Analytical application of the recursion and moments methods to the electronic structure of C\textsubscript{60}:
Exact solution for the \(\pi\) and \(\sigma\) states

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The recursion and moments methods are applied analytically to study the electronic structure of a neutral C\textsubscript{60} molecule. We employ a tight-binding Hamiltonian which considers both the \(s\) and \(p\) valence electrons of carbon. From the recursion method, we obtain exact results for the \(\pi\) and \(\sigma\) eigenvalues and eigenfunctions, including the highest occupied molecular orbital and the lowest unoccupied molecular orbital states. We also compute the Green’s function in analytic closed form and obtain the local density of states around several ring clusters, which can be probed experimentally by using, for instance, a scanning tunneling microscope. From the method of moments, identical results for the energy spectrum are also derived. In addition, the local density of states on one carbon atom is obtained; from this we can derive the degree of degeneracy of the energy levels.

I. INTRODUCTION AND SUMMARY OF RESULTS

Since the discovery of a simple technique for the production in bulk quantities of fullerenes, undoped and doped C\textsubscript{60} molecules have generated enormous interest among chemists, physicists, and materials scientists. In C\textsubscript{60}, carbon atoms sit at the 60 vertices of the pentagons and hexagons of a truncated icosahedron. The carbon-carbon bonds are of two different lengths: 1.46 Å for the single bonds (bonds on the pentagons) and 1.40 Å for the double bonds (bonds on the hexagons not shared by a pentagon). The single (double) bonds are denoted by solid (dotted) lines throughout the figures in this paper. The literature on C\textsubscript{60} is vast, and here we do not attempt a review. The interested reader is referred to Refs. 1–7 and papers listed therein.

In this work, we focus on an analytical study of the electronic structure of a single neutral C\textsubscript{60} molecule. We model this system through a tight-binding Hamiltonian [Eq. (1)] which considers both the \(s\) and \(p\) valence electrons of carbon. For decades, the recursion method and method of moments have been successfully applied to the electronic structure calculations in a variety of physical systems. However, most of these applications have been purely numerical. Furthermore, the relationship between these two methods has rarely been investigated thoroughly. The goal of this paper is to analytically apply these two methods to study the electronic structure of a C\textsubscript{60} molecule. Relations between these two approaches will be discussed.

This paper is organized as follows. In Sec. II, we discuss the physical nature and types of interaction between these valence electrons, with a total number of 240. The couplings can be separated into two main contributions: coming from the \(\pi\)-bonded and \(\sigma\)-bonded electrons.

We first focus on the \(\pi\) states. In Sec. III we use the recursion method to analytically solve the Hamiltonian for the \(\pi\) electrons. We derive closed-form expressions for their energy eigenvalues and eigenfunctions—including the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)—for two cases: equal and unequal hopping integrals for the single and double bonds. The main results concerning the \(\pi\)-state eigenvalues and eigenfunctions are summarized in Tables III, IV, and V. The physical nature of the wave functions of the HOMO and LUMO is discussed in Sec. III D. The beauty of the recursion method for C\textsubscript{60} lies in the fact that the recurrence is simple and terminates very quickly (e.g., after four iterations only), providing exact and very concise expressions for the parameters of the recursion. Thus, the dimensionality of the problem is reduced by a factor of 15, namely from 60\times60 to 4\times4.

The same results for the energy spectrum of the \(\pi\) states are derived in Sec. IV by using the method of moments. The main ingredient in this approach is the analytical computation of sums over contributions from all paths starting and ending at the same site, each one with its corresponding kinetic energy. The spirit of this approach follows Feynman’s program: to compute physical quantities from sums over all paths. In addition, the local density of states (LDOS) on one carbon atom is obtained; from this we can derive the degree of degeneracy of the energy levels.

In the two sections mentioned above, we provide detailed descriptions of the steps (e.g., the choice of appropriate starting states incorporating the physical properties of the system, and the iteration schemes) employed in the analytic application of the recursion and moments methods to C\textsubscript{60}. Furthermore, every step of either approach is exact. All the calculations are done analytically, either by hand or with the assistance of computer symbolic manipulation software. Diagonalizations are achieved by iteratively applying the Hamiltonian on simple initial states.

The relations between the recursion and moments methods are discussed in Sec. V. There it will be seen that while these two approaches are related to each other, each one has its own advantages. These methods are significantly different from the ones used so far. Furthermore, they are neither numerical nor require the use of group theory. For a lucid and clear account of a very different approach, based on group theory and focused only on the \(\pi\) states, the reader is referred to Ref. 3.

In Sec. VI, we present the precise algebraic expressions, derived from the Green’s functions, as well as plots of the LDOS around several ring clusters (i.e., a carbon atom, a
pentagon ring, and a hexagon ring; also for two opposite carbon atoms, pentagons, and hexagons). We find that around a pentagon ring the LDOS is large at low energies. This is related to the fact that a pentagon has zero double bonds and five single bonds. On the other hand, around a hexagon ring the LDOS is large at high energies. This is because a hexagon has three double bonds and three single bonds. The LDOS is relevant to the several important experimental techniques which probe the local spectroscopy of molecules; for instance, by using a scanning tunneling microscope, as described in the review in Ref. 9.

In Sec. VII we discuss the solutions of the $\sigma$-states Hamiltonian Eq. (3). To describe the $\sigma$ states, the coupling between orbitals on the same atom and that between orbitals along the same bond are both taken into account. By following a "one band—two band" transformation, the eigenvalues and eigenfunctions for the $\sigma$ states are then analytically obtained.

II. ELECTRONIC STATES

To investigate the electronic properties of a single C$_{60}$ molecule, we consider the four carbon valence electrons 2$s$, 2$p_x$, 2$p_y$, and 2$p_z$ in the tight-binding Hamiltonian

$$H_T = \sum_{i,\alpha} \epsilon_{\alpha} c_{i\alpha}^+ c_{i\alpha} + \sum_{(ij),\alpha,\beta} t_{\alpha\beta} c_{i\alpha}^+ c_{j\beta}. \quad (1)$$

Here, $i$ denotes the carbon site and $\alpha$ denotes the valence orbitals 2$s$, 2$p_x$, 2$p_y$, and 2$p_z$. Also, $\epsilon_{\alpha}$ is the orbital energy and $t_{\alpha\beta}$ is the hopping matrix element between orbitals on the nearest-neighboring sites $i$ and $j$. The 60 2$p_z$ orbitals, each pointing along the outward radial direction, are hybridized to form $\pi$ states. The other three orbitals 2$s$, 2$p_x$, and 2$p_y$, distributed on the plane tangential to the surface of the molecule, are hybridized along the lattice bonds to form $\sigma$ bonding and antibonding states.

Let us assume that the mixture of these three orbitals at each site produces three $sp^2$ hybrid orbitals: $sp^2_z$ along the double bond and $sp^2_x$ and $sp^2_y$ along the two single bonds, respectively. From a physical point of view, the 60 outer $\pi$ orbitals are relevant to the conducting properties of the molecules and the 180 $\sigma$ orbitals are mainly responsible for the elastic properties. The former are also responsible for the bond dimerization. Also, only $\pi$ states occur around the Fermi energy.

As a result of its planar structure, the $\pi$ electrons in graphite contain only pure 2$p_z$ orbitals. Nevertheless, in the curved structure of C$_{60}$, an extra small component from 2$s$, 2$p_x$, and 2$p_y$, is induced along the radial direction due to the surface curvature. The interaction between the $\pi$ orbitals in C$_{60}$ is then slightly increased in comparison to that in graphite. However, since this component is very small, the overlap integral between $\pi$ and $\sigma$ orbitals is negligible. The nonzero Hamiltonian parameters used here are the same ones as in Ref. 2.

The original Hamiltonian Eq. (1) can thus be written in terms of $H_\pi$ and $H_\sigma$ as $H_T = H_\pi \oplus H_\sigma$, where

$$H_\pi = -\sum_{(ij)} t_{ij} c_{i\pi}^+ c_{j\pi}, \quad (2)$$

and

$$H_\sigma = -V_1 \sum_{i,\alpha,\beta} c_{i\alpha}^+ c_{i\beta} - V_2 \sum_{(ij)} c_{i\alpha}^+ c_{j\alpha}. \quad (3)$$

The electronic $\pi$-states Hamiltonian Eq. (2) describes the kinetic energy of the 2$p_z$ electrons hopping on the 60 vertices of a C$_{60}$ fullerene and $t_{ij}$ is the hopping integral between nearest-neighboring atoms $i$ and $j$. The hopping integrals are considered unequal for single and double bonds. Also, $c_{i\alpha}^+$ is the electron operator creating a 2$p_z$ orbital on the atom located at vertex $i$. A constant term corresponding to the onsite 2$p_z$ orbital energy is omitted in Eq. (2). In the $\sigma$-states Hamiltonian Eq. (3), $\alpha = sp^2_x$, $sp^2_y$, and $sp^2_z$ denotes the hybridized orbitals. Also, $V_1$ stands for the hopping integral between orbitals on the same carbon atom and $V_2$ stands for that between orbitals on different atoms that are associated with the same bond (the length difference between single and double bonds is neglected here). A more detailed discussion on the origin of $V_1$ and $V_2$ is presented in Appendix A.

Admittedly, this is a simplified model (like the "Ising model") for the electronic structure of C$_{60}$, the "hydrogen atom" of the main fullerene family of C$_{60n2z}$ molecules. However, its understanding is a convenient stepping stone to the study of more complex models. The spectroscopy of, for instance, the hydrogen atom can be analytically solved by using several different approaches. These lead to the same analytical expressions for the eigenvalues and eigenvectors. In spite of the fact that modern computers can easily obtain numerical expressions for them, it is useful to have analytic results. In fact, analytical solutions have always been pursued in the area of spectroscopy of atoms, molecules, and clusters. In this paper, we pursue several approaches to the analytical study of the spectroscopy of an important molecule. We would like to emphasize that the approaches described here are not intended to substitute more traditional methods, but to present alternative viewpoints and complementary results.

III. RECURSION METHOD APPROACH

A. Formulation

We first focus on the $\pi$-states Hamiltonian Eq. (2). Let us begin with a brief outline of the recursion method for obtaining the eigenvalues and eigenfunctions. First, one must choose an appropriate normalized starting state $|f_0\rangle$. Further states are iteratively generated by the three-term recurrence relation

$$H|f_n\rangle = a_n |f_n\rangle + b_{n+1} |f_{n+1}\rangle + b_n |f_{n-1}\rangle, \quad (4)$$

with the condition $b_n |f_{n-1}\rangle \equiv 0$. Here, the real parameters $a_n$ and $b_{n+1}$ are determined by

$$a_n = \langle f_n | H | f_n \rangle \quad (5)$$

and

$$b_{n+1} = \langle f_n | H | f_{n+1} \rangle = \langle f_{n+1} | H | f_n \rangle. \quad (6)$$

By convention, the $b$’s are chosen to be positive. The process terminates at $|f_{N-1}\rangle$ with the last recurrence $H|f_{N-1}\rangle = a_{N-1} |f_{N-1}\rangle + b_{N-1} |f_{N-2}\rangle$. The constructed orthonormal
states \( \{|f_0\rangle, |f_1\rangle, \ldots, |f_{N-1}\rangle\} \) along with the parameters \( \{a_0, a_1, \ldots, a_{N-1}\} \) and \( \{b_1, b_2, \ldots, b_{N-1}\} \) thus constitute the "chain model" of a given Hamiltonian. The representation of \( \mathbf{H} \) in the new basis \( \{|f_n\rangle\} \) is in a tridiagonal form.

The energy levels can be achieved by constructing the following polynomials with \( P_{-1}(E) = 0 \) and \( P_0(E) = 1 \):

\[
P_{n+1}(E) = \frac{(E-a_n)P_n(E) - b_nP_{n-1}(E)}{b_{n+1}}.
\]

The eigenvalues \( E_\lambda \) are determined by the \( N \) zeros of the last polynomial \( P_N(E) = 0 \), with an arbitrary nonzero \( b_N \). It follows then that the eigenfunctions are

\[
\frac{1}{\mathcal{N}_\lambda} \sum_{n=0}^{N-1} P_n(E_\lambda)|f_n\rangle,
\]

where \( \mathcal{N}_\lambda = [\sum_{n=0}^{N-1} P_n^2(E_\lambda)]^{1/2} \) are the normalization constants for the eigenfunctions, and \( P_0(E_\lambda) \) always equals 1.

So far, we have briefly outlined the recursion method. We now come to the application of this approach to the electronic structure of a fullerene molecule. For convenience, we work in units of the single-bond hopping integral. The hopping amplitude is therefore 1 for every single bond and \( t \) for each double bond. It has been pointed out that the value of \( t \) is about 1.1. We will use two alternative sets (denoted by \( \mathcal{A} \) and \( \mathcal{B} \)) of starting states. Each set consists of two initial states from which the whole energy spectrum can be derived, and the final results do not depend on the choice of initial bases. Both sets lead to the same solutions for the eigenvalues and eigenfunctions. From the physical point of view, this consistency ensures the equivalent interpretation of the results from these two sets of initial states. We denote by \( |j\rangle \) the \( 2p_z \) orbital centered at the \( j \)th atom. For convenience of visualization, in all our figures we flatten the truncated icosahedral structure of \( \text{C}_{60} \) into a plane. Note that labelings vary according to the different choices of initial states.

### B. Case \( \mathcal{A} \)

The first set of initial states starts from a five-atom pentagon ring [see Fig. 1(a)] and a six-atom hexagon ring [see Fig. 1(b)]. Starting from a pentagon ring, we choose the initial state \( |u_0\rangle \) as a linear combination of the five orbitals on it,

\[
|u_0\rangle = \frac{1}{\sqrt{5}} \sum_{j=1}^{5} |j\rangle.
\]

Here the labeling is as shown in Fig. 1(a). From now on, \( \mathbf{H} \) will denote \( \mathbf{H}_\mathcal{A} \) unless specified otherwise (e.g., \( \mathbf{H}_\mathcal{B} \)). As an illustration, we present here the calculation of the first recurrence,

\[
\mathbf{H}|u_0\rangle = -\frac{1}{\sqrt{5}} [(1|2) + |5\rangle + t|6\rangle + (|1\rangle + |3\rangle + t|7\rangle) + (2|4\rangle + t|8\rangle) + (|3\rangle + |5\rangle + t|9\rangle) + (|1\rangle + |4\rangle + t|10\rangle)]
\]

We then obtain \( a_0 = -2 \), \( b_1 = t \), and \( |u_1\rangle = -1/\sqrt{5} \sum_{j=6}^{10} |j\rangle \). Following the same procedure, we can construct further states and obtain the parameters \( a \)’s and \( b \)’s at the same time. The beauty of the recursion method for \( \text{C}_{60} \) lies in the fact that the recurrence terminates very quickly, exactly at \( |u_7\rangle \). As a result, we have exact and very concise formulas for \( a_0 \) through \( a_7 \), and \( b_1 \) through \( b_7 \).
TABLE I. States and parameters for case $\varphi$ in the recursion method approach. It is interesting to notice that $a_n = a_{7-n}$ and $b_n = b_{8-n}$ for \( n = 4,5,6,7 \).

<table>
<thead>
<tr>
<th>( n )</th>
<th>Starting from a pentagon ring</th>
<th>( \Delta a_n )</th>
<th>( \Delta b_n )</th>
<th>Starting from a hexagon ring</th>
<th>( \Delta a_n )</th>
<th>( \Delta b_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( \frac{1}{\sqrt{5}} \sum_{j=1}^6 (-1)^{j+1}</td>
<td>j\rangle )</td>
<td>-2</td>
<td></td>
<td>( \frac{1}{\sqrt{6}} \sum_{j=1}^6 (-1)^{j+1}</td>
<td>j\rangle )</td>
</tr>
<tr>
<td>1</td>
<td>( \frac{1}{\sqrt{2}} \sum_{j=1}^6 (-1)^{j+1}</td>
<td>j\rangle )</td>
<td>0</td>
<td>( t )</td>
<td>( \frac{1}{\sqrt{6}} \sum_{j=1}^{15} (-1)^{j+1}</td>
<td>j\rangle )</td>
</tr>
<tr>
<td>2</td>
<td>( \frac{1}{\sqrt{6}} \sum_{j=0}^{14} (-1)^{j+1}</td>
<td>j\rangle )</td>
<td>( \sqrt{2} )</td>
<td></td>
<td>( \frac{1}{\sqrt{6}} \sum_{j=2}^{24} (-1)^{j+1}</td>
<td>j\rangle )</td>
</tr>
<tr>
<td>3</td>
<td>( \frac{1}{\sqrt{6}} \sum_{j=0}^{14} (-1)^{j+1}</td>
<td>j\rangle )</td>
<td>-1</td>
<td>1</td>
<td>( \frac{1}{\sqrt{6}} \sum_{j=2}^{24} (-1)^{j+1}</td>
<td>j\rangle )</td>
</tr>
<tr>
<td>4</td>
<td>( \frac{1}{\sqrt{6}} \sum_{j=0}^{14} (-1)^{j+1}</td>
<td>j\rangle )</td>
<td>-1</td>
<td>( t )</td>
<td>( \frac{1}{\sqrt{6}} \sum_{j=2}^{24} (-1)^{j+1}</td>
<td>j\rangle )</td>
</tr>
<tr>
<td>5</td>
<td>( \frac{1}{\sqrt{6}} \sum_{j=0}^{14} (-1)^{j+1}</td>
<td>j\rangle )</td>
<td>-1</td>
<td>( t )</td>
<td>( \frac{1}{\sqrt{6}} \sum_{j=2}^{24} (-1)^{j+1}</td>
<td>j\rangle )</td>
</tr>
<tr>
<td>6</td>
<td>( \frac{1}{\sqrt{6}} \sum_{j=0}^{14} (-1)^{j+1}</td>
<td>j\rangle )</td>
<td>( \sqrt{2} )</td>
<td></td>
<td>( \frac{1}{\sqrt{6}} \sum_{j=2}^{24} (-1)^{j+1}</td>
<td>j\rangle )</td>
</tr>
<tr>
<td>7</td>
<td>( \frac{1}{\sqrt{6}} \sum_{j=0}^{14} (-1)^{j+1}</td>
<td>j\rangle )</td>
<td>-2</td>
<td>( t )</td>
<td>( \frac{1}{\sqrt{6}} \sum_{j=2}^{24} (-1)^{j+1}</td>
<td>j\rangle )</td>
</tr>
</tbody>
</table>

Similarly, starting from a linear combination of the six orbitals on a hexagon ring, we have the initial state \(|v_0\rangle\) as

\[
|v_0\rangle = \frac{1}{\sqrt{6}} \sum_{j=1}^6 (-1)^{j+1} |j\rangle,
\]

where the labeling is referred to Fig. 1(b). The choice of alternating signs, \((-1)^{j+1}\), meets the threefold symmetry requirement of a hexagon ring in \( C_{60} \), with alternating single and double bonds. Again, the recurrence terminates at \(|v_7\rangle\).

We then obtain another group of parameters \( a' \)'s and \( b' \)'s. All these \(|u_n\rangle\) and \(|v_n\rangle\) states, as well as their respective parameters \( a_n \) and \( b_{n+1} \), are summarized in Table I.

Through these two groups of \( a' \)'s and \( b' \)'s, we can, respectively, construct two polynomials \( P^P(E) \) and \( P^H(E) \) which are of eighth degree in \( E \). Here the superscript \( p \) for pentagon (h for hexagon) refers to the polynomial constructed from the group of \( a' \)'s and \( b' \)'s generated by \(|u_0\rangle\) (\(|v_0\rangle\)). The roots of these two polynomials can be analytically obtained and correspond to the electronic energy levels. It follows then that we have a total of 16 distinct eigenvalues. When \( t = 1 \), a common root \(-1\) exists for both polynomials \( P^P \) and \( P^H \). We thus have 15 distinct energy levels. It is also straightforward to obtain the eigenvectors through Eq. (8).

C. Case $\varphi$

In this approach, we exploit the symmetry property that the inversion operator leaves the \( C_{60} \) molecule invariant. We therefore take the first (second) starting state \(|\phi_0\rangle\) (\(|\varphi_0\rangle\)) as a linear combination of the orbitals on two opposite (i.e., antipodes) pentagon (hexagon) rings

\[
|\phi_0\rangle = \frac{1}{\sqrt{10}} \sum_{j=1}^5 (|j\rangle + \varphi |j\rangle'),
\]

where the site labels are presented in Fig. 1(a) [1(b)] for the first (second) starting state. Here \( \varphi \) stands for parity, with the value \(+1\) or \(-1\). Note that atom \( j \) and atom \( j' \) are antipodes. Following the same procedure, we find the very convenient and remarkable result that the recurrence terminates even faster at \(|\phi_3\rangle\) (\(|\varphi_3\rangle\)) for the first (second) initial state. Due to the two possible values of \( \varphi \), we have two different results for \( a_3 \) for each starting state. In Appendix B we present the calculation of the last recurrence, namely those for \(|\phi_3\rangle\) and \(|\varphi_3\rangle\). It can be clearly seen that \( H|\phi_3\rangle \) generates two possible values for \( a_3 \) and no further state; and so does \( H|\varphi_3\rangle \). As a consequence, we obtain four groups of \( \{a_0, a_1, a_2, a_3\} \) and \( \{b_1, b_2, b_3\} \).

All the states \(|\phi_0\rangle\) and \(|\varphi_0\rangle\), as well as their respective parameters \( a_n \) and \( b_{n+1} \), are listed in Table II. It follows that we can construct four polynomials \( P_4^{P+}(E) \), \( P_4^{P-}(E) \), \( P_4^{H+}(E) \), and \( P_4^{H-}(E) \). Each one is of fourth degree in \( E \). The superscript \( p \) stands for the polynomial constructed from \(|\phi_0\rangle\) with \( \varphi \) equal to \(+1\), and similarly for the others. With the choice of \( b_1 = 1/b_2 b_3 \), these polynomials can be explicitly written as

\[
P_4^{P+}(E) = E^4 + (2t + 3)E^3 + (5t - 1)E^2 - (2t^3 - t^2 + 8)E
\]

\[-(t + 2)(t^3 - t^2 + t + 2),
\]

\[
P_4^{P-}(E) = E^4 + (2t^2 + 1)E^3 - (5t^2 - 4t + 8)E
\]

\[+(t - 1)(t^3 + t^2 - 4)t - 4),
\]

\[
P_4^{H+}(E) = E^4 - 2(t + 1)E^3 + (3t - 1)E^2 - (2t^3 + t^2 + 2)E
\]

\[-(t^2 + 1)(t^2 + t - 1),
\]

and

and
On the other hand, the threefold degenerate LUMO state is obtained from the initial state \( u \) with a threefold symmetry axis passing through their centers.

As to the eigenfunctions, we present in Table V those for the HOMO and LUMO in terms of the single-bond hopping integral \( t_1 \) and the double-bond hopping integral \( t_2 \). Thus, eigenvalues for the limiting cases \( t_1 = 0 \) or \( t_2 = 0 \) can also be readily inferred.

It is interesting to notice that the fivefold degenerate HOMO state is obtained from the initial state \( |\phi_0\rangle \) (with negative parity), made of orbitals on two opposite hexagons with a threefold symmetry axis passing through their centers. On the other hand, the threefold degenerate LUMO state is obtained from the initial state \( |\phi_0\rangle \) (with negative parity), consisting of orbitals on two opposite pentagons with a fivefold symmetry axis passing through their centers.

As to the eigenfunctions, we present in Table V those for the HOMO and LUMO in terms of \( t = t_1 / t_2 \), the ratio of the hopping matrix elements for single and double bonds. Since the respective degree of degeneracy for each eigenvalue can be acquired from the local density of states on a carbon atom (discussed in a later section), the other degenerate eigenvectors can be generated by standard group theory analysis. This is outside the scope of the present paper. We therefore only present these eigenfunctions derived from the pure application of the recursion method.

By analytically solving these four polynomials, we obtain the same 16 eigenvalues obtained above (case \( \mathcal{R} \)). Similarly we can obtain the eigenvectors, which are also equal to those obtained from the alternative set \( \mathcal{R} \) of initial states.

### D. Results for the \( \pi \)-state eigenvalues and eigenfunctions of \( \text{C}_{60} \)

In Table III, we summarize the eigenvalues and the corresponding eigenvectors for the case \( t = 1 \). In Table IV, we present the closed-form eigenvalues—including the HOMO and LUMO energies—explicitly expressed in terms of the single-bond hopping integral \( t_1 \) and the double-bond hopping integral \( t_2 \). Thus, eigenvalues for the limiting cases \( t_1 = 0 \) or \( t_2 = 0 \) can also be readily inferred.

It is interesting to note that the fivefold degenerate HOMO state is obtained from the initial state \( |\varphi_0\rangle \) (with negative parity), made of orbitals on two opposite hexagons with a threefold symmetry axis passing through their centers. On the other hand, the threefold degenerate LUMO state is obtained from the initial state \( |\phi_0\rangle \) (with negative parity), consisting of orbitals on two opposite pentagons with a fivefold symmetry axis passing through their centers.

As to the eigenfunctions, we present in Table V those for the HOMO and LUMO in terms of \( t = t_1 / t_2 \), the ratio of the hopping matrix elements for single and double bonds. Since the respective degree of degeneracy for each eigenvalue can be acquired from the local density of states on a carbon atom (discussed in a later section), the other degenerate eigenvectors can be generated by standard group theory analysis. This is outside the scope of the present paper. We therefore only present these eigenfunctions derived from the pure application of the recursion method.

It is instructive to notice that the following points further support the results for the degeneracy. They are (1) the sum of the product of energy and its corresponding degeneracy equals the trace of the Hamiltonian, which is zero; (2) the number of states with even parity equals that with odd parity; and (3) the behavior of the eigenvalues can be easily studied in the limits when either \( t_1 = 0 \) or \( t_2 = 0 \).

### E. Relations between alternatives \( \mathcal{R} \) and \( \mathcal{B} \)

It is worthwhile to point out the following relations between the cases \( \mathcal{R} \) and \( \mathcal{B} \) presented before. First, \( P_4^B(E) = P_4^B(E) P_4^B(E) \) and \( P_4^B(E) = P_4^B(E) P_4^B(E) \) up to an overall constant factor. In other words, roots solved from \( P_4^B(E) \) are identical to those solved from \( P_4^B(E) \) and \( P_4^B(E) \). Second, from Tables I and II we can see that, for \( n = 0, 1, 2 \) and \( 3 \),

\[
|\phi_n\rangle = \frac{1}{\sqrt{2}} (|u_n\rangle - \mathcal{R}|u_{7-n}\rangle)
\]

and

### Table II. States and parameters for case \( \mathcal{B} \) in the recursion method approach. The parity \( \mathcal{R} \) can be \( +1 \) or \( -1 \).

| \( n \) | \( |\phi_n\rangle \) | \( a_n \) | \( b_n \) |
| --- | --- | --- | --- |
| 0 | \( \frac{1}{\sqrt{10}} \sum_{j=1}^{5} |j\rangle + \mathcal{R}|j\rangle \) | -2 | |
| 1 | \( \frac{1}{\sqrt{10}} \sum_{j=6}^{10} |j\rangle + \mathcal{R}|j\rangle \) | 0 | \( t \) |
| 2 | \( \frac{1}{\sqrt{20}} \sum_{j=11}^{20} |j\rangle + \mathcal{R}|j\rangle \) | -\( t \) | \( \frac{\sqrt{2}}{2} \) |
| 3 | \( -\frac{1}{\sqrt{20}} \sum_{j=21}^{30} |j\rangle + \mathcal{R}|j\rangle \) | \(-1 + \mathcal{R} \) | 1 |

### Starting from two opposite hexagon rings

| \( n \) | \( |\varphi_n\rangle \) | \( a_n \) | \( b_n \) |
| --- | --- | --- | --- |
| 0 | \( \frac{1}{\sqrt{12}} \sum_{j=1}^{6} (-1)^{j+1} |j\rangle + \mathcal{R}|j\rangle \) | 1 + \( t \) | |
| 1 | \( \frac{1}{\sqrt{12}} \sum_{j=7}^{12} (-1)^{j+1} |j\rangle + \mathcal{R}|j\rangle \) | 0 | 1 |
| 2 | \( \frac{1}{\sqrt{12}} \sum_{j=13}^{18} (-1)^{j+1} |j\rangle + |j+3\rangle + |j+6\rangle + \mathcal{R}(|j\rangle + |j+3\rangle + |j+6\rangle) \) | 1 | \( t \) |
| 3 | \( \frac{1}{\sqrt{12}} \sum_{j=19}^{24} (-1)^{j+1} |j\rangle + |j+3\rangle + |j+6\rangle + \mathcal{R}(|j\rangle + |j+3\rangle + |j+6\rangle) \) | \( \mathcal{R} \) | 1 |
Third, for those eigenvalues $E_A$ which are common roots of $P^a_8$ and $P^{a+}_4$, or common roots of $P^b_8$ and $P^{b+}_4$,

$$P_{7-n}(E_A) = -P_n(E_A).$$

Also for those eigenvalues $E_A$ which are common roots of $P^a_8$ and $P^{a-}_4$, or common roots of $P^b_8$ and $P^{b-}_4$,

$$P_{7-n}(E_A) = P_n(E_A).$$

Here, all the $P_n(E_A)$’s refer to the polynomials constructed in the case $\mathcal{A}$ and $n=0,1,2$, and 3. Fourth, $P_1(E_A)$, $P_2(E_A)$, and $P_3(E_A)$ calculated from the two alternatives $\mathcal{A}$ and $\mathcal{B}$ are the same. Fifth, for the eigenvector with respect to the same eigenvalue, the normalization constants $\mathcal{A}$ and $\mathcal{B}$, calculated in $\mathcal{A}$ and $\mathcal{B}$, respectively, satisfy $\mathcal{A} \mathcal{B} = \sqrt{2} \mathcal{B} \mathcal{A}$.

From the above five properties, the equivalence of results from both alternatives becomes clear. As an example, for an eigenvalue $E_A$ which is a common root of $P^a_8$ and $P^{a+}_4$, we can obtain the eigenvector $\{|\Psi_A\rangle\}$ from $\mathcal{A}$ as

$$|\Psi_A\rangle = \frac{1}{\sqrt{2}} \sum_{n=0}^{7} P_n(E_A) |u_n\rangle$$

where the last equality is just the result obtained directly from $\mathcal{B}$. In fact, from the results of alternative $\mathcal{B}$, we can understand the parity property associated with $C_{60}$.

### IV. METHOD OF MOMENTS APPROACH

#### A. Methodology and application

In this method, the first and central task is the computation of moments, defined by

$$\mathcal{M}_l = \langle j | H | j \rangle,$$

where the order $l$ is a positive integer. Note that $\mathcal{M}_0 = 1$ when $l = 0$. The physical meaning of the above quantum-mechanical expectation value is as follows. The Hamiltonian

| $E_A$ | $P_1(E_A)$ | $P_2(E_A)$ | $P_3(E_A)$ | $\mathcal{A} \mathcal{B}^2$ | $|f_n\rangle$ |
|-------|------------|------------|------------|-----------------|------------|
| $-3$  | $-1$       | $\sqrt{2}$ | $-\sqrt{2}$ | 6               | $|\phi_5^+\rangle$ |
| $-1$  | $1$        | $-\sqrt{2}$ | $-\sqrt{2}$ | 6               | $|\phi_6^+\rangle$ |
| $(-1 + \sqrt{13})/2$ = 1.303 | $(3 + \sqrt{13})/2$ | $\sqrt{2}(3 + \sqrt{13})/4$ | $\sqrt{2}/2$ | $(39 + 9 \sqrt{13})/4$ | $|\phi_7^+\rangle$ |
| $(-1 - \sqrt{13})/2$ = -2.303 | $(3 - \sqrt{13})/2$ | $\sqrt{2}(3 - \sqrt{13})/4$ | $\sqrt{2}/2$ | $(39 - 9 \sqrt{13})/4$ | $|\phi_8^+\rangle$ |
| $(-3 + \sqrt{5} + \alpha)/4$ = 1.438 | $5 + \sqrt{5} + \alpha$ | $\sqrt{2}[6 + 2 \sqrt{5} + (\sqrt{5} + 1)\alpha]$ | $\sqrt{2}[4 + 8 \sqrt{5} + (\sqrt{5} - 1)\alpha]$ | $95 + 5 \sqrt{5} + (25 + \sqrt{5})\alpha$ | $|\phi_9^+\rangle$ |
| $(-3 + \sqrt{5} - \alpha)/4$ = -1.820 | $5 + \sqrt{5} - \alpha$ | $\sqrt{2}[6 + 2 \sqrt{5} - (\sqrt{5} + 1)\alpha]$ | $\sqrt{2}[4 - 8 \sqrt{5} - (\sqrt{5} - 1)\alpha]$ | $95 + 5 \sqrt{5} + (25 - \sqrt{5})\alpha$ | $|\phi_9^-\rangle$ |
| $(-3 + \sqrt{5} + \beta)/4$ = 0.139 | $5 - \sqrt{5} + \beta$ | $\sqrt{2}[6 - 2 \sqrt{5} - (\sqrt{5} - 1)\beta]$ | $\sqrt{2}[4 - 8 \sqrt{5} - (\sqrt{5} + 1)\beta]$ | $95 - 5 \sqrt{5} + (25 + \sqrt{5})\beta$ | $|\phi_9^-\rangle$ |
| $(-3 - \sqrt{5} - \beta)/4$ = -2.757 | $5 - \sqrt{5} - \beta$ | $\sqrt{2}[6 - 2 \sqrt{5} - (\sqrt{5} - 1)\beta]$ | $\sqrt{2}[4 - 8 \sqrt{5} + (\sqrt{5} + 1)\beta]$ | $95 - 5 \sqrt{5} + (25 - \sqrt{5})\beta$ | $|\phi_9^-\rangle$ |
| 2    | 0          | -1         | -1         | 3               | $|\phi_{10}^+\rangle$ |
| $-1$  | 3          | -3         | -2         | 15              | $|\phi_{10}^+\rangle$ |
| $(3 + \sqrt{5})/2$ = 2.618 | $(1 + \sqrt{5})/2$ | $(-1 + \sqrt{5})/2$ | $(3 - \sqrt{5})/2$ | $(15 - 5 \sqrt{5})/2$ | $|\phi_{10}^-\rangle$ |
| $(3 - \sqrt{5})/2$ = 0.382 | $(-1 - \sqrt{5})/2$ | $(-1 - \sqrt{5})/2$ | $(3 + \sqrt{5})/2$ | $(15 + 5 \sqrt{5})/2$ | $|\phi_{10}^-\rangle$ |
| $(1 + \sqrt{5})/2$ = 1.618 | $(-3 + \sqrt{5})/2$ | $(-1 + \sqrt{5})/2$ | $(1 - \sqrt{5})/2$ | $(15 - 3 \sqrt{5})/2$ | $|\phi_{10}^-\rangle$ |
| $(1 - \sqrt{5})/2$ = -0.618 | $(-3 - \sqrt{5})/2$ | $(-1 + \sqrt{5})/2$ | $(1 + \sqrt{5})/2$ | $(15 + 3 \sqrt{5})/2$ | $|\phi_{10}^-\rangle$ |
| $(1 + \sqrt{17})/2$ = 2.562 | $(-3 + \sqrt{17})/2$ | $(5 - \sqrt{17})/2$ | $-4 + \sqrt{17}$ | 51 - 12 $\sqrt{17}$ | $|\phi_{10}^-\rangle$ |
| $(1 - \sqrt{17})/2$ = -1.562 | $(-3 - \sqrt{17})/2$ | $(5 + \sqrt{17})/2$ | $-4 - \sqrt{17}$ | 51 + 12 $\sqrt{17}$ | $|\phi_{10}^-\rangle$ |
TABLE IV. The eigenvalues and the corresponding degree of degeneracy for $C_{60}$ with a single-bond hopping-integral $t_1$ and a double-bond hopping-integral $t_2$. Note that $t_2 = 1.1 t_1$. The characteristic polynomials from which these eigenvalues are solved are indicated in the left-hand column. Here $\tau = \{16 \, t_2^2 - 8(1 + \sqrt{5}) \, t_1 + 10(3 + \sqrt{5}) \, t_1^2\}$ and $\gamma = \{16 \, t_2^2 - 8(1 - \sqrt{5}) \, t_1 + 10(3 - \sqrt{5}) \, t_1^2\}$. Also $\eta$ and $\xi$ satisfy $(16 \, t_2^2 - 24 \, t_1 t_2 + 12 \, t_1^2 + 25 \, t_1^4) = 54(\eta^2 - 3 \, \eta \, \xi)$ and $[3 \, (64 \, t_1^2 - 160 \, t_2 t_1 + 288 \, t_1^2) - 200 \, t_2 t_1 + 125 \, t_1^2] = 18(3 \, \eta^2 - \xi)$. Notice that the fivefold degenerate HOMO (threefold degenerate LUMO) energy, as indicated, is solved from the polynomial constructed from the starting state $|\phi_{\alpha_0}(\eta)|$—with negative parity—which consists of orbitals on two opposite hexagons (pentagons) with a threefold (fivefold) symmetry axis passing through their centers.

<table>
<thead>
<tr>
<th>Energy</th>
<th>Degeneracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-(2 t_1 + t_2)$</td>
<td>1</td>
</tr>
<tr>
<td>$-(t_1 + t_2)/3 - \eta + \sqrt{3} \xi$</td>
<td>3</td>
</tr>
<tr>
<td>$-(t_1 + t_2)/3 - \eta - \sqrt{3} \xi$</td>
<td>3</td>
</tr>
<tr>
<td>$-\tau/4$</td>
<td>3</td>
</tr>
<tr>
<td>$-\gamma/4$</td>
<td>3</td>
</tr>
<tr>
<td>$P_{4 , \alpha}^h$</td>
<td>3</td>
</tr>
<tr>
<td>$P_{4 , \alpha}^h$</td>
<td>3</td>
</tr>
<tr>
<td>$P_{4 , \alpha}^h$</td>
<td>3</td>
</tr>
</tbody>
</table>

$H$ is applied $l$ times to an initial $2p_z$ electron state $|j\rangle$, localized at carbon site $j$. Each time $H$ is applied, the electron gains a certain amount of kinetic energy depending upon the bond (single or double) it travels. This enables the electron to hop through $l$ bonds, reaching the final state $H^l |j\rangle$. The moment $\.\langle j|l|$ just equals the total kinetic energy gained by the electron returning to the starting site $j$ after hopping $l$ steps.

It is obvious that $\.\langle j|0|$ will be zero when the $l$-hops path does not return to the starting site. In other words, $\.\langle j|1|$ is the absolute value of the moment $\.\langle j|$ the total number of closed paths of $l$ steps starting and ending at the same site. The spirit of this approach follows Feynman’s program: to compute physical quantities from sums over paths.

The moments can be calculated analytically by hand, as well as by computer using a symbolic manipulation program. Below we describe these two implementations starting from the former. Let us first examine the action of the Hamiltonian on an arbitrary state $|j\rangle$. This results in three nearest-neighbor atom states with an additional factor accounting for the respective bond hopping energy. For example,

**FIG. 2.** Site labels used in the moments method. Independent vertices are those with $j$ running from 1 to 24.
the adjacent nearest-neighboring vertices. Also the factor on each vertex is the sum of the factors on the three nearest-neighbor vertices times the bond hopping integral between vertices. It is then straightforward, with the aid of “the flattened C\textsubscript{60} graph,” to obtain all the factors on the available vertices for any power of the Hamiltonian. From its definition, it is evident that the moment of order \(l\) is just the factor on the vertex 1 for \(H'\). For example, \(\mathcal{M}_1 = 0\) (i.e., the number of closed paths obtained by moving one step is zero) and \(\mathcal{M}_2 = 2 + r^2\). By following this strategy, we can generate, one by one, all the moments to any order.

It is worthwhile to notice the mirror-symmetry between the left and right halves of C\textsubscript{60} for the atom vertices and bonds. So we need only concern ourselves with the factors on the vertices in the right part. Furthermore, because of the geometrical equivalence, with respect to vertex 1, of eight pairs of vertices (\(j\) and \(j'\) in Fig. 2), the total number of independent vertices can be reduced to 24. All calculations up to this point can be done analytically by hand.

An alternative analogous procedure can be implemented by using symbolic manipulation software on a computer. First, we define an auxiliary quantity, \(W_l(j)\), which is the sum over all possible paths of \(l\) steps on which an electron may hop from the vertex 1 to the vertex \(j\). From the connectivity of C\textsubscript{60}, we can then construct 24 independent recurrence relations. For instance, \(W_{l + 1}(1) = -tW_l(2) - 2W_l(3), \ W_{l + 1}(2) = -tW_l(1) - 2W_l(4), \ W_{l + 1}(3) = -tW_l(4) - W_l(1) - W_l(5)\). The recurrence relations state that the vertex \(j\) can be reached by taking the (1\(+l\))th step from the three nearest-neighbor vertices. The factors \(-t\) and \(-1\) account for the connecting bond-hopping integral. With the initial conditions \(W_0(1) = 1\) and \(W_0(j) = 0\) for the rest of \(j\)‘s, we can obtain the moments to any order as \(\mathcal{M}_l = W_l(1)\). We list \(\mathcal{M}_3\) through \(\mathcal{M}_9\) here: 0, \(t^4 + 8t^2 + 6, -2, t^6 + 18t^4 + 4t^3 + 48t^2 + 20, -14t^2 - 14, t^8 + 32t^6 + 16t^4 + 184t^2 + 48t^3 + 256t^2 + 70, \) and \(-54t^4 + 18t^3 - 162t^2 - 72, \) for \(l = 3, 4, \ldots, 9\). The moments \(\mathcal{M}_{10}\) through \(\mathcal{M}_{32}\) (the highest order moment needed to obtain the entire energy spectrum) are not presented here.

The correctness of the calculated moments \(\mathcal{M}_l\) is assured by the consistency of the results from these two approaches. It is evident that through these two implementations we can also obtain the quantities \(\langle 1|H'|j\rangle\) for \(j \neq 1\) which can be appropriately interpreted as the “sum-over-paths” between sites 1 and \(j\). For instance, \(\langle 1|H'|j\rangle\) just equals \(W_l(j)\).

To obtain the energy spectrum, we again utilize Eq. (7). So the next step is to express the parameters \(a_n\) and \(b_{n+1}\) in terms of the moments. We employ the following formulas: \(M_{n+1} = M_n + \sum_{k=0}^{l-1} M_{n+k}M_{n-1-k}\), \(n \geq 1; l = 0, 1, \ldots\) (14)

The \(a_n\)‘s and \(b_{n+1}\)‘s are obtained from the elements of the second and third columns as

| TABLE VI. Parameters \(a_n\) and \(b_n\) for \(n=0,1,\ldots,9\) calculated from the moments \(\mathcal{M}_l\) with \(l=1\) in the moment method for C\textsubscript{60}. Numbers in the denominator are relatively prime to those in numerator and all numbers in square root are primes.

<table>
<thead>
<tr>
<th>(n)</th>
<th>(a_n)</th>
<th>(b_n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>(\sqrt{3})</td>
</tr>
<tr>
<td>2</td>
<td>(-\frac{1}{2})</td>
<td>(\sqrt{2})</td>
</tr>
<tr>
<td>3</td>
<td>(\frac{1}{2})</td>
<td>(\frac{1}{\sqrt{2}})</td>
</tr>
<tr>
<td>4</td>
<td>(-\frac{1}{2})</td>
<td>(\frac{1}{\sqrt{2}})</td>
</tr>
<tr>
<td>5</td>
<td>(-\frac{1}{2})</td>
<td>(\frac{1}{\sqrt{2}})</td>
</tr>
<tr>
<td>6</td>
<td>(-\frac{1}{2})</td>
<td>(\frac{1}{\sqrt{2}})</td>
</tr>
<tr>
<td>7</td>
<td>(-\frac{1}{2})</td>
<td>(\frac{1}{\sqrt{2}})</td>
</tr>
<tr>
<td>8</td>
<td>(-\frac{1}{2})</td>
<td>(\frac{1}{\sqrt{2}})</td>
</tr>
<tr>
<td>9</td>
<td>(-\frac{1}{2})</td>
<td>(\frac{1}{\sqrt{2}})</td>
</tr>
</tbody>
</table>

\[ a_n = M_{n,1} \] (15)

and

\[ b_{n+1} = M_{n,2} - M_{n,1}^2, \] (16)

here \(n=0,1,2,\ldots\). Note that elements in the first column \(M_{n,0}\) are always equal to 1.

We find analytically that \(b_{15}^2\) exactly equals 0 for \(t=1\) and \(b_{16}^2\) exactly equals 0 for an arbitrary \(t\). Below we discuss the \(t=1\) case and similar results can be obtained for \(t \neq 1\). The exact vanishing of \(b_{15}^2\), in the case \(t=1\), indicates the truncation at \(b_{15}\). Thus, we expect 15 eigenvalues. It also turns out that the highest order of moment we need is \(l = 30\). The moments \(\mathcal{M}_{24}\) through \(\mathcal{M}_{30}\) for \(t=1\) are 15, \(-2, 91, -28, 607, -306, 4274, -3080, 31227, -29718, 234559, -279100, 180375, -2572542, 1414989, -2339880,\) and 113056535. The moments \(\mathcal{M}_{21}\) through \(\mathcal{M}_{30}\) were computed but are not shown here. Through the calculated parameters \(\{a_0, a_1, \ldots, a_{14}\}\) and \(\{b_1, b_2, \ldots, b_{14}\}\) (we only present \(\{a_0, \ldots, a_9\}\) and \(\{b_1, \ldots, b_9\}\) in Table VI), we can construct the polynomial \(P_{15}(E)\) by using Eq. (7). By solving \(P_{15}(E)=0\), we thus obtain 15 energy levels. The results are exactly identical to those obtained from the recursion method approach.

**B. Alternative application of the moments method**

In the above description of the moments approach, the main ingredient is the computation of the moments for a natural choice of state \(|1\rangle\) centered at the atom labeled by 1. However, it is worthwhile to incorporate the inversion symmetry property. Therefore, instead of focusing on a single localized state, we turn to the computation of the moments with respect to states

\[ |I_{\pm}\rangle = \frac{1}{\sqrt{2}}(|1\rangle \pm |24\rangle), \] (17)

where atoms labeled by 1 and 24 in Fig. 2 are antipodes. It is a simple exercise to construct the following identity for the moments defined by \(\langle 1|H'|I_{\pm}\rangle\),

\[ \langle I_{\pm}|H'|I_{\pm}\rangle = \langle 1|H'|1\rangle \pm \langle 1|H'|24\rangle. \] (18)
TABLE VII. Parameters $a_n$ and $b_n$ computed from the moments $\langle I_2 | 1 | H | I_2 \rangle$ with $t = 1$.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$a_n$</th>
<th>$b_n$</th>
<th>$a_n$</th>
<th>$b_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>$\sqrt{3}$</td>
<td>0</td>
<td>$\sqrt{3}$</td>
</tr>
<tr>
<td>2</td>
<td>$-\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$-\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
</tr>
<tr>
<td>3</td>
<td>$\frac{11}{88}$</td>
<td>$\frac{1}{2} \sqrt{23}$</td>
<td>$\frac{11}{88}$</td>
<td>$\frac{1}{2} \sqrt{23}$</td>
</tr>
<tr>
<td>4</td>
<td>$-\frac{19007}{39320}$</td>
<td>$\frac{1}{5} \sqrt{2 \times 19}$</td>
<td>$-\frac{19007}{39320}$</td>
<td>$\frac{1}{5} \sqrt{2 \times 19}$</td>
</tr>
<tr>
<td>5</td>
<td>$-\frac{12651157040}{227097}$</td>
<td>$\frac{1}{10} \sqrt{3 \times 5 \times 23 \times 137 \times 283}$</td>
<td>$-\frac{12651157040}{227097}$</td>
<td>$\frac{1}{10} \sqrt{3 \times 5 \times 23 \times 137 \times 283}$</td>
</tr>
<tr>
<td>6</td>
<td>$-\frac{342588}{39320}$</td>
<td>$\frac{1}{5} \sqrt{2 \times 13 \times 19}$</td>
<td>$-\frac{342588}{39320}$</td>
<td>$\frac{1}{5} \sqrt{2 \times 13 \times 19}$</td>
</tr>
<tr>
<td>7</td>
<td>$-\frac{16361}{22709}$</td>
<td>$\frac{1}{10} \sqrt{37 \times 2 \times 17 \times 47}$</td>
<td>$-\frac{16361}{22709}$</td>
<td>$\frac{1}{10} \sqrt{37 \times 2 \times 17 \times 47}$</td>
</tr>
</tbody>
</table>

These moments can then be readily obtained since the quantities $\langle 1 | H | 1 \rangle$ and $\langle 1 | H | 24 \rangle$ are already available. Note that the lowest order for the appearance of a nonzero $\langle 1 | H | 24 \rangle$ is $l=9$. This is because the shortest path for vertex 1 to reach vertex 24 contains 9 steps. We thus obviously have $\langle I_2 | 1 | H | I_2 \rangle = \infty$ for $l \leq 8$.

For the case $t=1$, the highest order we need for $\langle I_2 | 1 | H | I_2 \rangle$, $\langle I_2 | 1 | H | I_2 \rangle$ is $l=14$ (16), because $b_2^7$, $b_2^8$ calculated from the moment $\langle I_2 | 1 | H | I_2 \rangle$ gives exactly 0. Through the computed parameters $\{a_0, \ldots, a_6\}$ and $\{b_1, \ldots, b_6\}$, analytically obtain 7 (8) eigenvalues which are identical to those belonging to the $\mathcal{R} = +1$ ($\mathcal{R} = -1$) category from the recursion method. The moments $\langle I_2 | 1 | H | I_2 \rangle$, for $l=9, \ldots, 14$, are $-312$, $4319$, $-3278$, $32339$, $-33436$, and $252339$. Also the moments $\langle I_2 | 1 | H | I_2 \rangle$ are $-300$, $4231$, $-2882$, $30115$, $-26000$, $216779$, $-225080$, and $1571823$, respectively, for $l=9, \ldots, 16$. Their respective set of parameters $a_n$'s and $b_{n+1}$'s are presented in Table VII. The result that $a_n$ and $b_{n+1}$ for $n=0,1,2,$ and 3 in Table VII are identical to those in Table VI comes from the fact $\langle I_2 | 1 | H | I_2 \rangle = \infty$ for $l \leq 8$.

For an arbitrary $t$, we need the moments $\langle I_2 | 1 | H | I_2 \rangle$ up to order 16. The moments $\langle I_2 | 1 | H | I_2 \rangle$, $\langle I_2 | 1 | H | I_2 \rangle$ through $\langle I_2 | 1 | H | I_2 \rangle$ are listed in Table VIII, while $\langle I_2 | 1 | H | I_2 \rangle$, $\langle I_2 | 1 | H | I_2 \rangle$, and $\langle I_2 | 1 | H | I_2 \rangle$ were computed but are not presented here. We analytically find that $b_2^7$, $b_2^8$ calculated from these two sets of moments exactly equals 0 in both cases. Consequently, consistent results for the eigenvalues are recovered.

In this section, we have presented an unconventional choice of initial states and concentrated on the moments with respect to these states. It is shown that this approach is even more efficient in analytically obtaining the energy eigenvalues.

V. RELATIONSHIP BETWEEN THE RECURSION AND MOMENTS METHODS

Generally speaking, the moments method is closely related to the recursion method, especially in the aspect that both methods lead to the same results for the parameters $a_n$ and $b_{n+1}$. In this section, we illustrate this point by showing that the same expressions for the parameters in the recursion method case $\mathcal{R}$ can be obtained through the moments method. As the initial states are $|\phi_0\rangle$ and $|\varphi_0\rangle$ in this case.

TABLE VIII. Moments (sums over paths) $\langle I_2 | 1 | H | I_2 \rangle$, with an arbitrary $t$, for $l=9, \ldots, 13$.

| Order ($l$) | Moment ($\langle I_2 | 1 | H | I_2 \rangle$) |
|------------|----------------------------------|
| 9          | $-54 t^4 - 35 t^2 - 162 t - 72$ |
| 10         | $t^{10} + 50 t^8 + 40 t^6 + 500 t^4 + 304 t^2$ + $1490 t^4 + 400 t^3 + 1280 t^2 + 254$ |
| 11         | $-154 t^6 - 176 t^4 - 990 t^2 - 396 t^1 - 1232 t^2 - 330$ |
| 12         | $t^{12} + 72 t^{10} + 80 t^8 + 1110 t^6 + 1104 t^4 + 5784 t^2$ + $3648 t^4 + 10560 t^3 + 2840 t^2 + 6192 t^1 + 948$ |
| 13         | $-364 t^8 - 728 t^6 - 4212 t^4 - 4056 t^2$ - $10920 t^4 - 3952 t^3 - 7774 t^2 - 1430$ |

$\mathcal{R}$, the moments we now need to compute are $\langle \phi_0 | 1 | H | \phi_0 \rangle$ and $\langle \varphi_0 | 1 | H | \varphi_0 \rangle$. It is straightforward to find that

\[ \langle \phi_0 | 1 | H | \phi_0 \rangle = 2 \langle 1 | H | 1 \rangle + 2 \langle 1 | H | 3 \rangle + 2 \langle 1 | H | 5 \rangle \]

\[ + \mathcal{R} (2 \langle 1 | H | 24 \rangle + 2 \langle 1 | H | 22 \rangle + 2 \langle 1 | H | 19 \rangle) \]

(19)

and

\[ \langle \varphi_0 | 1 | H | \varphi_0 \rangle = 2 \langle 1 | H | 1 \rangle - 2 \langle 1 | H | 2 \rangle - 2 \langle 1 | H | 3 \rangle - 2 \langle 1 | H | 7 \rangle + 2 \langle 1 | H | 4 \rangle \]

\[ + \mathcal{R} (2 \langle 1 | H | 24 \rangle - 2 \langle 1 | H | 23 \rangle - 2 \langle 1 | H | 22 \rangle - 2 \langle 1 | H | 20 \rangle). \]

(20)

Notice that the site labels on the right-hand sides of the above two equations refer to Fig. 2. Through the techniques for the calculation of these quantities previously discussed, the moments $\langle \phi_0 | 1 | H | \phi_0 \rangle$ and $\langle \varphi_0 | 1 | H | \varphi_0 \rangle$ can be readily obtained.

Anticipating the termination at $b_2^7$, we only need these moments up to order 8. In Table IX we give the moments with respect to $|\phi_0\rangle$ and $|\varphi_0\rangle$. By utilizing Eqs. (14)–(16), we thus obtain $a_n$'s and $b_{n+1}$'s which are consistent with those (in Table II) derived directly from the recursion method. To illustrate this consistency, we explicitly present here the results for the $b_{n+1}$'s. From $\langle \phi_0 | 1 | H | \phi_0 \rangle$, we have
same results for the parameters $a$ and $b$ when the recursion method is applied to some starting states, for example, a single carbon atom state $\phi_0$. We thus demonstrate the fact that the moments after the moments are obtained.

| TABLE IX. Moments (sums over paths) $\langle \phi_0| H^4 |\phi_0 \rangle$ and $\langle \phi_0| H^8 |\phi_0 \rangle$ for $l=1, \ldots , 8$. |
|-------------------------------|-------------------|
| Order ($l$) | Moment $\langle \phi_0| H^l |\phi_0 \rangle$ |
| 1 | $-2$ |
| 2 | $t^2 + 2 t + 2$ |
| 3 | $t^3 + 3 t^2 + 5 t + 3$ |
| 4 | $t^4 + 4 t^3 + 10 t^2 + 5 t + 4$ |
| 5 | $t^5 + 5 t^4 + 16 t^3 + 25 t^2 + 20 t + 8$ |
| 6 | $t^6 + 6 t^5 + 24 t^4 + 48 t^3 + 60 t^2 + 38 t + 13$ |
| 7 | $t^6 + 7 t^5 + 33 t^4 + 84 t^3 + (133 + \beta) t^2 + 133 t + 71 + 21 t$ |
| 8 | $t^8 + 8 t^7 + 44 t^6 + 132 t^5 + (266 + 4 \beta) t^4 + (336 + 4 \beta) t^3 + 284 t^2 + 130 t + 34$ |

For the state $|\phi_0\rangle$, we have $b_1 = 1$, $b_2 = t^2$, $b_3 = 1$, and $b_4 = (1 - \beta^2) t^2 = 0$. From $\langle \phi_0| H^4 |\phi_0 \rangle$, we have $b_1 = 1$, $b_2 = t^2$, $b_3 = 1$, and $b_4 = (1 - \beta^2) t^2 = 0$. We thus demonstrate the fact that the same results for the parameters $a_n$ and $b_{n+1}$ can be obtained by using either the recursion or moments methods. The advantage of the recursion method lies in the fact that we can simultaneously generate the states and the parameters. However, it is sometimes difficult to derive the states and parameters when the recursion method is applied to some starting state, for example, a single carbon atom state $|j\rangle$, while the moment method provides standard procedures to calculate the parameters after the moments are obtained.

$G_{0}(E) = \left( \frac{1}{E - \mathbf{H}} \right)_{\phi_0} = \left\{ \begin{array}{c} t^2 \\ -t^2(\text{E} + 1 - \{ \text{E} + \text{t} - 2 \{ \text{E} - t^2(\text{E} + 2)^{-1} \}^{-1} \}^{-1} - 1) \\ \end{array} \right.$ for the state $|\phi_0\rangle$

and

$G_{0}(E) = \left( \frac{1}{E - \mathbf{H}} \right)_{u_0} = \left\{ \begin{array}{c} t^2 \\ t^2(\text{E} - \{ \text{E} - 1 - t^2(\text{E} - (\text{E} - \text{t} - 1)^{-1} \}^{-1} - 1)^{-1} - 1 \\ \end{array} \right.$ for the state $|u_0\rangle$, respectively.
The LDOS around these ring-clusters are plotted in Fig. 3 and Fig. 4. Notice that around a pentagon (hexagon) ring the LDOS is large at low (high) energies. This is related to the fact that a pentagon (hexagon) has zero (three) double bonds and five (three) single bonds. Also from the moments approach, the local density of states on two antipode carbon atoms are plotted in Fig. 5. In principle, they are experimentally accessible by using a scanning tunneling microscope.\(^9\)

In one of the moments method approaches, the initial state is a \(2p_z\) orbital on a carbon atom. The local density of states in the case \(t=1\) is plotted in Fig. 6. From Fig. 6, we can obtain the degree of degeneracy for each energy level, which is the respective LDOS value times 2. The common factor of 2 comes from the consideration that the total number of \(\pi\) electrons is 60. For \(t\neq 1\), conclusions for the degeneracy can be similarly drawn.

VII. SOLUTION FOR THE ELECTRONIC \(\sigma\) STATES

It is apparent that the Hamiltonian \(H_\sigma\) is more complex than \(H_\pi\) due to the two different couplings. However, an analytic transformation of this Hamiltonian into a simpler one with a single “renormalized” hopping parameter between sites can be established.\(^10\) The energy states can then be readily solved. Below we first present the transformation of the \(\sigma\)-states Hamiltonian into a \(\pi\)-type one. As a consequence, the resulting solutions of the eigenvalues for the \(\sigma\) states are obtained.

We first write the \(\sigma\) states eigenfunctions as

\[
|\Psi_\sigma\rangle = \sum_i \zeta_{i,\alpha} |i,\alpha\rangle,
\]

where \(\zeta=a,b,\) and \(c\) represents, respectively, the corresponding coefficient for the orbital \(\alpha=sp^z_A,sp^z_B,\) and \(sp^z_C\) at each site \(i\). Let us now focus attention on a given atom labeled \(i\). Also let atoms \(j,k,\) and \(l\) be the three adjacent nearest neighbors of the \(i\) atom. The energy eigenvalue equation \(H_\sigma|\Psi_\sigma\rangle = \epsilon|\Psi_\sigma\rangle\) then reads

\[
\epsilon a_i = -V_2 a_j - V_1 (b_i + c_i),
\]

\[
\epsilon b_i = -V_2 c_k - V_1 (a_i + c_i),
\]

\[
\epsilon c_i = -V_2 b_l - V_1 (a_i + b_i),
\]

and

\[
\epsilon a_j = -V_2 a_i - V_1 (b_j + c_j),
\]

\[
\epsilon c_k = -V_2 b_i - V_1 (a_k + b_k),
\]

\[
\epsilon b_l = -V_2 c_i - V_1 (a_l + c_l),
\]

and so on. We then define

\[
A_i = a_i + b_i + c_i
\]

as the sum of the coefficients for orbitals at the site \(i\), and

\[
B_i = a_j + c_k + b_l
\]

as the sum of the coefficients for orbitals on the bonds associated with the site \(i\). Similar equations hold for the other \(A\)’s and \(B\)’s. In the first place, Eqs. (26) and (29) can be rewritten as

\[
(e - V_1)a_i + V_2a_j = -V_1A_i
\]

and

\[
V_2a_i + (e - V_1)a_j = -V_1A_j.
\]

FIG. 3. The local density of states around ring clusters: (a) a pentagon, (b) a hexagon. They are obtained by using the recursion method. Notice that around a pentagon (hexagon) ring the LDOS is large at low (high) energies. This is related to the fact that a pentagon (hexagon) has zero (three) double bonds and five (three) single bonds.
When the situation $A_i = A_j = 0$ occurs, the secular equation immediately yields
\[ e = V_1 \pm V_2. \tag{36} \]

In all, there are 30 pairs of similar equation sets. We thus have two energy levels: $V_1 - V_2$ belonging to the bonding states, and $V_1 + V_2$ belonging to the antibonding states, each having a degree of degeneracy equal to 30. Furthermore, by respectively summing up Eqs. (26) through (28) and Eqs. (29) through (31), we have
\[ \epsilon A_i = -V_2 B_i - 2V_1 A_i \tag{37} \]
and
\[ (\epsilon - V_1) B_i = -V_2 A_i - V_1 (A_j + A_k + A_l). \tag{38} \]

By substituting Eq. (37) into Eq. (38), we obtain
\[ [(\epsilon + 2V_1)(\epsilon - V_1) - V_2^2] A_i = V_1 V_2 (A_j + A_k + A_l). \tag{39} \]

It can be directly recognized that Eq. (39) is entirely equivalent to the problem of a tight-binding Hamiltonian with one state per atom and a single nearest-neighbor hopping integral, whose eigenvalue and eigenvector solutions are already fully explored in previous sections. Let $E_\lambda (\lambda = 1, 2, \ldots, 15)$ stand for the eigenvalues listed in Table III. It follows then that
\[ (\epsilon_\lambda + 2V_1)(\epsilon_\lambda - V_1) - V_2^2 = V_1 V_2 E_\lambda. \tag{40} \]
Thus, we obtain
\[
\epsilon_\lambda = - \frac{V_1}{2} \pm \frac{\sqrt{V_1^2 + 2V_1^2 + V_1V_2E_\lambda}}{4}
\]
\[
= - \frac{V_1}{2} \pm V_2 \sqrt{1 + \frac{V_1^2E_\lambda}{V_2^2} + \frac{9V_1^2}{4V_2^2}}.
\]  

The minus sign designates the bonding states, and the plus sign designates the antibonding states.

Summarizing, in this section we obtain 90 bonding \( \sigma \) states and 90 antibonding \( \sigma \) states. Among the bonding (antibonding) states, 30 states are lumped together at the energy level \( V_1 - V_2 (V_1 + V_2) \). The other 60 \( \sigma \) bonding and 60 \( \sigma \) antibonding states are closely related to the energy spectrum for the \( \pi \) states. Finally, in the limit \( V_2 \gg V_1 \), we have
\[
\epsilon_\lambda = - \frac{V_1}{2} \pm V_2 \pm \frac{V_1}{2}E_\lambda.
\]  

It is also straightforward to obtain the corresponding eigenvector for an eigenvalue \( \epsilon_\lambda \). Since all the \( A_i \)'s are already known, the initial coefficients \( a_i, \ b_i, \) and \( c_i \) can be calculated.

**VIII. CONCLUSION**

In conclusion, we use several approaches based on the recursion and moments methods in order to explore the electronic structure of a \( \text{C}_{60} \) molecule, obtaining exact closed-form expressions for the \( \pi \) and \( \sigma \) eigenvalues and eigenfunctions, including the HOMO and LUMO states, as well as the Green's functions and LDOS through alternative methods. These quantities are relevant to the several important experimental techniques which probe the local spectroscopy of molecules; for instance, by using a scanning tunneling microscope, as described in the review in Ref. 9. For comparison purposes, we have also done a direct numerical diagonalization of the full Hamiltonian and the results obtained are consistent with those from the previous analytical methods. However, the much more elegant and powerful recursion and moments methods provide valuable insights and closed-form expressions for various quantities characterizing the elec-
tronic structure of C\textsubscript{60}. Finally, a generalized version of the recursion method can be used to greatly simplify the calculation of the electronic properties of large C\textsubscript{60} fullerene (i.e., C\textsubscript{240}, C\textsubscript{540}, C\textsubscript{960}, C\textsubscript{1500}, C\textsubscript{2160}, and C\textsubscript{2940}).\textsuperscript{13}

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APPENDIX A: ORIGIN OF \(V_1\) AND \(V_2\)

In this appendix we examine more closely the physical interpretation for the hopping integrals \(V_1\) and \(V_2\). Let \(|i,a\rangle\) be a hybrid orbital located at site \(i\). We have

\[
|i,sp_a^2\rangle = a_i^\dagger |2s\rangle + a_i^\dagger |2p_a\rangle + a_i^\dagger |2p_y\rangle, \quad (A1)
\]

\[
|i,sp_b^2\rangle = b_i^\dagger |2s\rangle + b_i^\dagger |2p_b\rangle + b_i^\dagger |2p_y\rangle, \quad (A2)
\]

and

\[
|j,sp_a^2\rangle = a_j^\dagger |2s\rangle + a_j^\dagger |2p_a\rangle + a_j^\dagger |2p_y\rangle, \quad (A3)
\]

where \(i\) and \(j\) are nearest neighbors. We also assume that orbitals \(|i,sp_a^2\rangle\) and \(|j,sp_a^2\rangle\) lie along the bond connecting \(i\) and \(j\). It is straightforward to obtain

\[-V_1=\langle i,sp_a^2|H_a|i,sp_a^2\rangle = a_i^\dagger b_i^\dagger \epsilon_o + (a_i^\dagger b_i^\dagger + a_j^\dagger b_j^\dagger)\epsilon_p, \quad (A4)\]

and

\[
-V_2=\langle i,sp_a^2|H_a|j,sp_a^2\rangle \\
= a_i^\dagger a_i^\dagger t_{p_x} + a_i^\dagger a_i^\dagger t_{p_y} + a_i^\dagger a_i^\dagger t_{p_y} \\
+ (a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger) t_{p_z} + (a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger) t_{p_y} \\
+ (a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger) t_{p_z} \quad (A5)
\]

Here \(\epsilon_o\) and \(\epsilon_p\) are the \(2s\)-level and \(2p\)-level energies and the \(t\)’s are hopping matrix elements between orbitals on nearest-neighbor sites. It is evident that, with a suitable choice of a local coordinate system, we can always have

\[
\langle i,sp_a^2|H_a|i,sp_a^2\rangle = \langle i,sp_a^2|H_a|i,sp_a^2\rangle = \langle i,sp_a^2|H_a|i,sp_a^2\rangle \quad (A6)
\]

and

\[
\langle i,sp_a^2|H_a|j,sp_a^2\rangle = \langle i,sp_a^2|H_a|k,sp_a^2\rangle = \langle i,sp_a^2|H_a|l,sp_a^2\rangle. \quad (A7)
\]

In the above equation, we have assumed that orbitals \(|i,sp_a^2\rangle, |k,sp_a^2\rangle\) lie along the bond connecting \(i\) and \(k\) and orbitals \(|i,sp_a^2\rangle, |l,sp_a^2\rangle\) along the bond connecting \(i\) and \(l\).

APPENDIX B: CALCULATION OF \(H|\phi_3\rangle\) AND \(H|\phi_3\rangle\)

In this appendix we present the calculation of the recurrence relations for states \(|\phi_3\rangle\) and \(|\phi_3\rangle\) in the recursion method case. It is shown that the recurrence terminates at these states and two solutions for \(a_3\) are constructed from each state. First,

\[
H|\phi_3\rangle = |\phi_3\rangle + \frac{1}{\sqrt{20}} \sum_{j=1}^{20} (|j\rangle + \mathcal{R}|j\rangle) + \frac{1}{\sqrt{20}} \sum_{j=21}^{30} (|j\rangle + t|j\rangle) + \mathcal{R} \sum_{j=21}^{30} (|j\rangle + |j\rangle)
\]

\[
= |\phi_2\rangle - \frac{1}{\sqrt{20}} \sum_{j=21}^{30} [(1 + \mathcal{R})|j\rangle + (t + \mathcal{R})|j\rangle]
\]

\[
= |\phi_2\rangle - \frac{1}{\sqrt{20}} \sum_{j=21}^{30} [(1 + \mathcal{R})|j\rangle + (1 + \mathcal{R})|j\rangle]
\]

\[
= |\phi_2\rangle - (1 + \mathcal{R})|\phi_3\rangle.
\]

We thus obtain \(a_3 = - (1 + \mathcal{R})\) and \(b_3 = 1\). Second,

\[
H|\phi_3\rangle = |\phi_2\rangle + \frac{1}{\sqrt{12}} [r(|23\rangle - |24\rangle + |26\rangle + |27\rangle + |29\rangle - |30\rangle) + \mathcal{R}(|23\rangle - |24\rangle + |26\rangle - |27\rangle - |29\rangle)]
\]

\[
= |\phi_2\rangle + \mathcal{R} \frac{1}{\sqrt{12}} [r(|23\rangle - |24\rangle + |26\rangle - |27\rangle + |29\rangle - |30\rangle) + \mathcal{R}(|23\rangle - |24\rangle + |26\rangle - |27\rangle - |29\rangle)]
\]

\[
= |\phi_2\rangle + \mathcal{R} |\phi_3\rangle.
\]

Therefore, we have \(a_3 = \mathcal{R}\) and \(b_3 = 1\).
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9 J.H. Weaver, Acc. Chem. Res. 25, 143 (1992), and references therein.


