Factorization of the Hückel Hamiltonian Matrix for Highly Symmetrical Molecules

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A simple approach to the group-theoretical factorizing of the Hamiltonian matrix of highly symmetrical molecules is presented. This approach, which is based on the Lanczos method, requires only a symmetry-adapted linear combination (SALC) for each category of irreducible representation (IR) of the molecular point-group, while it reduces the size of the problem by more than one order of magnitude. We demonstrate the treatment by applying it to the study of electronic structures of the Goldberg type-II fullerenes, $C_{80}$, $C_{180}$, $C_{320}$, $C_{500}$ and $C_{980}$ within the Hückel tight-binding framework. The results, in terms of the factor characteristic polynomial (or the subspectrum) for each category of irreducible representation, are presented for these giant molecules.

INTRODUCTION

Stimulated by the experimental observation of Buckminsterfullerene\(^1\) and the spheroidal concentric graphitic structures,\(^2,3\) the energetics and configurations of $I_h$-symmetrical carbon cages (Goldberg type-I and type-II fullerenes)\(^4-7\) have been the focus of numerous theoretical investigations.\(^5-40\) Among them, calculations\(^8-29\) based on the Hückel (tight-binding) molecular orbital theory provide preliminary results for the topological analysis of their stability.

The central theme of quantum mechanical calculations for a molecule is known to be the determination of the eigenvalues and eigenvectors of its

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Hamiltonian. With the Hückel approximation, the Hamiltonian matrix is of dimension \( N \), the number of atoms. Consequently, when we are dealing with giant molecules, for instances, \( C_{720} \) and \( C_{980} \) direct diagonalization of the Hückel Hamiltonian matrix becomes unfavorable due to the limited capacity of an ordinary computer. One of the traditional ways of reducing this difficulty is to factorize (reduce) the Hamiltonian matrix into the block-diagonal form and to solve the eigenproblem of smaller blocks.

Thus, the problem arises of how to factorize the Hamiltonian matrix in an efficient way. There have been several solutions to this problem thus far.\(^{19-29}\) In this work, we prefer a treatment based on the Lanczos method. Its efficiency and facility will be illustrated by several giant Goldberg fullerenes.

**APPROACH**

First, let us give a brief review of the group factorization problem of the Hamiltonian matrix within the Hückel framework. Assume \( \phi_i \) (\( i = 0, 1, ..., N-1 \)) are the basis functions for the molecule under consideration. The Hamiltonian matrix will be of dimension \( N \) and the matrix elements are

\[
H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle.
\]

The basis functions \( \{ \phi_i \} \) span a reducible representation space of the Hamiltonian, which decomposes to a sum of irreducible representations

\[
\Gamma = \bigoplus_{\alpha = 1}^{h} f_{\alpha} \Gamma_{\alpha}
\]

where \( \Gamma_{\alpha} \) stands for the \( \alpha \)-th irreducible representation (IR) of the point group and \( f_{\alpha} \) denotes its repetitive frequency, and the sum runs over the \( h \) categories of IRs of the point group. The structure of \( \Gamma \) implies that, on adopting a set of mutually-orthogonal symmetry-adapted linear combinations of atomic orbitals (SALCs) as new basis functions, the Hamiltonian matrix \( H \) decomposes into the direct sum of submatrices

\[
H = \bigoplus_{\alpha = 1}^{h} l_{\alpha} H_{\alpha}
\]

where \( l_{\alpha} \) is the dimensionality of the irreducible representation \( \Gamma_{\alpha} \) and \( H_{\alpha} \) the corresponding Hamiltonian submatrix of order \( f_{\alpha} \). At the same time, the secular determinant of the molecule, \( \text{det}(xI-H) \), is factorized in the following manner.
\[
\det(xI-H) = \prod_{\alpha=1}^{h} \left[ \det(xI_{\alpha} - H_{\alpha}) \right]_{\alpha} = \prod_{\alpha=1}^{h} \left[ P_{\alpha}(x) \right]_{\alpha}.
\] (4)

It is obvious that the \( f_{\alpha} \) roots of the \( \alpha \)-th sub-determinant equation

\[
P_{\alpha}(x) = \det(xI_{\alpha} - H_{\alpha}) = 0
\] (5)

will make up the subspectrum for IR \( \Gamma_{\alpha} \) and each of the roots will be \( l_{\alpha} \)-degenerate in the entire molecular energy spectrum.

Now, it is clear that the essential step to attain the factorization described by Eq. (3) or (4) is to find a complete set of SALCs to be employed as new basis functions. As far as we know, constructing all the SALCs required for the factorization has been a somewhat cumbersome task in the case of highly symmetrical giant molecules, either through the linear combinations of the spherical harmonics\textsuperscript{41-43} or by utilizing the complete projection operator technique.\textsuperscript{44} However, as it will be seen in this paper, if one applies the Lanczos method\textsuperscript{45,46} all the SALCs required can be easily generated in a recursive way. As a result, the Hamiltonian matrix will be readily factorized.

As we know, the Lanczos method can be applied to the tridiagonalization of the Hamiltonian matrix. It begins with an arbitrary starting state \( u_{0} \), rendering a set of mutually orthogonal states \( \{u_{i}\} \) through the following recursive process. The first of the states \( u_{1} \) is derived as follows,

\[
u_{1} = H u_{0} - a_{0} u_{0}
\] (6)

where coefficient \( a_{0} \) can be determined in accordance with the orthogonality condition, \textit{i.e.} \( \langle u_{i}|u_{j}\rangle = 0, \) for \( i \neq j \). So we have

\[
a_{0} = \frac{\langle u_{0}|H|u_{0}\rangle}{\langle u_{0}|u_{0}\rangle}.
\] (7)

The second and the subsequent states are constructed one by one by the recursion formula

\[
u_{k+1} = H u_{k} - a_{k} u_{k} - b_{k} u_{k-1}
\] (8)

where coefficients \( a_{k}, b_{k} \) are determined by

\[
a_{k} = \frac{\langle u_{k}|H|u_{k}\rangle}{\langle u_{k}|u_{k}\rangle}, \quad b_{k} = \frac{\langle u_{k-1}|H|u_{k}\rangle}{\langle u_{k-1}|u_{k-1}\rangle}.
\] (9)
The recursion process will terminate at some step when \( u_n = 0 \). In this way, one obtains a set of states \( \{u_i\} \). In quantum mechanics, one prefers the normalized states defined as

\[
\{ |k\rangle \} = \frac{u_k}{\langle u_k|u_k\rangle^{1/2}}.
\]  

(10)

In terms of this new orthogonal set \( \{ |k\rangle \} \), the Hamiltonian matrix corresponds to a tridiagonal form, where only the diagonals and their nearest neighboring entries are not equal to zero, \textit{i.e.},

\[
H_{mm} = \langle m|H|m\rangle = \frac{\langle u_m|H|u_m\rangle}{\langle u_m|u_m\rangle} = \alpha_m
\]  

(11)

\[
H_{m-1,m} = H_{m,m-1} = \langle m-1|H|m\rangle = \frac{\langle u_{m-1}|H|u_m\rangle}{\langle u_{m-1}|u_{m-1}\rangle^{1/2} \langle u_m|u_m\rangle^{1/2}} = b_m^{1/2}
\]  

(12)

\[
H_{mm'} = 0, \quad \text{if} \quad |m - m'| > 1.
\]  

(13)

Moreover, it can be easily proved that the above transformation process preserves the symmetry of the starting state, \textit{i.e.} if \( u_0 \) is a SALC of irreducible representation \( \Gamma_\alpha \), the derived states \( u_1, u_2, \ldots, u_n \) are also SALC belonging to the same row of irreducible representation \( \Gamma_\alpha \). In this way, the Lanczos method can be generally applied to deriving \( f_\alpha \) SALCs belonging to the same row of irreducible representation, \( \Gamma_\alpha \).

Now, this approach for the group-theoretical factorizing of the Hamiltonian can be better summarized as a three-step scheme:

1. Construct a SALC for each category of irreducible representation;

2. For each category of irreducible representation \( \Gamma_\alpha \), use the corresponding SALC as the starting state to start the recursive process, and derive the other SALC belonging to the same row of irreducible representation, evaluate the corresponding tridiagonal Hamiltonian submatrix \( H_\alpha \) of dimension \( f_\alpha \). As a whole, the Hamiltonian matrix of the molecule falls into the block-diagonal form as in Eq. (3).

3. Solve the eigenproblem of each tridiagonal submatrix separately.

At this stage, the factor characteristic polynomials and, thus, the subspectrum referring to each category of IR are obtained.
TREATMENT OF GOLDBERG TYPE-II FULLERENES

In the 30’s, Goldberg\(^4\) noted a class of polyhedra possessing only trivalent vertices, and only pentagonal and hexagonal faces. He showed that there are exactly twelve pentagons and that the remaining faces are hexagonal. The number of vertices of these polyhedrons, \(N\), is given by \(20(a^2 + ab + b^2)\), with \(a, b\) non-negative integers.\(^9,13\) If \(a\) equals \(b\) (type-I, \(N = 60k^2\)) or \(ab\) equals 0 (type-II, \(N = 20k^2\)), the polyhedron will be of \(I_h\) symmetry. If carbon atoms are placed on the vertices of these polyhedrons, Goldberg fullerenes result. In a topological sense, the carbon atoms of Goldberg fullerenes are distributed on the twenty triangles of a master icosahedron. In Figure 1, one of the triangles is depicted for six Goldberg type-II fullerenes, \(C_{20k^2}\) \((k = 2, 3, ..., 7)\).

Figure 2. Repeat units of Goldberg type-II fullerenes (each repeat unit is made up of two neighboring structural units).
Resulting from the $S_{10}$ subgroup symmetry of these molecules, a fragment with $2k^2$ carbon atoms (see Figure 2) can be regarded as the repeat unit for $C_{20k^2}$, and the carbon atoms can be labelled in a circulant way so that the Hückel Hamiltonian matrix is a circulant matrix\textsuperscript{47-49} as follows:

\[
H = \begin{pmatrix}
U & V & W & 0 & 0 & 0 & 0 & 0 & W^T & V^T \\
V^T & U & V & W & 0 & 0 & 0 & 0 & W^T & V^T \\
W^T & V^T & U & V & W & 0 & 0 & 0 & 0 & 0 \\
0 & W^T & V^T & U & V & W & 0 & 0 & 0 & 0 \\
0 & 0 & W^T & V^T & U & V & W & 0 & 0 & 0 \\
0 & 0 & 0 & W^T & V^T & U & V & W & 0 & 0 \\
0 & 0 & 0 & 0 & W^T & V^T & U & V & W & 0 \\
W & 0 & 0 & 0 & 0 & W^T & V^T & U & V & W \\
V & W & 0 & 0 & 0 & 0 & W^T & V^T & U & V \\
\end{pmatrix}
\]  

\[ (14) \]

where $U$, $V$, $W$, $V^T$, $W^T$ are all of dimension $2k^2$, $U$ describes the internal connectivity in the repeat unit in Figure 2, $V$ and $W$ describe the connectivity between the neighboring repeat units, and $V^T$, $W^T$ are their transposes.

It can be easily proved that this representative of the Hamiltonian is a reducible one with respect to $I_h$ group, decomposing according to the following formula

\[
\Gamma_k = \frac{k^2 + 3k + 2\delta_{k, 3m+1}}{6} A_g \oplus \frac{k^2 - k}{2} T_{1g} \oplus \frac{k^2 - k}{2} T_{2g} \oplus \frac{2k^2 + \delta_{k, 3m+1}}{3} G_g \\
\oplus \frac{5k^2 + 3k - 2\delta_{k, 3m+1}}{6} H_g \oplus \frac{k^2 - 3k + 2\delta_{k, 3m+1}}{6} A_u \oplus \frac{k^2 + k}{2} T_{1u} \\
\oplus \frac{k^2 + k}{2} T_{2u} \oplus \frac{2k^2 + \delta_{k, 3m+1}}{3} G_u \oplus \frac{5k^2 - 3k - 2\delta_{k, 3m+1}}{6} H_u
\]  

\[ (15) \]

The repetitive frequencies of IRs in Eq. (15), which depend on $k$, are collected up to $k \leq 7$ in Table I. One may notice that the $A_u$ irreducible representation doesn’t appear in $C_{80}$ and $C_{180}$, but does appear one or more times in $C_{320}$ and larger cages.

Now, we apply the approach, described in the last section, to the factorization of the Hamiltonian matrix for these fullerene molecules. In a previous work\textsuperscript{28} by using the projection operator technique, we constructed a set of SALCs as starting states for the nine IRs occurring in $C_{80}$ which are contributed by the sixty equivalent atomic orbitals on 12 pentagons. These
TABLE I

Repetitive frequencies of irreducible representations for Goldberg type-II fullerenes within the Hückel tight-binding approximation

<table>
<thead>
<tr>
<th>k</th>
<th>N (=20k²)</th>
<th>A_g</th>
<th>T_{1g}</th>
<th>T_{2g}</th>
<th>G_g</th>
<th>H_g</th>
<th>A_u</th>
<th>T_{1u}</th>
<th>T_{2u}</th>
<th>G_u</th>
<th>H_u</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>80</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>4</td>
<td>0</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>6</td>
<td>9</td>
<td>0</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>320</td>
<td>5</td>
<td>6</td>
<td>6</td>
<td>11</td>
<td>15</td>
<td>1</td>
<td>10</td>
<td>10</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>5</td>
<td>500</td>
<td>7</td>
<td>10</td>
<td>10</td>
<td>17</td>
<td>23</td>
<td>2</td>
<td>15</td>
<td>15</td>
<td>17</td>
<td>18</td>
</tr>
<tr>
<td>6</td>
<td>720</td>
<td>9</td>
<td>15</td>
<td>15</td>
<td>24</td>
<td>33</td>
<td>3</td>
<td>21</td>
<td>21</td>
<td>24</td>
<td>27</td>
</tr>
<tr>
<td>7</td>
<td>980</td>
<td>12</td>
<td>21</td>
<td>21</td>
<td>33</td>
<td>44</td>
<td>5</td>
<td>28</td>
<td>28</td>
<td>33</td>
<td>37</td>
</tr>
</tbody>
</table>

Starting states can be also applied to higher members of C_{20k²} due to the structural similarity, that is, the sixty atoms on the 12 pentagons of these cages are also equivalent and distributed analogously on an icosahedron (see Figure 1.). As a result, similar SALCs can be constructed as the starting states for any higher member of C_{20k²}, which are also linear combinations of atomic orbitals on pentagons, with the same coefficients of SALCs of C_{80}, which were tabulated in ref. 28. The starting state for A_u which appears in C_{320} and larger ones can also be constructed with the 120 atoms which are

TABLE II

Factor characteristic polynomials (FCPs) of C_{80} and their related eigenvalues

<table>
<thead>
<tr>
<th>IR</th>
<th>FCPs</th>
<th>Eigenvalues</th>
</tr>
</thead>
<tbody>
<tr>
<td>A_g</td>
<td>x² - 2x - 3</td>
<td>3, -1</td>
</tr>
<tr>
<td>T_{1g}</td>
<td>x + \frac{1 - \sqrt{5}}{2}</td>
<td>0.618</td>
</tr>
<tr>
<td>T_{2g}</td>
<td>x + \frac{1 + \sqrt{5}}{2}</td>
<td>-1.618</td>
</tr>
<tr>
<td>G_g</td>
<td>x³ + x² - 4x + 1</td>
<td>1.377, 0.274, -2.651</td>
</tr>
<tr>
<td>H_g</td>
<td>x⁴ - x³ - 6x² + 3x + 7</td>
<td>2.473, 1.463, -1, -1.935</td>
</tr>
<tr>
<td>T_{1u}</td>
<td>x³ - \frac{3 + \sqrt{5}}{2} x² - (4 - \sqrt{5})x + \frac{9 - \sqrt{5}}{2}</td>
<td>2.818, 1, -1.200</td>
</tr>
<tr>
<td>T_{2u}</td>
<td>x³ - \frac{3 - \sqrt{5}}{2} x² - (4 + \sqrt{5})x + \frac{9 + \sqrt{5}}{2}</td>
<td>2.081, 1, -2.699</td>
</tr>
<tr>
<td>G_u</td>
<td>x³ + x² - 4x - 3</td>
<td>1.912, -0.714, -2.199</td>
</tr>
<tr>
<td>H_u</td>
<td>x² + x - 1</td>
<td>0.618, -1.618</td>
</tr>
</tbody>
</table>
TABLE III

Factor characteristic polynomials (FCPs) of C\textsubscript{180} and their related eigenvalues

<table>
<thead>
<tr>
<th>IR</th>
<th>FCPs</th>
<th>Eigenvalues</th>
</tr>
</thead>
<tbody>
<tr>
<td>A\textsubscript{g}</td>
<td>(x^3 - 3x^2 - 3x + 9)</td>
<td>3, 1.732, -1.732</td>
</tr>
<tr>
<td>T\textsubscript{1g}</td>
<td>(x^2 + \frac{3 - \sqrt{5}}{2}x^2 - \frac{3 + \sqrt{5}}{2}x + \frac{3 - \sqrt{5}}{2})</td>
<td>1.514, -0.144, -1.752</td>
</tr>
<tr>
<td>T\textsubscript{2g}</td>
<td>(x^3 + \frac{3 + \sqrt{5}}{2}x^2 - \frac{3 - \sqrt{5}}{2}x + \frac{3 + \sqrt{5}}{2})</td>
<td>0.916, -1.251, -2.283</td>
</tr>
<tr>
<td>G\textsubscript{g}</td>
<td>(x^6 + x^5 - 9x^4 - 5x^3 + 20x^2 + 6x - 11)</td>
<td>2.202, 1.475, 0.737, -1.078, -1.508, -2.828</td>
</tr>
<tr>
<td>H\textsubscript{g}</td>
<td>(-72x^4 - 53x^3 + 75x^2 + 18x - 21)</td>
<td>2.762, 2.270, 1.551, 1, 0.595, -0.698, -1.099, -1.913, -2.470</td>
</tr>
<tr>
<td>T\textsubscript{1u}</td>
<td>(x^6 - \frac{3 + \sqrt{5}}{2}x^5 - \frac{(9 - \sqrt{5})x^4 + 21 + 5\sqrt{5}}{2}x^3)</td>
<td>2.919, 1.980, 1.269, -0.067, -1.386, -2.098</td>
</tr>
<tr>
<td>T\textsubscript{2u}</td>
<td>(\frac{41 - 9\sqrt{5}}{2}x^2 - (14 + 3\sqrt{5})x - \frac{23 - 9\sqrt{5}}{2})</td>
<td>2.569, 1.889, 1.157, -0.920, -1.464, -2.849</td>
</tr>
<tr>
<td>G\textsubscript{u}</td>
<td>(x^6 + x^5 - 9x^4 - 7x^3 + 18x^2 + 6x - 9)</td>
<td>2.503, 1.123, 0.724, -0.940, -1.799, -2.613</td>
</tr>
<tr>
<td>H\textsubscript{u}</td>
<td>(x^6 + x^5 - 6x^4 - 4x^3 + 9x^2 + 3x - 3)</td>
<td>1.864, 1.162, 0.512, -0.817, -1.465, -2.257</td>
</tr>
</tbody>
</table>

the second nearest neighbors with respect to the pentagons by the projection operator technique.

Due to the circulant property of the Hamiltonian matrix (see Eq. (14)), only smaller matrices \(U, V, W\) and their transposes will be used in the factorization. On the other hand, as indicated in Table I, the dimension of the resulting Hamiltonian submatrices will be no larger than \(k^2\) (one twentieth of the dimension of the Hamiltonian matrix). Therefore, this approach reduces the size of the problem by more than one order of magnitude. In reality, it takes only several minutes to attain the factorization for giant molecules such as \(C_{720}\) and \(C_{980}\) on a PC 486/33. In Tables II–IV, the factor characteristic polynomials (FCPs) in analytical form and their related eigenvalues are presented for \(C_{80}\), \(C_{180}\) and \(C_{320}\); while for the other three Goldberg type-II fullerenes, the subspectra instead of FCPs are given to save space.
### Table IV

Factor characteristic polynomials (FCPs) of $C_{320}$ and their related eigenvalues

<table>
<thead>
<tr>
<th>IR</th>
<th>FCPs</th>
<th>Eigenvalues</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g$</td>
<td>$x^5 - 3x^4 - 6x^3 + 18x^2 + 5x - 15$</td>
<td>3, 2.236, 1, -1, -2.236</td>
</tr>
<tr>
<td>$T_{1g}$</td>
<td>$x^6 + \frac{3 - \sqrt{5}}{2} x^5 - \frac{11 + \sqrt{5}}{2} x^4 - (6 - 2\sqrt{5})x^3$ $+ \frac{17 + \sqrt{5}}{2} x^2 + (5 - 2\sqrt{5})x - \frac{9 - \sqrt{5}}{2}$</td>
<td>2.122, 1, 0.765, -0.708, -1.305, -2.256</td>
</tr>
<tr>
<td>$T_{2g}$</td>
<td>$x^6 + \frac{3 + \sqrt{5}}{2} x^5 - \frac{11 - \sqrt{5}}{2} x^4 - (6 + 2\sqrt{5})x^3$ $+ \frac{17 - \sqrt{5}}{2} x^2 + (5 + 2\sqrt{5})x - \frac{9 + \sqrt{5}}{2}$</td>
<td>1.559, 1, 0.575, -1.285, -1.898, -2.570</td>
</tr>
<tr>
<td>$G_g$</td>
<td>$x^{11} + x^{10} - 16x^9 - 13x^8 + 89x^7 + 59x^6$ $- 211x^5 - 111x^4 + 207x^3 + 84x^2 - 65x - 20$</td>
<td>2.538, 2.083, 1.555, 1.122, 0.740, -0.281, -0.806, -1.226, -1.772, -2.054, -2.898</td>
</tr>
<tr>
<td>$H_g$</td>
<td>$x^{15} + 2x^{14} + 22x^{13} + 41x^{12} + 190x^{11} - 323x^{10}$ $- 834x^9 + 1258x^8 + 2020x^7 - 2579x^6 - 2716x^5$ $+ 2767x^4 + 1887x^3 - 1398x^2 - 526x + 239$</td>
<td>2.866, 2.579, 2.120, 1.669, 1.541, 1.150, 1, 0.331, -0.784, -1, -1.216, -1.491, -1.736, -2.341, -2.689</td>
</tr>
<tr>
<td>$A_u$</td>
<td>$x^5 + 5x^4 + 3x^3 + 5x^2 + x$</td>
<td>-1</td>
</tr>
<tr>
<td>$T_{1u}$</td>
<td>$x^{10} + \frac{117 - 33\sqrt{5}}{2} x^9 - \frac{275 + 29\sqrt{5}}{2} x^8 + \frac{27 + 3\sqrt{5}}{2} x^7 + (33 + 5\sqrt{5})x^6$ $+ \frac{147 - 153\sqrt{5}}{2} x^5 - \frac{41 - 65\sqrt{5}}{2} x^4 - 101x - \frac{2}{2}$</td>
<td>2.955, 2.402, 1.937, 1.264, 1, 0.578, -1, -1.054, -1.992, -2.473</td>
</tr>
<tr>
<td>$T_{2u}$</td>
<td>$x^{10} + \frac{117 + 33\sqrt{5}}{2} x^9 - \frac{275 - 29\sqrt{5}}{2} x^8 + \frac{27 + 3\sqrt{5}}{2} x^7 + (33 - 5\sqrt{5})x^6$ $+ \frac{147 + 153\sqrt{5}}{2} x^5 - \frac{41 + 65\sqrt{5}}{2} x^4 - 101x - \frac{2}{2}$</td>
<td>2.754, 2.341, 1.860, 1.438, 1, -0.632, -1, -1.471, -1.998, -2.910</td>
</tr>
<tr>
<td>$G_u$</td>
<td>$x^{11} + x^{10} - 16x^9 - 13x^8 + 89x^7 + 51x^6$ $- 219x^5 - 71x^4 + 239x^3 + 20x^2 - 89x + 12$</td>
<td>2.717, 1.817, 1.342, 1.279, 0.710, 0.148, -0.925, -1.458, -1.587, -2.271, -2.774</td>
</tr>
<tr>
<td>$H_u$</td>
<td>$x^{11} + 2x^{10} - 12x^9 - 23x^8 + 49x^7 + 89x^6$ $- 84x^5 - 140x^4 + 63x^3 + 88x^2 - 18x - 17$</td>
<td>2.335, 1.844, 1.254, 0.883, 0.689, -0.466, -1, -1.286, -1.646, -2.056, -2.552</td>
</tr>
</tbody>
</table>
Figure 3. Hückel subspectra of C_{500}.

Figure 4. Hückel subspectra of C_{720}.
DISCUSSION AND CONCLUSION

From the calculations in the last section, it is quite clear that upon utilizing the Lanczos method, a series of Symmetry-adapted Linear Combinations (SALCs) can be generated recursively from one SALC, and thus the Hückel Hamiltonian matrix of a highly symmetrical molecule can easily be group factorized into a direct sum of the smallest submatrices. Therefore, in this paper, we have suggested a simple but efficient approach for solving the Hückel eigenvalue problem for highly symmetrical molecules.

To our knowledge, besides this approach, there have already been several other approaches dealing with the Hückel eigenvalue problem of fullerenes: the direct diagonalization of the Hamiltonian matrix; reducing the molecule into subsystems by the use of its $Z_2$ or $S_{10}$ symmetry;\textsuperscript{17–22} deriving the characteristic polynomial referring to each irreducible representation on the basis of the character table and the multiplication table,\textsuperscript{23} and so on. We notice that the approach advanced by Lin and Nori\textsuperscript{25,26} also employs the Lanczos method. The chief difference between our work and theirs lies in the choice of the starting state. Our choice emphasizes the symmetry of the starting state in order to attain idealized factorization rendering maximum analytical results. It seems to us that the approach in this work may have a wider application and can be applied to other quantum chemical problems.

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REFERENCES

SAŽETAK

Faktorizacija matrice Hückelova hamiltoniana za visoko simetrične molekule

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Prikazan je jednostavan pristup faktorizaciji matrice hamiltoniana visoko simetričnih molekula s pomoću teorije grupa. Postupak, zasnovan na Lanczosovoj metodi, zahtijeva samo simetrijski prilagođenu linearnu kombinaciju (SALC) za svaku kategoriju ireducibilne reprezentacije (IR) molekulske grupe, a smanjuje veličinu problema za više od jednog reda veličine. Primjena tog postupka prikazana je u proučavanju elektronske strukture Goldbergovih fullerena II. tipa: C_{80}, C_{180}, C_{320}, C_{500}, C_{720} i C_{980}, unutar Hückellove koncepcije jake veze. Rezultati za ove velike molekule prikazani su kao faktori karakterističnog polinoma (odnosno podspektri) za svaku kategoriju ireducibilne reprezentacije.