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A Facile Hückel Molecular Orbital Solution of Buckminsterfullene Using Chemical Graph Theory

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In the *Content of Undergraduate Physical Chemistry Courses* published by ACS in April 1985, it was stated (5) that quantum mechanics, spectroscopy, and statistical thermodynamics should be contracted by "... presenting solution to energy level calculations in quantum mechanics without the mathematical details." Organic chemists over the years have employed the qualitative aspects of molecular graphs (graphs representing molecules) to guide their chemical thinking, in devising syntheses, and in studying reaction mechanisms. According to this model, bonds (edges) are lines connecting atomic nuclei (vertices) and represent pairs of localized electrons shared between the corresponding pairs of nuclei. Merging the qualitative/intuitive approach of the organic chemist with mathematical graph theory, one can accomplish what this ACS document suggests. We will illustrate this approach by giving a total Hückel molecular orbital solution to the three-dimensional aromatic C_{60} species without employing group theory (*1*, *2*). The reader should compare our simpler solution with that of Davidson who uses the Z_2 automorphism reduction of the truncated icosahedron (*3*).

Terminology

Consider the HMO solution of ethene. Its 2 × 2 secular determinant is

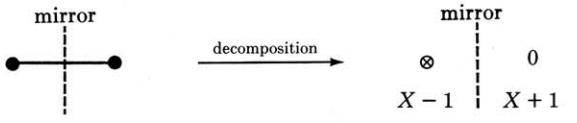
$$\begin{vmatrix} \alpha - \epsilon & \beta \\ \beta & \alpha - \epsilon \end{vmatrix} = 0$$

where α is the Coulomb integral, ϵ is the energy level variable, and β is the exchange or resonance integral (*4*). Dividing each term in the secular determinant by $-\beta$ gives

$$\begin{vmatrix} X & -1 \\ -1 & X \end{vmatrix} = 0 = X^2 - 1 = P(C_2H_4; X)$$

where $X = (\epsilon - \alpha)/\beta$ is the eigenvalue variable and $X^2 - 1$ is the characteristic polynomial $P(C_2H_4; X)$ of ethene.

Throughout this paper, we will show only the σ C–C bond skeleton of molecules (molecular graphs). Mirror plane decomposition of ethene is illustrated by the following operation:



where $X - 1$ is the characteristic polynomial of the left fragment and $X + 1$ of the right fragment.

Mirror Plane Decomposition of Buckminsterfullerene

McClelland has described the following rules for decomposition of a molecule with a plane of symmetry into simpler graph fragments for the purpose of simplifying the characteristic polynomial or secular determinant (*5*).

(1) The mirror plane divides a molecular graph into left and right fragments.
(2) Vertices on the plane of symmetry are included in the left fragment.

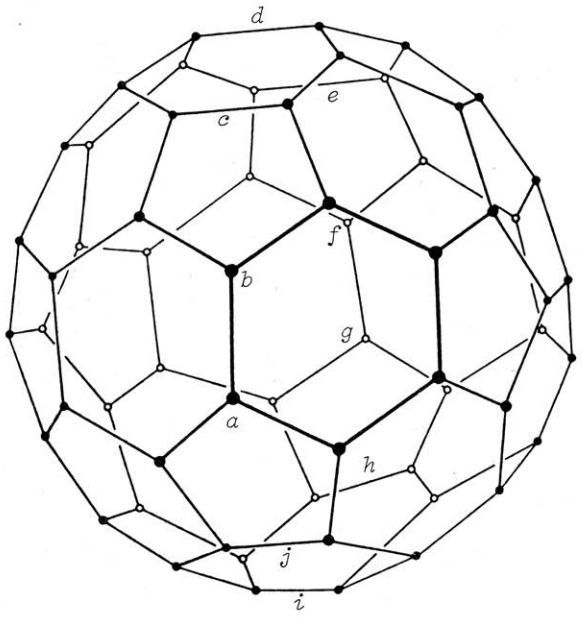


Figure 1. The truncated icosahedron or Buckminsterfullerene C_{60} species.

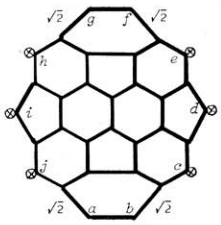
(3) The weight of the edge between a vertex lying on the plane of symmetry and a vertex in the left fragment is $\sqrt{2}$.
(4) If the symmetry plane bisects an edge originally connecting the left and right fragments, the vertex in the left fragment is weighted +1 and the vertex in the right fragment is weighted −1.
(5) The eigenvalues of the original graph equals the eigenvalues of the fragment graphs.

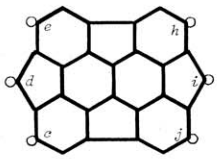
We will now use McClelland's rules for computing the eigenvalues of the truncated icosahedron, i.e., Buckminsterfullerene, shown in Figure 1.

Mirror plane fragmentation of BM-C_{60} through vertices a, b, f, g and edges c, d, e, h, i, j in Figure 1 leads to the C_{28} and C_{32} fragments shown in Figure 2. Because of the high symmetry associated with the truncated icosahedron, these fragments can be submitted to successive mirror plane fragmentation as shown in Figures 3 and 4. The size of the eight final fragments range from nine to six vertices, which can be easily solved using methods previously published by us (*6–9*). Note that fragments **2** (Fig. 3) and **7** (Fig. 4) can be mirror-plane-fragmented further, and fragments **1, 4,** and **6** are identical, as are **3, 5,** and **8.**

Eigenvalues of Buckminsterfullerene

The roots to the characteristic polynomials for the graph fragments **1–8** in Figures 3 and 4 taken together constitute the set of eigenvalues belonging to BMF-C_{60} and are presented in the table. These roots can easily be obtained by iteration on a hand calculator/programmable computer or by a simplified version of a basic program for finding roots of a polynomial.





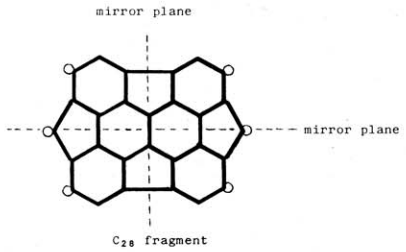
O vertex of weight -1
⊠ vertex of weight +1

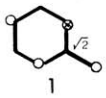
Figure 2. Mirror-plane fragments of the truncated icosahedron or the Buckminsterfullerene C_{60} species.

The HMO Eigenvalues (β) of the Truncated Icosahedrane, C_{60} (*3*)

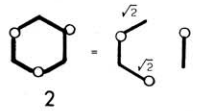
Major Doubly Degenerate Subsets		Unmatched Subset
−2.61803	−2.61803	−2.61803
−2.562	−2.562	−1.61803
−2.562	−2.562	−1.438
−2.0	−2.0	−1.303
−2.0	−2.0	−0.382
−1.61803	−1.61803	−0.139
−1.61803	−1.61803	0.61803
−1.438	−1.438	1.0
−1.303	−1.303	1.820
−1.303	−1.303	2.303
−0.382	−0.382	2.757
−0.139	−0.139	3.0
0.61803		0.61803
0.61803		0.61803
1.0	1.0	
1.0	1.0	
1.0	1.0	
1.0	1.0	
1.562	1.562	
1.562	1.562	
1.820	1.820	
2.303	2.303	
2.303	2.303	
2.757	2.757	

If the eigenvalues of a smaller graph are contained among the eigenvalue spectrum of a larger graph, then the smaller graph is said to be subspectral to the larger one (*6*). Previously, it was shown that molecular graphs with greater than twofold symmetry possessed doubly degenerate eigenvalue subsets (*10–12*). Whenever a molecular graph possesses degenerate eigenvalue subsets, a (zero) node vertex can be obtained at any selected molecular graph position by taking an appropriate linear combination of these degenerate eigenvalues subsets. Deletion of any atomic vertex or placement of any heteroatom or polyene substitutent at any position on a molecular graph having doubly degenerate eigenvalue subsets will lead to successor molecular graphs still retaining one of these eigenvalue subsets (*9*). Thus, deletion of any vertex from BMF-C_{60} (Fig. 1) gives a successor molecular graph that will still retain one of the doubly degenerate subsets given in the table. Furthermore, deletion of up to four vertices (a, b, f, g in Fig. 1) lying the vertical mirror plane of BMF-C_{60} leads to the structure given in Figure 5, which still possesses the same right-hand mirror-plane fragment given in Figure 3 and its associated eigenvalues; the dangling bonds formed in the vertex-deleted successor molecular graphs of BMF-C_{60} can be compensated for by bond-

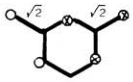



1

$X^7+2X^6-8X^5-14X^4+16X^3+20X^2-11X-6$


2

$(X^4+2X^3-4X^2-5X+4)(X^2+X-1)$


3

$X^8-X^7-12X^6+10X^5+42X^4-28X^3-47X^2+23X+4$

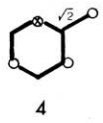
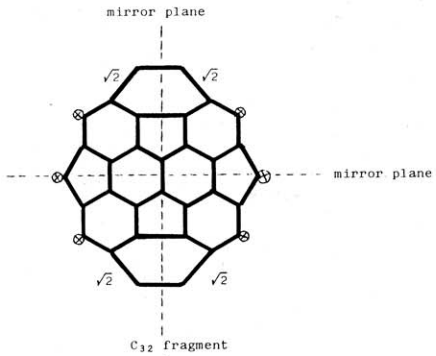
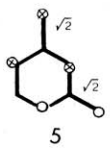

4

Figure 3. Further mirror-plane fragmentation of the C_{28} fragment of the truncated C_{60} icosahedron.

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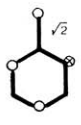
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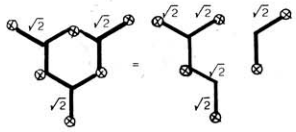

7

$(X^6-4X^5-3X^4+23X^3-8X^2-27X+18)(X^3-2X^2-2X+3)$

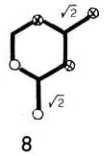

8

Figure 4. Further mirror-plane fragmentation of the C_{32} fragment from the C_{60} truncated icosahedron.

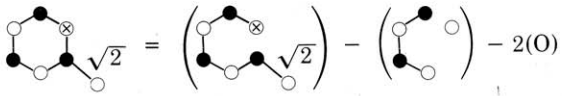
ing hydrogen to them. The consequence of this eigenvalue retention is that BMF-C_{60} and any of its six vertex-deleted successor molecular graphs will all have very similar, if not identical, electronic spectra, and the impact of this observation on the suggestion that BMF-C_{60} may be responsible for diffuse stellar bands found in absorption spectra of the Milky Way should be obvious (*1*).

Graph Theoretical Decomposition of the Fragment Graphs of Buckminsterfullerene

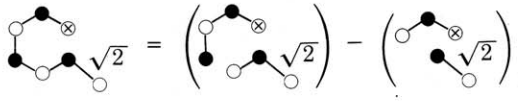
We will give a complete solution to **1**. The following decomposition equation will be employed for the characteristic polynomial of graph G

$$P(G; X) = P(G - e; X) - k^2P(G - (e); X) - 2k\sum P(G - Z; X)$$

where $G - e$ is graph G with its edge e deleted, $G - (e)$ is graph G with its edge e and associated vertices deleted, k is the weight of the edge e, and $G - Z$ is the graph G with the cycle Z containing e deleted (*7*, *12*). Application of this decomposition to the graph of **1** gives



The goal here is to reduce graph **1** into subgraphs of five or less vertices that give determinants of size 5×5 or less that can be easily solved using Laplace's expansion by minors. The subgraph $G - e$ still possesses seven vertices and can be divided by another successive application of the above equation to give



where the absence of cycles in this graph results in the third term being zero. The secular determinant of the 4×4 subgraph is submitted to Laplace's expansion to give

$$P(\ ; X) =$$

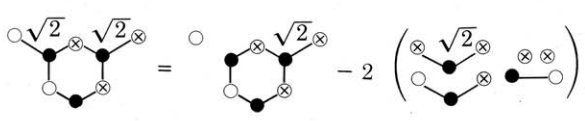
$$\begin{vmatrix} X & -1 & 0 & 0 \\ -1 & (X+1) & -1 & 0 \\ 0 & -1 & X & -1 \\ 0 & 0 & -1 & (X-1) \end{vmatrix}$$

$$= \begin{vmatrix} X & -1 \\ -1 & (X+1) \end{vmatrix} \begin{vmatrix} X & -1 \\ -1 & (X-1) \end{vmatrix} - \begin{vmatrix} X & -1 \\ 0 & -1 \end{vmatrix} \begin{vmatrix} -1 & 0 \\ -1 & (X-1) \end{vmatrix}$$

$$= X^4 - 4X^2 + X + 1$$

Combining the characteristic polynomials of the subgraphs obtained per the above prescription leads to the characteristic polynomial of fragment **1** given in Figure 3.

As another example, consider the solution of **3** in Figure 3. Successive application of the above decomposition equation gives



The first fragment above has seven vertices and also appears as fragment **12** found in Figure 6, which can be mirror-plane decomposed into easily solvable fragments.

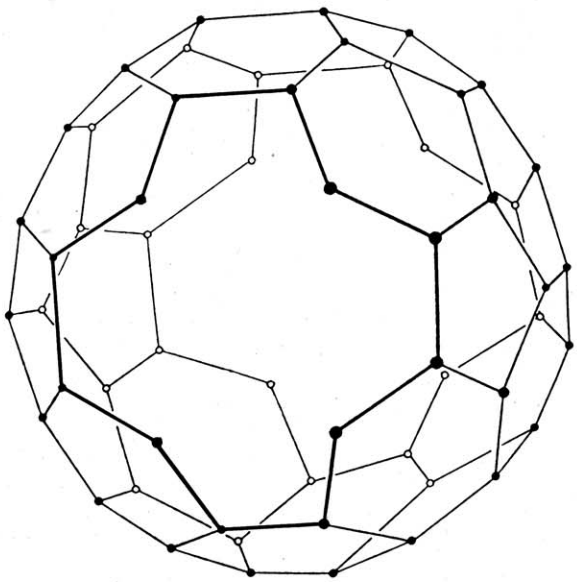
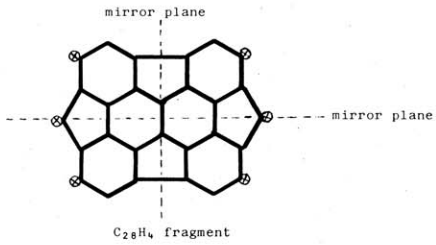


Figure 5. The tetravertex-deleted truncated icosahedron $C_{56}H_8$ species.



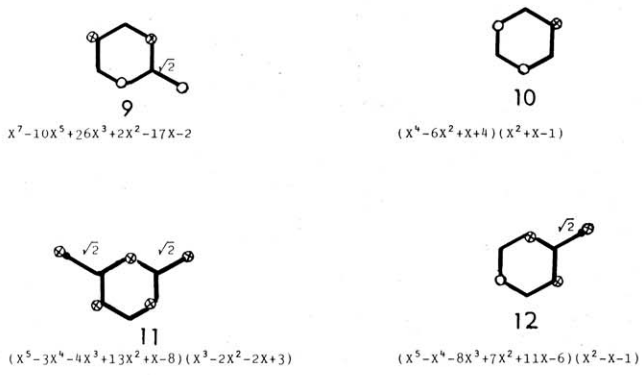


Figure 6. Fragmentation of the left mirror fragment of the $C_{56}H_8$ species.

Resonance Energy per Electron (REPE)

If one uses the Hess and Schaad method (*13*) for computing the reference energy for BMF-C_{60}, then one obtains a REPE of 0.031β, which may be compared to the values of 0.0658β for benzene and 0.053β for coronene and graphite. Thus, it appears that BMF-C_{60} has significant aromatic character, and the chemical inertness of BMF-C_{60} is due to both this and the unavailability of replaceable hydrogens capable of electrophilic and oxidative reaction normally characteristic of aromatic compounds (*14*).

Summary

It should be evident from this paper that chemical graph theory provides a different avenue for conceptualizing chemical phenomena. Although the application of chemical graph theory is accompanied by some specialized terminology, the result is an easily understood, intuitive method. Herein, two methods of molecular graph decomposition for the purpose of obtaining the HMO energy levels have been illustrated, mirror-plane decomposition and the use an more general form of an equation due to Heilbronner (*15*). Both these approaches circumvented the need to use group theory.

Literature Cited

1. Smalley, R. E. *Chem. Eng. News* **1985,** (Dec. 23), 20; **1988,** (Aug. 29), 33.
2. Schmalz, T.; Seitz, W.; Klein, D. J.; Hite, G. *J. Am. Chem. Soc.* **1988,** *110*, 1113.
3. Davidson, R. A. *Theoret. Chim. Acta* **1981,** *58*, 193.
4. Roberts, J. D. *Molecular Orbital Calculations*; Benjamin: New York, 1962.
5. McClelland, B. *J. Chem. Soc., Faraday Trans. II* **1974,** *70*, 1453.
6. Dias, J. R. *J. Chem. Educ.* **1987,** *64*, 213.
7. Dias, J. R. In *Graph Theory and Topology in Chemisry*; King, R. B.; Rouvray, D., Eds.; Elsevier: Amsterdam, 1988; pp 466–475.
8. Dias, J. R. In *Applications of Discrete Mathematics*; Ringeisen, R.; Roberts, F. S., Eds.; SIAM: Philadelphia, 1988; pp 148–162.
9. Dias, J. R. *Handbook of Polycyclic Hydrocarbons, Parts A and B*; Elsevier: Amsterdam, 1987 and 1988.
10. D'Mato, S. *Theoret. Chim. Acta* **1979,** *53*, 319.
11. Trinajstic', N. *Chemical Graph Theory*; CRC: Boca Raton, FL, 1983.
12. Dias, J. R. *J. Molec. Struct. (THEOCHEM)* **1988,** *165*, 125.
13. Hess, B. A.; Schaad, L. *J. Org. Chem.* **1986,** *51*, 3902; *J. Am. Chem. Soc.* **1971,** *93*, 305 and 2413.
14. Randic', M.; Nikolic', S.; Trinajstic', N. *Croat. Chem. Act* **1986,** *60*, 595.
15. Heilbronner, E. *Helv. Chim. Acta* **1953,** *36*, 170.