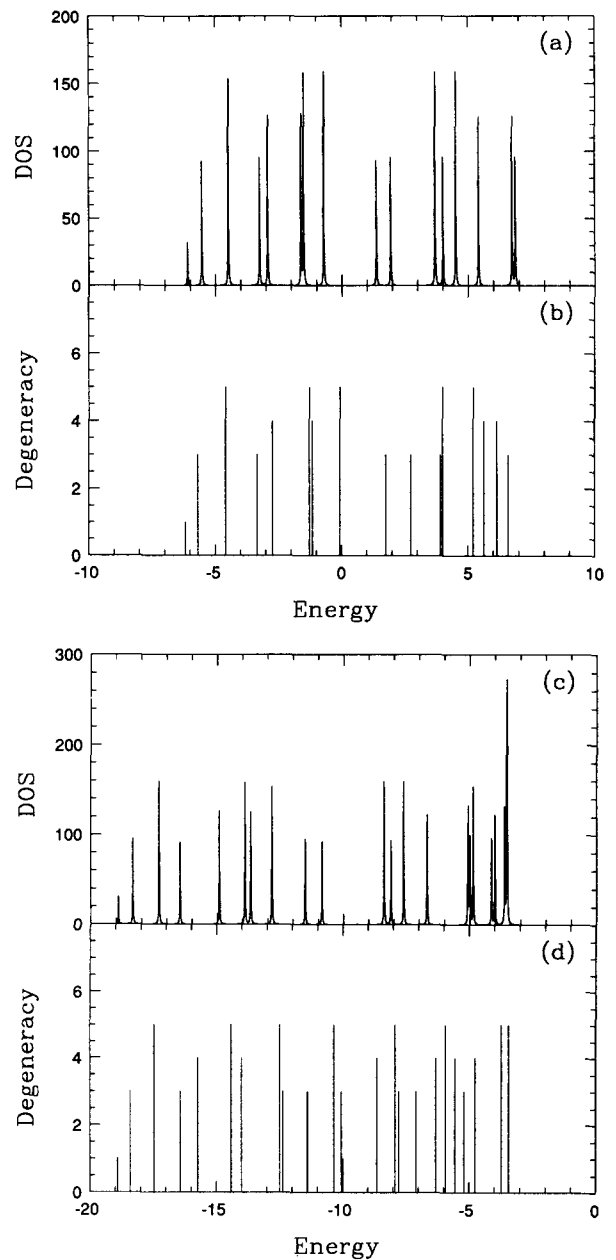

Figure 3. Electronic structures of the dimerized C_{60} molecule. (a) DOS (arbitrary units) of the π states, for which $\varepsilon = 0.8$ eV, $t_\pi^{(1)} = -2.2$ eV, and $t_\pi^{(2)} = -2.5$ eV; (b) energy levels of the π states obtained by the local density approximation (LDA) (Ref. [7]); (c) DOS (arbitrary units) of the σ bonding states, for which $\varepsilon_\sigma = -9$ eV, $t_\sigma^{(1)} = -3$ eV, and $t_\sigma^{(2)} = -2.2$ eV; (d) energy levels of the σ bonding states obtained by the LDA (Ref. [7]).

results reasonably match those obtained by the LDA calculations, especially in the lower-energy regions of the spectra of the σ bonding and π states.

Finally, we turn to the C_{70} molecule [see Fig. 1(b)]. As in the C_{60} molecule, two types of nearest-neighbor
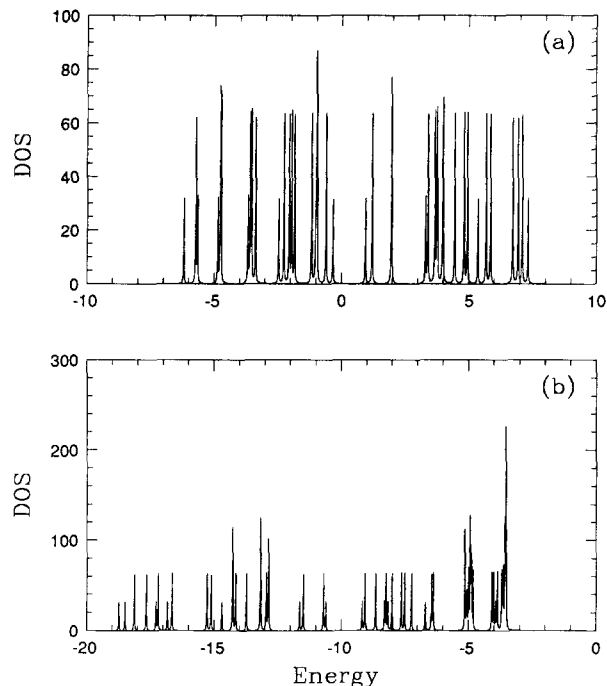
Figure 4. DOS (arbitrary units) of the C_{70} molecule. (a) π states, for which $\varepsilon = 0.8$ eV, $t_\pi^{(1)} = -2.2$ eV, and $t_\pi^{(2)} = -2.5$ eV; (b) σ bonding states, for which $\varepsilon_\sigma = -9$ eV, $t_\sigma^{(1)} = -3$ eV, $t_\sigma^{(2)} = -2.2$ eV, and $t_\sigma^{(3)} = -2$ eV.

hopping integrals are chosen for the π states, which correspond to the edges of the pentagons (single bond) in the C_{70} molecule and those of the hexagons that are not shared by the pentagons (double bond), respectively. This is an approximation since C_{70} has more than two edge lengths. In Fig. 4(a) we present the DOS of the π states for the C_{70} molecule. The parameters of the site hopping Hamiltonian are chosen to be the same as those for the π states of the C_{60} molecule, namely, $\varepsilon = 0.8$ eV, $t_\pi^{(1)} = -2.2$ eV, and $t_\pi^{(2)} = -2.5$ eV. Comparing Fig. 4(a) with Fig. 3(a), one sees that the number of peaks in the DOS becomes much larger for the C_{70} molecule. This can be understood from the group-theoretical point of view. For a molecule with high point

group symmetry, its degeneracy in eigenstates will be high. When the point group becomes lower, the degeneracies for some eigenstates are partly, or completely, removed. Since the point group of the C_{70} molecule is lower than that of the C_{60} molecule and, in addition, the C_{70} molecule has more carbon atoms, the number of eigenvalues will be much larger for the C_{70} molecule and thus there are many more peaks in the DOS.

As for the σ bonding or antibonding states of the C_{70} molecule, there are three types of nearest-neighbor bond-to-bond configurations, i.e., single-bonded to single-bonded, double-bonded to single-bonded, and double-bonded to double-bonded. The corresponding hopping integrals are here denoted by $t_\sigma^{(1)}$, $t_\sigma^{(2)}$, and $t_\sigma^{(3)}$, respectively. As an example, we present in Fig. 4(b) the DOS of the σ bonding states of the C_{70} molecule, where the parameters of the bond hopping Hamiltonian are chosen to be $\varepsilon_\sigma = -9$ eV, $t_\sigma^{(1)} = -3$ eV, $t_\sigma^{(2)} = -2.2$ eV, and $t_\sigma^{(3)} = -2$ eV. It can be seen that the number of the peaks in the DOS of the σ bonding states for the C_{70} molecule is much larger than that for the C_{60} molecule [compare Fig. 4(b) with Fig. 3(c)], just as in the case of the π states.

In summary, we have studied the electronic structures of the C_{60} and C_{70} molecules within the tight-binding approximation. The approach is based on recursive evaluations of the generating functions of the systems which directly determine their DOS. The π states are associated with a site-hopping Hamiltonian. There are 60 π states for the C_{60} molecule and 70 π states for the C_{70} molecule. For the σ states, the Hamiltonian can also be written in the site-hopping form, but it is more complex due to $ss\sigma$, $sp\sigma$, and $pp\sigma$ hopping integrals between sites. In this paper, we have proposed a simpler way to deal with this problem, namely, to transform the site-hopping Hamiltonian to a bond-hopping model. In the C_{60} and C_{70} molecules, there exist 90 and 105 bonds, respectively. Thus, there are 180 σ states (90 bonding and 90 antibonding) for the C_{60} molecule and 210 σ states (105 bonding and 105 antibonding) for the C_{70} molecule. Our results for C_{60} are consistent with previous calculations using very different methods, and we have also obtained results for the much-less-studied C_{70} case.

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