PHYSICAL REVIEW B VOLUME 49, NUMBER 7 15 FEBRUARY 1994-I

Electronic structure of single- and multiple-shell carbon fullerenes

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(Received 16 August 1993)

We study the electronic states of giant single-shell and the recently discovered nested multiple-shell carbon fullerenes within the tight-binding approximation. We use two different approaches, one based on iterations and the other on symmetry, to obtain the π-state energy spectra of large fullerene cages: C_{240}, C_{540}, C_{960}, C_{1500}, C_{2160}, and C_{2940}. Our iteration technique reduces the size of the problem by more than one order of magnitude (factors of $\sim$ 12 and 20), while the symmetry-based approach reduces it by a factor of 10. We also find formulas for the highest occupied and lowest unoccupied molecular orbital energies of C_{60n^2} fullerenes as a function of n, demonstrating a tendency towards a metallic regime for increasing n. For multiple-shell fullerenes, we analytically obtain the eigenvalues of the intershell interaction.

INTRODUCTION

The discovery of a simple technique[1] for the production in bulk quantities of fullerenes has triggered intensive research on these carbon molecules and the search for other forms of carbon. Subsequently, a type of carbon multiple-shell structure composed of multilayered needlelike tubes has been discovered by high-resolution transmission electron microscopy.[2] Quite recently, giant nested shells of multiple-shell fullerenes (also called hyperfullerenes[3]) have been synthesized by intense electron-beam irradiation.[4] Essentially they consist of a composition of concentric spherical fullerene cages. The innermost cage is a C_{60} molecule which is encapsulated by giant fullerenes C_{240}, C_{540}, ..., one following the other.[4,5] The interlayer spacing coincides with that for bulk graphite (3.34 Å). A recent investigation[6] on the stability of these diverse forms of carbon shows that multiple-shell structures are most energetically favorable among them. Specifically, a very recent paper[7] shows that a stability transition from single to multilayer fullerenes occurs when the number of atoms exceeds $\sim$ 6000. Moreover, the concentric carbon multiple-shell structure containing no dangling bonds provides a challenge to graphite (comprising flat sheets of carbon hexagons) for the most stable form of pure carbon.

The structures and energies for several multiple-shell carbon molecules have recently been carried out by using realistic atomic potentials[7] and molecular mechanics calculations.[8] As yet there has been little spectroscopic information available regarding the electronic properties of the multiple-shell fullerenes, besides total energy calculations. The exact diagonalization of a local orbital matrix scales as N^3 (for an N-dimensional matrix). The orthonormalization step in plane-wave methods also scales as N^3. These two examples illustrate typical bottlenecks encountered when studying one of the central issues of condensed matter theory: to compute the energetics of very large systems. Different suggestions on how to minimize this formidable problem have recently attracted a lot of attention (see, e.g., Ref. 9). Here, we explore different ways to reduce this difficulty by using two very dissimilar approaches: one based on iterations and the other on symmetry considerations. *The iteration method reduces the size of the problem, N, by more than one order of magnitude (factors of $\sim$ either 12 or 20 depending on the chosen initial state).* For instance, it reduces N by about a factor of 20, from 2940 to 154, for the C_{2940} fullerene molecule. Furthermore, it can provide some precise analytic results for the eigenvalues. By using a different method based only on symmetry arguments, we can reduce N by a factor of 10. These two approaches give the same results for the energy eigenvalues. However, several distinct features of the first method that make it very convenient include the following: it requires the diagonalization of a fewer number of matrices, each one of them smaller in size, and every one of them with all their elements real.

Here we focus on a simple model of the electronic states of the giant single-shell fullerenes, and multiple-shell carbon molecules with the number of shells up to seven. The strategy used in this work includes two parts. First, we treat each C_{60n^2} fullerene as a $60n^2$-site nearest-neighbor tight-binding model. Each site corresponds to one radially directed carbon π orbital. Since the π orbitals provide the dominant contribution to the conducting properties of the molecules, the σ orbitals (being mainly responsible for the elastic properties) are not taken into account. In spite of the slight differences between bond lengths and structure curvature in these molecules, we have assumed a uniform hopping amplitude t for all the fullerenes under consideration. This assertion is motivated by the fact that results in C_{60} changed insignificantly by considering the two different hopping integrals. These icosahedrally-symmetric C_{60n^2} molecules will be studied for $n = 1, 2, \ldots, 7$ (i.e., C_{60}, C_{240}, C_{540}, C_{960}, C_{1500}, C_{2160}, and C_{2940}).

In the last part of this work, we use an intermolecular tight-binding model to account for the weak intershell interaction between the fullerene layers and analytically obtain its eigenvalues. It is important to stress that the sim-

0163-1829/94/49(7)/5020(4)/$06.00

ple tight-binding approximation yields reasonable quantitative results for the energy levels of each individual fullerene,[10–12] especially for those near the Fermi level. Furthermore, the intermolecular tight-binding model has also been applied to the electronic states of solid C_{60}.

SINGLE-SHELL GIANT FULLERENES

In the description of the electronic states of C_{60n^2} molecules, we employ a tight-binding Hamiltonian (Hückel theory as, for instance, used for fullerenes in Refs. 10–12) written as $H = -\sum_{\langle ij \rangle} t\, c_i^\dagger c_j$. Admittedly, this is a simplified Hamiltonian: the "Ising model" for the electronic structure. However, its understanding is a convenient stepping stone to the study of more complex models. Also, simple models are more accessible for analytical or semianalytical approaches. Much more realistic and complicated tight-binding Hamiltonians can be found, for instance, in Ref. 13 and papers cited therein. For carbon C_{60}, we have obtained closed-form expressions of the eigenvalues and eigenfunctions for both π and σ states as well as the Green function and local density of states by using recursion and path-integral methods.[14] Here we focus on the giant fullerenes.

To obtain the energy spectrum, we use two entirely different approaches, each one with its advantages. The first approach we use here is our generalization of the recursion method,[15] which we call the "generalized block recursion method." Because of limited space, here we present only a brief outline of this approach. We start from two initial states, $|u_0\rangle$ and $|v_0\rangle$, formed as

$$|u_0\rangle = \frac{1}{\sqrt{10}} \sum_{j=1}^{5} [|j\rangle + \mathcal{P}\,|j'\rangle] \tag{1}$$

and

$$|v_0\rangle = \frac{1}{\sqrt{12}} \sum_{j=1}^{6} (-1)^{j+1}[|j\rangle + \mathcal{P}\,|j'\rangle]. \tag{2}$$

In $|u_0\rangle$ ($|v_0\rangle$), $|j\rangle$ denotes the π orbitals on a pentagon (hexagon), and $|j'\rangle$ denotes those on the opposite (i.e., j and j' are antipodes) pentagon (hexagon). Also $\mathcal{P}$ stands for parity, with the value $+1$ or -1. Notice that these two pentagon (hexagon) rings satisfy the prerequisite that a fivefold (threefold) symmetry axis passes through their centers. Further states are then iteratively generated by the general recurrence relation

$$H\,|f_m^\alpha\rangle = a_m^\alpha\,|f_m^\alpha\rangle + b_{m+1}^\beta\,|f_{m+1}^\beta\rangle + b_m^\gamma\,|f_{m-1}^\gamma\rangle, \tag{3}$$

where m designates states which are m hops away from the initial state. The superscript designates various suitable states. On the left-hand side of Eq. (3), at most three terms are nonzero for each application of H on $|f_m^\alpha\rangle$. Among them, β and γ can each take at most two values among their several possible ones. The process terminates after a finite number of iterations. The representation of H thus becomes a "block-tridiagonal" form. However, the dimensionality of each block is *not* necessarily the same. The main operational difference between this approach and the standard recursion method is that additional indices (α, β, and γ) are needed to fully specify the generated states, producing very simple values (i.e., ± 1, ± 2, and $\sqrt{2}$) for the coefficients a's and b's. Furthermore, the standard recursion method is extremely cumbersome to apply for C_{60n^2} (for $n > 1$), while very convenient for only $n = 1$.

The advantage of this approach lies in that it reduces the task of diagonalizing the extremely large original Hamiltonian matrix for C_{60n^2} to the diagonalization of four much smaller matrices and provides precise analytic results for some of the eigenvalues (e.g., ± 1, ± 2, -3). For instance, in order to obtain the whole energy spectrum of C_{240}, we only need to diagonalize two (due to $\mathcal{P} = \pm 1$) 14×14 (constructed from $|u_0\rangle$) and two 18×18 (constructed from $|v_0\rangle$) matrices instead of a 240×240 matrix. Thus, the dimensionality has been reduced by (factors of $\sim$ 12 and 20) more than one order of magnitude. In general, for C_{60n^2} the dimensionality is reduced from $60n^2$ to $3n^2 + n$ ($5n^2 - n$) starting from the initial state $|u_0\rangle$ ($|v_0\rangle$). The relative size reduction is $(3n^2+n)/60n^2 = 1/20 + 1/60n \simeq 1/20$ [$(5n^2-n)/60n^2 = 1/12 - 1/60n \simeq 1/12$] for $|u_0\rangle$ ($|v_0\rangle$). Therefore, the dimensionality of the original giant fullerene problem can be easily reduced by more than one order of magnitude. The lowest unoccupied molecular orbital (highest occupied molecular orbital) [LUMO (HOMO)] energy is solved from the matrix constructed from $|u_0\rangle$ ($|v_0\rangle$) with negative parity.

We also use another approach, which closely follows the method presented in Ref. 12. This alternative and quite different method is based on group theory analysis. For instance, for C_{240}, six 24×24 matrices (four of them with complex elements) are diagonalized to obtain the energy spectrum. This method reduces the dimensionality of the problem by a factor of 10. For comparison purposes, we also use a third different method for the smaller cages: direct exact diagonalization. This method runs into limitations for very large cages. Therefore, it is a desirable and useful goal to be able to first reduce the dimensionality of the problem by more than one order of magnitude, in order to study very large fullerene cages.

The energy levels from the first two methods for various fullerenes are shown in Fig. 1. In Table I, we summarize the following physically important quantities for the giant fullerenes: energies of the HOMO, LUMO, and their differences (i.e., the band gaps). As the size of the fullerene grows, it can be seen that the band gap becomes smaller. These results demonstrate the tendency towards metallic regime for very large fullerenes. The best logarithmic fit formulas of the HOMO and LUMO energies (in units of t) for C_{60n^2} molecules with n up to 7 are

$$E_{\mathrm{HOMO}} = -0.674\,02 n^{-0.729\,56} \tag{4}$$

and

$$E_{\mathrm{LUMO}} = 0.146\,70 n^{-1.3772}. \tag{5}$$

By taking t equal to the typical value of 2.5 eV, these ex-

TABLE I. $N_L = 3n^2 + n$ $(N_H = 5n^2 - n)$ is the dimensionality of the matrix constructed from $|u_0\rangle$ $(|v_0\rangle)$, which provide the LUMO (HOMO) energies. These are significantly smaller than the dimensionality $N = 60n^2$ of the original Hamiltonian. Energies of the HOMO, LUMO, and band gaps for C_{60n^2} fullerenes, with $n = 1, 2, \ldots, 7$. In the HOMO and LUMO columns, the first values are in units of t and those in parentheses are the results obtained by taking t equal to the typical value of 2.5 eV.

Molecule	N_L	N_H	HOMO		LUMO		Gap (eV)
C_{60}	4	4	−0.618033	(−1.545082)	0.138564	(0.346410)	1.891492
C_{240}	14	18	−0.436772	(−1.091930)	0.059657	(0.149142)	1.241072
C_{540}	30	42	−0.324099	(−0.810247)	0.033671	(0.084177)	0.894424
C_{960}	52	76	−0.255010	(−0.637525)	0.022169	(0.055422)	0.692947
C_{1500}	80	120	−0.209564	(−0.523910)	0.015971	(0.039927)	0.563837
C_{2160}	114	174	−0.177673	(−0.444182)	0.012192	(0.030480)	0.474662
C_{2940}	154	238	−0.154140	(−0.385350)	0.009690	(0.024225)	0.409575

pressions become $E_{\mathrm{HOMO}} = -1.685\,05 n^{-0.729\,56}$ eV and $E_{\mathrm{LUMO}} = 0.366\,75 n^{-1.3772}$ eV. Even though these fits are not very accurate for small n, we believe that Eqs. (4) and (5) provide good approximations for larger values of n $(n \geq 8)$ where calculations are very difficult. From them, the band gap can also be readily inferred.

MULTIPLE-SHELL CARBON FULLERENES

In this section, we study the effects of the interaction between consecutive shells on the electronic states of the fullerene shells. In the stackings on the multiple-shell structures, the pentagons are aligned[8] along the icosahedral directions of the twelve vertices, and the hexagons are stacked in a manner similar to the *AB* (or Bernal) structure of graphite. Nevertheless, and as verified in Ref. 8, the interlayer interaction is mainly between adjacent shells. Each single-shell fullerene is now assumed to be in its ground (lowest energy) state and here we focus on its HOMO. We assume an intermolecular hopping amplitude V_n between the pairs of fullerenes

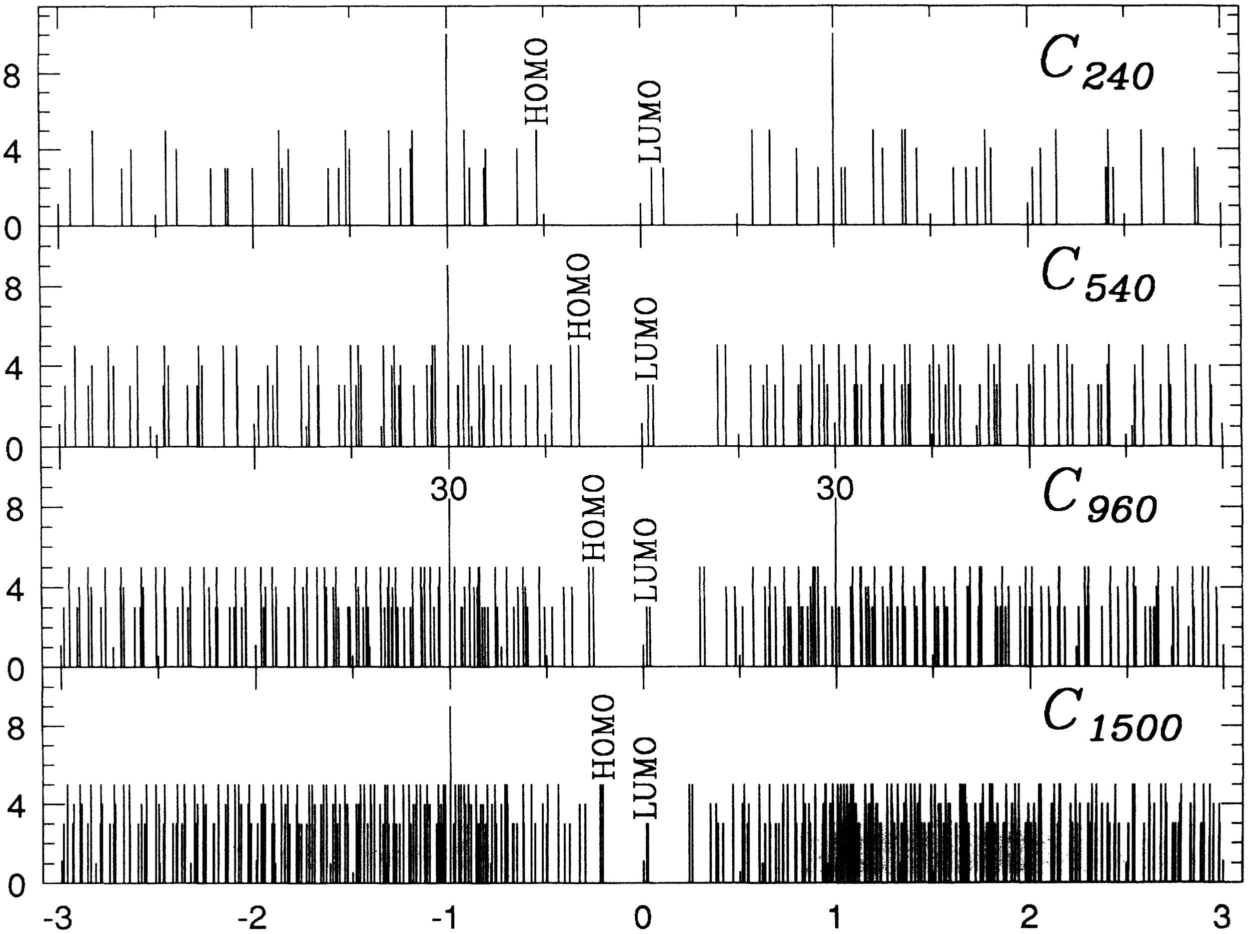

FIG. 1. The energy eigenvalues (horizontal axis) and their corresponding degrees of degeneracy (vertical axis) for various fullerenes. The energies are in units of carbon-carbon hopping integral t. The respective fivefold degenerate HOMO and threefold degenerate LUMO levels are indicated. For C_{60n^2}, there are approximately $60n^2/4 = 15n^2$ distinct energy levels.

TABLE II. The energy eigenvalues of H_I for various N_s.

N_s	Eigenvalues
2	$\pm V_1$
3	0 and $\pm\sqrt{V_1^2+V_2^2}$
4	$-\mathcal{A}\pm\mathcal{B}$ and $\mathcal{A}\pm\mathcal{B}$
5	0, $\pm\sqrt{\mathcal{S}-\mathcal{T}}$ and $\pm\sqrt{\mathcal{S}+\mathcal{T}}$

Here $\mathcal{A} = \sqrt{(V_1+V_3)^2+V_2^2}/2$, $\mathcal{B} = \sqrt{(V_1-V_3)^2+V_2^2}/2$, $\mathcal{S} = (V_1^2+V_2^2+V_3^2+V_4^2)/2$, and $\mathcal{T} = \sqrt{(V_1^2+V_2^2-V_3^2-V_4^2)^2+4V_2^2V_3^2}/2$.

C_{60n^2} and $C_{60(n+1)^2}$. A tight-binding approximation, $H_I = -\sum_{n=1}^{N_s-1} V_n\,(\,|\phi_n\rangle\langle\phi_{n+1}| + |\phi_{n+1}\rangle\langle\phi_n|\,)$, is then used to model the intershell interaction, where $|\phi_n\rangle$ denotes the HOMO of the C_{60n^2} molecule and N_s is the total number of shells. The V_n's can be obtained, for example, through an intermolecular resonance integrals calculation. At this moment, such calculations cannot yet be accurately done because of the lack of knowledge about the exact atomic positions. However, the V_n's are estimated to be of the order of a few hundred meV. Notice that while the multiplicity of the HOMO for each fullerene is five, the nonzero matrix element only exits between those belonging to the same representation. In other words, molecular states $|\phi_n\rangle$ and $|\phi_{n+1}\rangle$ in H_I must be in the same representation. Thus, for a N_s-shell carbon molecule, a small $N_s \times N_s$ matrix (constructed from H_I), with the mth row and nth column element $-V_{n-1}\delta_{m,n-1} - V_n\delta_{m,n+1}$, is sufficient to fully investigate the interaction between the $5N_s$ HOMO's. The eigenvalues for H_I can then be analytically solved. The results for various N_s are presented in Table II. This model with different hopping amplitudes can be readily applied to the threefold degenerate LUMO's.

In summary, we use two different approaches to study the π-state energy spectra of fullerene cages up to C_{2940}. We also find formulas for the HOMO and LUMO energies of fullerenes C_{60n^2} as a function of n. These approximations might be useful since experimentally obtained multiple-shell carbon molecules can have ~ 70 shells (with 294 000 atoms for the 70th shell, these systems are well beyond current computational capabilities). We obtain the gap energy as a function of n and show the tendency towards metallic regime for very large fullerenes. For multiple-shell carbon molecule, we analytically obtain the eigenvalues of the intershell interaction. The HOMO, LUMO, and gap energies (see Fig. 2), as well as the whole 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. 16) can be used to probe the local spectroscopy of fullerenes.

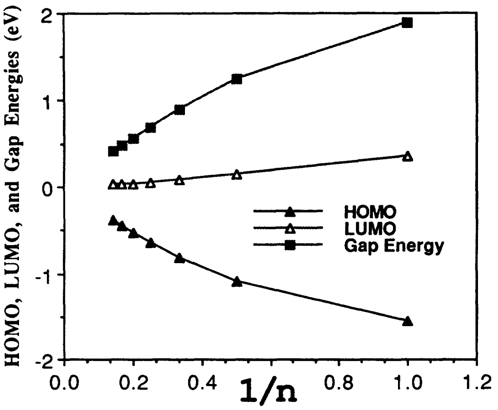

FIG. 2. The HOMO, LUMO, and gap energies (in units of eV) versus $1/n$ for various fullerenes C_{60n^2}.

The authors gratefully acknowledge stimulating and useful discussions with S. Fahy. FN acknowledges partial support from GE, the NSF through Grant No. DMR-90-01502, and SUN Microsystems.

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