

Electronic structure of C_{60} within the tight-binding approximation

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(Received 14 June 1991; revised manuscript received 25 July 1991)

We study the electronic states of the molecule C_{60} , with truncated icosahedral structure, using a simple tight-binding approximation. We compare our results for the energy levels with those obtained from a band-structure calculation within the local-density approximation (LDA). We find that using a value for the carbon-to-carbon electron-hopping matrix element $t_\pi = 2.50$ eV, many of the features of the LDA calculation of the π electrons can be reproduced. We also study the effects of bond dimerization on the molecule's electronic spectrum and on the degeneracy of states near the molecular Fermi level.

There exist carbon molecular structures involving many carbon atoms that follow "magic" numbers,¹ in particular, a C_{60} molecule with truncated icosahedral structure has been the subject of recent experimental activity. Kraätshmer *et al.*² have shown that these all-carbon molecules can be produced by evaporation of graphite and can be isolated as soluble well-defined crystals where the C_{60} molecules solidify in a nearly closed packed face-centered-cubic (fcc) lattice at room temperatures and undergo a structural transformation to a simple cubic with orientational order at a lower temperature.³ Hebard *et al.*⁴ and Rosseinsky *et al.*⁵ have demonstrated that when doping these materials with K and Rb new materials are formed (K_xC_{60} and Rb_xC_{60}) which superconduct at 18 and 28 K, respectively. The latter experimental discovery places these materials in the class of high- T_c superconductors and has made them interesting to a broader spectrum of physicists.

The Hückel molecular orbital theory has been used in the past to calculate the electronic structure of the icosahedral C_{60} molecule.⁶ Recently, total-energy and one-electron calculations within the local-density approximation (LDA) have been reported⁷ for both the molecule C_{60} and the fcc crystalline structure. Furthermore, molecular dynamics simulations⁸ for the solid C_{60} have been carried out using the LDA and the Car-Parrinello method. These calculations reveal the one-electron energy bands and they are very informative for the molecular electronic structure.

In order to make progress in understanding complex phenomena such as superconductivity in these systems, we need to describe the complexity of the one-body problem in terms of a simple model which captures the important features of the electronic structure of the molecule. Here, we shall study the extent to which the realistic features of the electronic structure of the molecule can be understood within the nearest-neighbor tight-binding Hamiltonian. We shall show that several important features of the electronic molecular levels and their degeneracies can be understood within such a simple model. We characterize the outer occupied and the lowest unoccupied electronic states (which form the conduction band when the doped material solidifies) with appropri-

ate quantum numbers characteristic to the icosahedral structure and we give their charge distribution. We also study the effects of bond dimerization on the degeneracy and the energy of the electronic levels.

It is believed and recently verified by nuclear-magnetic-resonance experiments⁹ that the molecule dimerizes, i.e., there are carbon-carbon bonds of two different lengths. The C_{60} molecule consists of twenty hexagons and twelve pentagons (Fig. 1). All the pentagon sides (60 sides), denoted in Fig. 1 by a single bond, have an approximate length or $r_1 = 1.46$ Å, while all the other 30 sides (which are those sides of the hexagons that are not shared by a pentagon) are of shorter length $r_2 = 1.40$ Å, and they are denoted by a double bond in Fig. 1.

We need to consider the four valence states $2s$, $2p_x$,

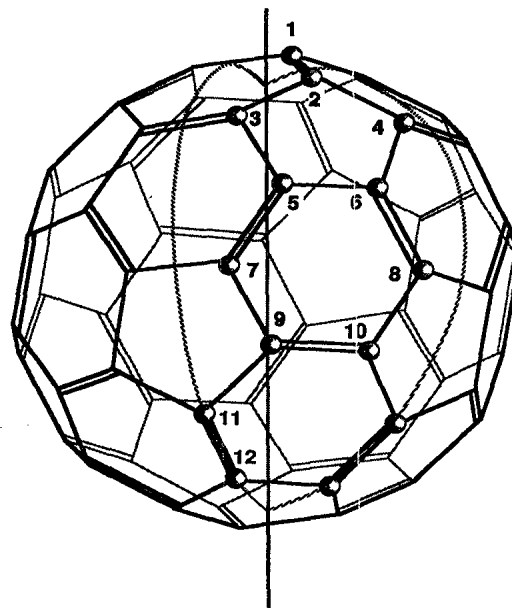


FIG. 1. The truncated icosahedral structure of the molecule C_{60} . A fivefold symmetry axis is shown and a slice which includes the 12 labeled atoms is shown. The electronic wave function can be written as given by Eq. (2) where the sum is over all five slices and within each slice the sum is over all twelve atoms.

$2p_y$, and $2p_z$. Let us use a local rectangular coordinate system where the z axis for each atom passes through the center of the icosahedron and the nucleus of the atom. Let the x axis be perpendicular to the z axis and lie on the plane defined by the z axis and the line joining the atom in question with the nearest atom of the nearest-neighbor pentagon. The directions of the bond joining the two pentagons and that of the x axis are almost the same. Let us define $t_\pi^{(1)}$ ($t_\pi^{(2)}$) to be the matrix element of the tight-binding Hamiltonian between the $2p_z$ states of each atom and its nearest atom of the nearest pentagon (same pentagon). In the case of dimerization, it is approximately true that¹⁰ $t_\pi^{(2)}/t_\pi^{(1)} \simeq (r_1/r_2)^2 \sim 1.1$. Because of the symmetry of the molecule, the overlap integral between these orbitals ($2p_z$) and different orbitals of nearest-neighbor atoms is very small. The $2p_z$ orbitals of all the carbon atoms will be mixed to form molecular orbitals and they will be nearly decoupled from the rest of the orbitals. The other three orbitals, namely, $2s$, $2p_x$, and $2p_y$, will be hybridized to form σ bonding and antibonding states (180 total number of σ states). We will return to the discussion of the nature of the σ states; let us first start by studying the π states.

Let us begin with a simple tight-binding Hamiltonian to describe the hybridization between the π electronic atomic orbitals in order to form the molecular states:

$$H = - \sum_{\langle ij \rangle, \sigma} t_{ij} (c_{i\sigma}^\dagger c_{j\sigma} + \text{H.c.}); \quad (1)$$

here t_{ij} is the carbon-to-carbon hopping matrix element and $c_{i\sigma}^\dagger$ creates electrons of spin σ on the i th local atomic carbon orbital. In general, we shall assume different hopping matrix elements t_{ij} for "single" and "double" bonds.

We write the electronic wave function in the tight-binding approximation (TBA) as

$$|\psi_{m, \sigma}\rangle = \frac{1}{\sqrt{5}} \sum_{n=1}^5 \exp\left(i \frac{2\pi}{5} mn\right) |n, \sigma\rangle, \quad (2)$$

where $|n, \sigma\rangle$ describes an electron state which is the linear combination

$$|n, \sigma\rangle = \sum_{i=1}^{12} a_i c_{i\sigma}^\dagger |\text{vacuum}\rangle. \quad (3)$$

Here the sum is over all twelve atomic orbitals localized at site i of the n th slice of the icosahedron, as shown in Fig. 1. The possible values of m are $m = 0, \pm 1, \pm 2$. It is straightforward to find the coefficient a_i , $i = 1, 2, \dots, 12$ and the energy eigenvalues numerically. For each value of m there are twelve eigenstates, among which some are degenerate. The parity of the states is determined as follows: Consider the i th atom within the first slice and the one located diametrically opposite on the icosahedron. Next, we map the second atom by a $\frac{4\pi}{5}$ rotation to a third atom which is its equivalent within the first slice. If the difference between the phase ϕ_i of the i th atom ($a_i = \sqrt{\rho_i} e^{i\phi_i}$) and the phase of the third atom, including the rotation angle of $\frac{4\pi}{5}$, is a multiple of 2π , the state has + (even) parity. If the difference in the phase is an odd multiple of π , the state has - (odd) parity.

In Table I and Fig. 2 we give the eigenvalues of the

TABLE I. The eigenvalues of the tight-binding Hamiltonian for the case of the C_{60} molecule. The numbers in parentheses denote degree of degeneracy. The energy is given in units of the carbon-carbon hopping matrix element t . The occupied states are separated from the unoccupied (for the π orbitals of C_{60}).

Degeneracy	Parity	Quantum number m	Energy (t)
Occupied			
1	+	0	-3.000 00
3	-	-1, 0, 1	-2.756 60
5	+	-2, -1, 0, 1, 2	-2.302 78
3	-	-2, 0, 2	-1.820 25
4	-	-2, -1, 1, 2	-1.561 56
9	+	-2(2), -1(2), 0, 1(2), 2(2)	-1.000 00
5	-	-2, -1, 0, 1, 2	-0.618 03
Unoccupied			
3	-	-1, 0, 1	0.138 56
3	+	-1, 0, 1	0.381 97
5	+	-2, -1, 0, 1, 2	1.302 78
3	-	-2, 0, 2	1.438 28
5	-	-2, -1, 0, 1, 2	1.618 03
4	+	-2, -1, 1, 2	2.000 00
4	-	-2, -1, 1, 2	2.561 55
3	+	-2, 0, 2	2.618 03

undimerized molecule (in units of the carbon-to-carbon hopping matrix element $t = t_\pi^{(1)} = t_\pi^{(2)}$), the corresponding quantum number m , the degree of degeneracy, and the parity of the states with respect to the center of the icosahedron. The ground state is singly degenerate, while the Fermi level for 60 electrons is fivefold degenerate. In Table I and Fig. 2, the occupied states are the negative energy states [in our Hamiltonian we have omitted the constant on-site energy from (1) for simplicity]. It is interesting to study the states closest to the Fermi

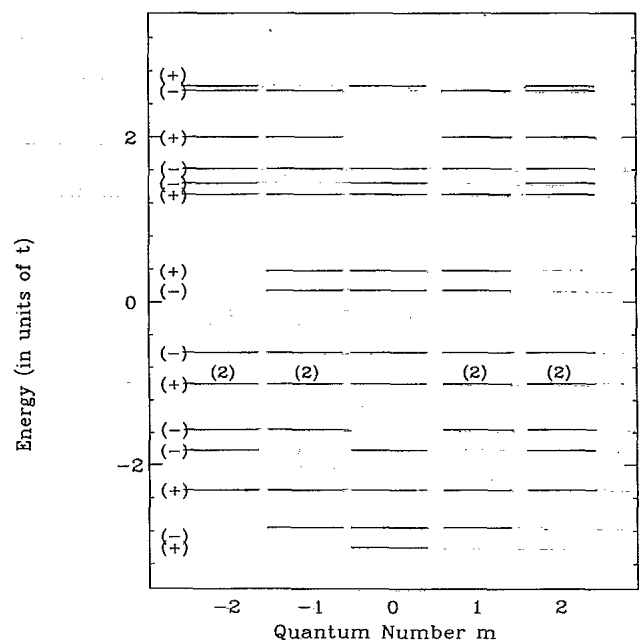


FIG. 2. The energy levels of the undimerized molecule in the tight-binding approximation.

TABLE II. We give the charge density $\rho_i = |a_i|^2$ of the conduction-electron eigenstates. If we include dimerization the $m = 0$ is the lowest conduction state and the $m = \pm 1$ remain degenerate with higher energy.

i	$m = 0$	$m = 1$
1	0.026 72	0.111 64
2	0.122 19	0.063 91
3	0.003 31	0.123 35
4	0.003 31	0.123 35
5	0.172 24	0.038 88
6	0.172 24	0.038 88
7	0.172 24	0.038 88
8	0.172 24	0.038 88
9	0.003 31	0.123 35
10	0.003 31	0.123 34
11	0.122 19	0.063 91
12	0.026 72	0.111 64

level that would be occupied by the additional electrons when doping with a metallic element occurs to form, for example, a negative C₆₀ ion; there is a threefold degenerate level just above zero (Fig. 2 and Table I) with $m = 0, \pm 1$. The difference in energy between C₆₀⁻ and C₆₀ is $\Delta E = 0.756 59t$. In Table II, we give the charge distribution $\rho_i = |a_i|^2$ on each atom for these states. As we shall discuss below, the threefold degeneracy of this outer state will be lifted when we include bond-dimerization effects and the $m = 0$ becomes the lowest energy state among these three. Electrons from the occupied states can be excited optically only to unoccupied states of opposite parity.

In Fig. 3, we compare the results of the tight-binding

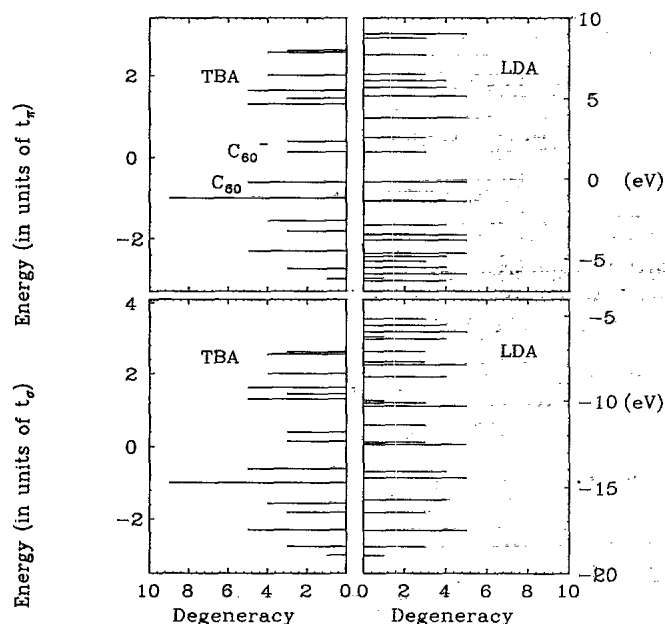


FIG. 3. The energy levels of the molecule in the tight-binding approximation (TBA) are compared with the results of the local density approximation (LDA) (Ref. 7). Top: the π -bonded states are compared with the results of the LDA calculation using $t_\pi = 2.50$ eV. Bottom: the lower σ -bonded states are compared using $t_\sigma = 2.11$ eV.

approximation with those recently obtained by LDA calculations.⁷ In this part of our calculation we have neglected bond-dimerization effects. Those will be included next in this paper. As already mentioned, there are two types of atomic states and overlap integrals: electron hopping between inner σ -bonded orbitals and hopping between outer π -bonded orbitals. The latter are the ones which cause bond dimerization and the “double” bonds. As discussed earlier, there are 180 σ states (there are 90 bonds and two σ states per bond) which correspond to the mixing of the orbitals defined as $2p_x, 2p_y$, and the $2s$. Since there are only 180 electrons to be distributed (three per atom) in these σ type states there will be 90

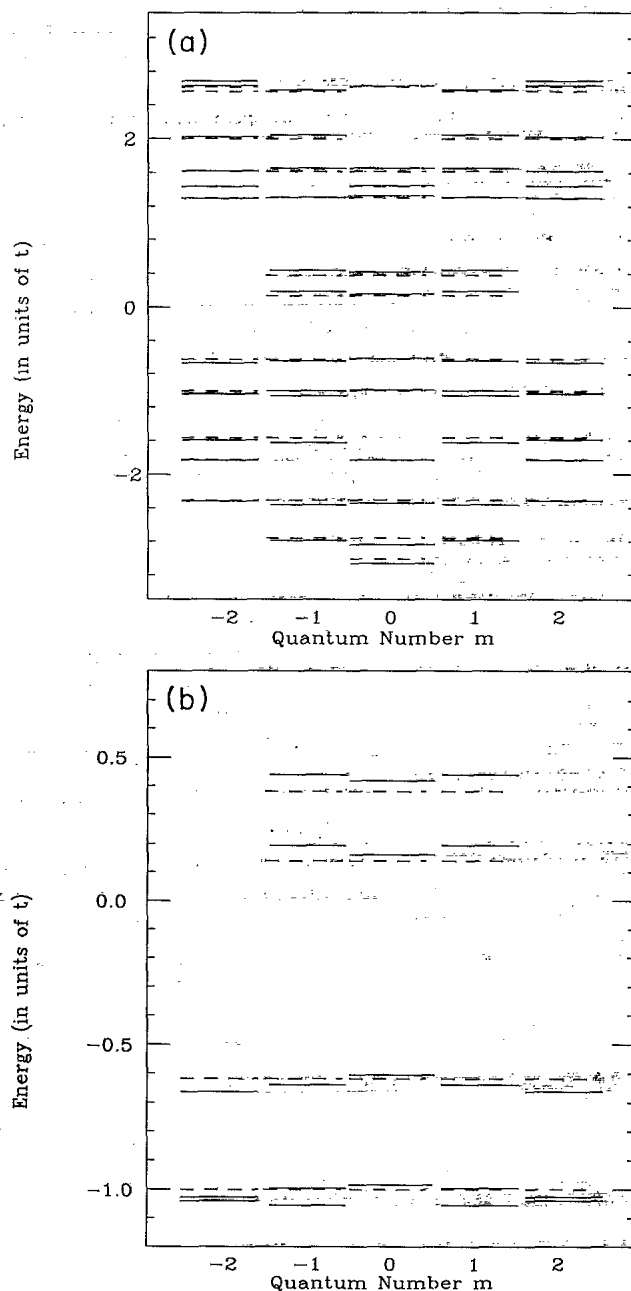


FIG. 4. (a) The energy levels of the dimerized (different bond lengths) molecule (solid lines) are compared with those of the undimerized molecule (dashed lines). (b) The same as (a) where we have enlarged the levels near the Fermi level.

such states below the Fermi level (occupied). Thus, below the Fermi level there are 120 states out of which 30 are of π and 90 of σ character. This counting is evident in the LDA calculation (Fig. 4 of Ref. 7).

First, in order to fit the π states, we choose the scale t_π in such a way as to reproduce the gap between the C_{60} and C_{60}^- state; we found that $t_\pi \simeq 2.50$ eV. In Fig. 3, we compare the results of the TBA (top left) and LDA (top right). The LDA calculation provides all 240 states (120 below the Fermi level), while this TBA calculation provides only the 60 π states (30 below the Fermi level). The constant on-site energy, omitted from Eq. (1) for simplicity, is also chosen properly by placing the Fermi level in both calculations at the same energy. Notice that the ninefold degenerate level below the Fermi level of the undoped C_{60} is very close to the two levels in the LDA calculation which are (5+4)-fold degenerate. In the TBA calculation with common t_{ij} for all nearest-neighbor bonds, this ninefold degeneracy is an accidental degeneracy of two energy levels, which are fivefold and fourfold degenerate. The energy level with fourfold degeneracy lying below the ninefold is also approximately reproduced. In addition the order of the levels and the degeneracies near the molecular Fermi level also agree.

We have one σ bonding state per bond and it corresponds to the deeper energy levels. We would like to notice that the order of the degeneracies of the lower σ bonding states are the same as those of the tight-binding model with one orbital per atom (Table I and Fig. 2). We have chosen an energy scale $t = t_\sigma$ in order to fit the difference between the lowest energy state and the first excited state of the bonding σ states (Fig. 4 of Ref. 7). We find $t_\sigma \simeq 2.11$ eV and the results are compared in the two lower parts of Fig. 3 (left corresponds to the TBA and the right to the LDA). Notice that the TBA calculation reproduces the degeneracies and the energies of the first four levels (12 states); the energy of the fifth level is somewhat different. The sixth level in our calculation is ninefold degenerate, while in the LDA calculation there are two energy levels (nine states total) close to each other, one level with fivefold and the other with fourfold degeneracy. The agreement becomes worse at higher energy states because of mixing with the other σ orbitals. It is interesting to notice that only higher energy states are mixed with the other orbitals; this indicates that from the lower energy levels, one set of σ states is separated from the other two sets of σ states. This might also

indicate that the lower σ -bonding states have mainly 2s character because the energy of these lower states is close to the energy of the 2s state in the single carbon atom ($E_s^{\text{atom}} \simeq -17.5$ eV). This is also supported by the fact that the value of t_σ for these states is small (almost the same with the t_π). The value of the overlap integrals t'_σ and t''_σ for the other two families of σ states which have strong admixture of $2p_x$ or $2p_y$ orbitals is expected to be larger.

In Fig. 4(a), we give the results (solid lines) of our calculation for the π states, where we have assumed that the hopping matrix element $t_\pi^{(2)}$ for the short bonds ("double" bonds) is larger than the matrix element $t_\pi^{(1)}$ corresponding to the longer bonds ("single" bonds), and for illustration we took $t_\pi^{(2)}/t_\pi^{(1)} = 1.1$. The dashed lines give the results obtained by taking these two matrix elements to be equal. Notice that the degeneracy of the levels near the Fermi level of the electron-doped molecule is lifted. Figure 4(b) gives an expanded version of Fig. 4(a) around the Fermi level. The valence level has one singly degenerate state with $m = 0$ and two doubly degenerate states characterized by $m = \pm 1$ and ± 2 . The conduction state with $m = 0$ is the lowest and there is a gap between this and the $m = \pm 1$ states which remain degenerate.

Finally, the LDA calculation is also approximate and thus more detailed comparison might not be appropriate. One of the purposes of this tight-binding calculation is to point out that most of the complex nature of the electronic states as revealed by the LDA calculation and in particular, their degeneracies and their quantum numbers can be understood in terms of a simple model of the molecular electronic structure.

This model can be extended to describe the fcc and the low-temperature phase of solid C_{60} and the doped materials. At the moment, however, the exact orientation of the molecules in the crystal is not experimentally clear. In order to perform a TBA calculation starting from the atom-to-atom hopping integrals, such information is needed.

I would like to thank Dr. E. Kaxiras and Dr. J. Skofronick for useful discussions. This work was supported in part by the Supercomputer Computations Research Institute of Florida State University which is partially supported by the U.S. Department of Energy under Contract No. DE-FC05-85ER-250000.

¹H. W. Kroto, *Science* **242**, 1139 (1988).

²W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and Hoffman, *Nature (London)* **347**, 354 (1990).

³P. A. Heiney, J. E. Fisher, A. R. Mcghee, W. J. Romanow, A. M. Denenstein, J. P. McCauley, Jr., A. B. Smith, and D. E. Cox, *Phys. Rev. Lett.* **66**, 2911 (1991).

⁴A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, and A. R. Kortan, *Nature (London)* **350**, 600 (1991).

⁵M. J. Rosseinsky, A. P. Ramirez, S. H. Glarum, D. W. Murphy, R. C. Haddon, A. F. Hebard, T. T. M. Palstra, A. R. Kortan, S. M. Zahurak, and A. V. Makhija, *Phys. Rev.*

Lett. **66**, 2830 (1991).

⁶R. C. Haddon, L. E. Brus, and K. Raghavachari, *Chem. Phys. Lett.* **125**, 459 (1986).

⁷S. Saito and A. Oshiyama, *Phys. Rev. Lett.* **66**, 2637 (1991).

⁸Q.-M. Zhang, J.-Y. Yi and J. Bernholc, *Phys. Rev. Lett.* **66**, 2633 (1991).

⁹R. D. Johnson, N. Yannoni, G. Meijer, and D. S. Bethune, *The MRS Late News Session-Buckeyballs: New Materials Made from Carbon Soot*, videotape (Materials Research Society, Pittsburgh, 1990).

¹⁰W. A. Harrison, *Electronic Structure and The Properties of Solids* (Freeman, San Francisco, 1980).