The Number of High-Energy Bands in the Photoelectron Spectrum of Alkanes

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Z. Naturforsch. **55a,** 973–977 (2000); received September 9, 2000

It was observed that within the Bieri-Dill-Heilbronner-Schmelzer model for the calculation of the ionization energies of alkanes C_nH_{2n+2}, there are exactly n C_{2s}-electron energy levels lying below the degenerate $\alpha - \beta$ manifold. We now show that, indeed, this regularity is obeyed by practically all alkane species. Exceptions do exist, but they must possess a (chemically infeasible) group of more than six mutually connected quaternary carbon atoms.

Key words: Hydrogen filled Molecular Graph; Inertia; Laplacian Spectrum.

Introduction

The communication industry employs lasers and fiber-optic cables to move data, sound, and even real-time motion pictures through backbone networks at the speed of light. These communications are slowed dramatically at their final destination when packets of light must be converted back into electrical impulses. Companies like Cisco Systems, JDS Uniphase, Lucent Technologies, and Nortel Networks are spending billions of dollars, looking for ways to overcome this technology bottleneck. The enormity of such applications has naturally stimulated renewed interest in everything photoelectric.

In 1977 Bieri, Dill, Heilbronner, and Schmelzer [1, 2] developed a simple equivalent-bond-orbital approximation (in what follows referred to as the BDHS model), capable of reproducing the experimental [3] photoelectron spectra of saturated hydrocarbons, especially the so-called "high-energy band" (HEB), lying in the range 17–26 eV. The HEB is believed to pertain to the 2s-orbitals of the carbon atoms, to the ionization of the C_{2s}-electrons.

The basic result of the BDHS model is the expression

$$E_j = \alpha + \beta x_j$$

where α and β are semiempirical parameters (whose proposed [1] values for alkanes are $\alpha = -16.10 \pm 0.08$ eV and $\beta = -2.11 \pm 0.03$ eV) and where x_j, $j = 1, 2, \ldots, 3n + 1$ are the eigenvalues of the line graph of the respective hydrogen-filled molecular graph. Throughout this paper the number of carbon atoms in the alkane molecules considered is denoted by n, hence, their formula is C_nH_{2n+2}.

In a hydrogen-filled molecular graph vertices represent both the heavy atoms (carbon etc.) and the hydrogen atoms. In Fig. 1 is depicted the hydrogen-filled molecular graph of 2,2,3,3,6,6-hexamethyl heptane and its line graph; for more details see elsewhere [1, 2, 4–6].

Within the BDHS model the energy level $\alpha - \beta$ is highly degenerate [5], and only the energy levels lying below the $\alpha - \beta$ manifold are of physical significance. In a recent study of the BDHS model [6] the following empirical observation was made:

Rule 1. Every alkane with n carbon atoms has exactly n energy levels lying below the degenerate $\alpha - \beta$ manifold.

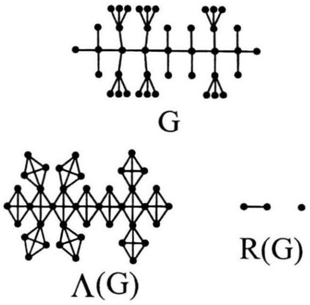

Fig. 1. The hydrogen-filled molecular graph G of 2,2,3,3,6,6-hexamethyl heptane $C_{13}H_{28}$, its line graph $\Lambda(G)$ and the subgraph $R(G)$, induced by the quaternary carbon atoms; $\Lambda(G)$ has 40 vertices and, consequently, within the BDHS model there are 40 energy levels; only 13 of these correspond to the HEB.

Bearing in mind that the BDHS model renders a total of $3n + 1$ energy levels (because the respective model Hamiltonian matrix is of order $3n + 1$), Rule 1 is far from being self-evident (and, as we shall see, is also not generally valid).

Another way to formulate Rule 1 is based on the result [6] that for alkanes,

$$x_i = y_i - 2$$

where y_i, $i = 1, 2, \ldots, 3n + 1$ are the non-zero Laplacian eigenvalues of the hydrogen-filled molecular graph. (Recall that x_i pertains to the line graph, cf. Figure 1). This implies:

Rule 1′. The hydrogen-filled molecular graph of an alkane with n carbon atoms has exactly n Laplacian eigenvalues greater than $+1$.

Basic Definitions and Statement of the Main Result

In this section we first give some basic definitions concerning Laplacian eigenvalues; for more mathematical and chemical details see the reviews [7] and [8], respectively.

Suppose $H = (V, E)$ is a graph on m vertices; $V = \{v_1, v_2, \ldots, v_m\}$. Denote by $A(H) = (a_{ij})$ its adjacency matrix, i.e., $a_{ij} = 1$ if v_i is adjacent to v_j, and $a_{ij} = 0$, otherwise. Denote by $d_H(v_i)$ the degree (= number of first neighbors) of the vertex v_i. Let $D(H) = \mathrm{diag}(d_H(v_1), d_H(v_2), \ldots, d_H(v_m))$ be the diagonal matrix of vertex degrees. The Laplacian matrix is $L(H) = D(H) - A(H)$. The m eigenvalues of $L(H)$ are called the Laplacian eigenvalues of the graph H. Of these eigenvalues one is always zero and none is negative. If H is connected, then it has $m - 1$ positive-valued Laplacian eigenvalues.

Now, if G is the hydrogen-filled molecular graph of an alkane, then it has $3n + 2$ vertices and $3n + 1$ edges, cf. Figure 1. For such a graph $d_G(v_i) = 4$ if v_i corresponds to a carbon atom, and $d_G(v_i) = 1$ if it corresponds to a hydrogen atom.

As a first step toward analyzing the Laplacian spectra of alkanes, we divide the vertices of a fixed but arbitrary hydrogen-filled molecular graph G into three types. Type 1 consists of the $p = 2n + 2$ vertices of degree 1. (When these vertices – and all the edges adjacent with them – are removed from G, what remains is the hydrogen-depleted molecular graph, the object usually employed in chemical graph theory [4].)

Type 2 vertices of G are the vertices of degree 4 that are adjacent to at least one vertex of degree 1. Denote by q the number of Type 2 vertices. The remaining $r = n - q$ vertices are of Type 3. So, Type 3 vertices are those vertices of degree 4, each of whose four neighbors also has degree 4. In other words, Type 3 vertices correspond to quaternary carbon atoms in the respective molecule.

If $r > 0$, denote by R the graph that remains after the vertices of G of Types 1 and 2 have been removed. Then R is a subgraph of G, induced by the Type 3 (quaternary carbon) vertices. Because G is a tree (a connected acyclic graph), R is a forest (a graph each of whose connected components in a tree). We will refer to the components of R as *quaternary segments* of the corresponding alkane. If $r = 0$, there are no quaternary carbon atoms and no quaternary segments.

An example of the subgraph R is found in Figure 1. It has two quaternary segments: a 2-vertex and a 1-vertex segment.

In what follows we demonstrate that Rule 1 is valid for practically all (chemically sound) alkane species. We namely prove

Theorem 1. Rule 1 is valid for any alkane whose molecular graph does not have a quaternary segment with more than six vertices.

In view of Rule 1′, what we actually prove is:

Theorem 1′. A hydrogen-filled molecular graph of an alkane with n carbon atoms, having no quaternary segment with more than six vertices, has exactly n Laplacian eigenvalues greater than $+1$.

Clearly, Theorems 1 and 1′ are equivalent.

Violations of Rule 1

It follows immediately from Theorem 1 that Rule 1 is valid for alkanes having a total of six or fewer quaternary carbon atoms, and for those having an arbitrary number, no two of which are adjacent. Together, these cases cover practically every alkane relevant to real-life chemistry.

As the proof will indicate, the number six in the statement of the theorem can almost certainly be replaced with a larger number. However, as we see in the following example, this larger number cannot be as big as 53.

Consider a (hypothetical) isomer $C_{161}H_{324}$ having 53 quaternary carbon atoms and a molecular graph G_6 that takes the form of a dendrimer (symmetric “starburst”) in

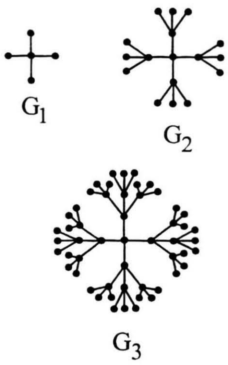

Fig. 2. The hydrogen-filled molecular graphs of the first three members of a hypothetical dendrimer series (G_1 and G_2 represent methane and *neo*-pentane, respectively); G_6, corresponding to a species with formula $C_{161}H_{324}$, provides a counterexample for Rule 1.

which four isomorphic branches extend from a central Type 3 (quaternary carbon) vertex, cf. the series G_1, G_2, $G_3, \ldots$ depicted in Figure 2.

Rule 1′ predicts that G_6 should have 161 Laplacian eigenvalues greater than 1. Calculations show that there are only 160 such eigenvalues, in addition to 109 and 216 eigenvalues less than and equal to 1, respectively. Hence, G_6 is a counterexample to Rule 1.

We mentiuon in passing that, in this case, the $\alpha - \beta$ manifold is 216-times degenerate.

Preparation for the Proof of Theorem 1

Recall that if M is a real symmetric matrix, then all of its eigenvalues are real. The inertia of M is an ordered triple, $\mathrm{in}(M) = (\pi, \nu, \zeta)$, where π, ν and ζ are the number of positive, negative and zero eigenvalues, respectively, of M, multiplicities included. Then $\pi + \nu + \zeta$ is the size of the (necessarily square) matrix M.

We will prove Theorem 1 by showing that if G is the hydrogen-filled molecular graph of an alkane that does not have a quaternary segment with more than six vertices, then

$$\mathrm{in}(L(G) - I_{3n+2}) = (q + r, q, p - q) \tag{1}$$

where I_{3m+2} denotes the unit matrix of order $3m + 2$. Eq. (1) may be rewritten as

$$\mathrm{in}(L(G) - I_{3n+2}) = (n, q, p - q) .$$

Beyond determining that n is the number of eigenvalues of $L(G)$ greater than 1, (1) shows that the multiplicity of the eigenvalue $y = 1$ of $L(G)$ is $p - q$, and that the number of eigenvalues of $L(G)$ less than 1 is precisely equal to the number of nonquaternary carbon atoms in the corresponding alkane. Apart from these observations, the proof is essentially qualitative in nature. It does not afford any information about, e.g., the magnitude of the largest eigenvalue $\mu(G)$.

On the other hand, independently of Theorem 1 and its proof, we offer the following upper bound for $\mu(G)$:

Theorem 2. Let G be the hydrogen-filled molecular graph for a fixed but arbitrary alkane with n carbon atoms. If $\mu(G)$ is its largest Laplacian eigenvalue then, independently of n, $\mu(G) \le 8$. If quaternary carbon atoms are absent, then $\mu(G) \le 7.25$.

Proof. Let $H = (V, E)$ be an arbitrary graph. If $v \in V$, denote by $m_H(v)$ the average of the degrees of the vertices of H adjacent to v. Then [9]

$$\mu(G) \le \max_{v \in V} \, [d_H(v) + m_H(v)] . \tag{2}$$

For our molecular graph, $\max\,[d_G(v)] = 4$, so $\max\,[m_H(v)] \le 4$, and $\mu(G) \le 8$. On the other hand, if every vertex of degree 4 is adjacent to at least one vertex of degree 1, then $\max\,[d_G(v) + m_G(v)] \le 7.25$. □

Proof of Theorem 1

Let G be the hydrogen-filled molecular graph of some fixed but arbitrary alkane. Recall that $G = (V, E)$ has $p = 2n + 2$ vertices of Type 1 (corresponding to hydrogen atoms), q vertices of Type 2 (afforded by nonquaternary carbon atoms), and $r = n - q$ vertices of Type 3 (arising from quarternary carbon atoms). Let $V = \{v_1, v_2, \ldots, v_{3n+2}\}$ where, without loss of generality, we may assume that $v_{p+1}, v_{p+2}, \ldots, v_{p+q}$ are the Type 2 vertices, $v_{p+q+1}, v_{p+q+2}, \ldots, v_{p+q+r}$ are the Type 3 vertices (if there are any), and that for $1 \le i \le q$ the (only) vertex adjacent to v_i is v_{p+i}. With this vertex numbering, $L(G) - I_{3n+2}$ is the 4×4 block partitioned matrix

$$(A_{ij}) = \begin{bmatrix} 0 & 0 & -I_q & 0 \\ 0 & 0 & B & 0 \\ -I_q & B^t & D & C \\ 0 & 0 & C^t & E \end{bmatrix} , \tag{3}$$

where $A_{23} = B$ is a $(p - q) \times q$ matrix, each entry of which is -1 or 0; provided $r > 0$, $A_{34} = C$ is a $q \times r$ matrix of -1's and 0's; $A_{33} = D$ and $A_{44} = E$ are $q \times q$ and $r \times r$

blocks, respectively; B^t and C^t are the transposes of B and C, respectively; and each 0 represents an appropriately sized block of zeros. As we have observed (Eq. (1)), to prove Theorem 1 it suffices to show that $\mathrm{in}(A_{ij}) = (q + r, q, p - q)$.

Recall that a real symmetric matrix M is congruent to the matrix M' if there exists an invertible matrix U such that $M' = U^t M U$. While congruent matrices need not share the same spectrum, they must share the same inertia [10].

Thus it is enough to show that $\mathrm{in}(Y) = (q + r, q, p - q)$ for some matrix Y congruent to (A_{ij}). Because every invertible matrix is a product of elementary matrices, and since $(M_1 M_2)^t = M_2^t M_1^t$, any matrix conguent to (A_{ij}) can be obtained from it by a sequence of congruencies by elementary matrices. This is equivalent to a sequence of modifications obtained by performing an elementary row operation followed by the same elementary operation applied to the columns. For example, because $A_{13} = -I_q$ is the only nonzero block in the first row, and $A_{31} = -I_q$ is the only nonzero block in the first column, elementary operations using these blocks can be employed to annihilate B and B^t, as well as C and C^t. It other words, $L(G) - I_{3n+2} = (A_{ij})$ is congruent to the matrix

$$\begin{bmatrix} 0 & 0 & -I_q & 0 \\ 0 & 0 & 0 & 0 \\ -I_q & 0 & D & 0 \\ 0 & 0 & 0 & E \end{bmatrix}.$$

Similarly, the rows and columns of the $-I_q$'s can be used to zero out all the nondiagonal entries of D. After permuting rows and columns, this produces the congruent matrix

$$\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & -I_q & 0 \\ 0 & -I_q & 3I_q & 0 \\ 0 & 0 & 0 & E \end{bmatrix}. \tag{4}$$

Finally, adding 1/3 of $3I_q$ first to row 2 and then to column 2 of the block partitioned matrix in (4), we obtain the congruent matrix $Y =$

$$\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & (-1/3)I_q & 0 & 0 \\ 0 & 0 & 3I_q & 0 \\ 0 & 0 & 0 & E \end{bmatrix}. \tag{5}$$

Using vector language, we see from (5) that

$$\mathrm{in}(Y) = (q, q, p - q) + \mathrm{in}(E).$$

Fig. 3. The subgraph induced by the quaternary carbon atoms of 2,2,3,3,4,5,5-heptamethyl-4-*t*-butyl hexane.

If there are no quaternary carbons in the alkane considered, then $r = 0$, $q = n$, E does not appear, and the proof is finished. Otherwise, we must prove that $\mathrm{in}(E) = (r, 0, 0)$.

If $r > 0$ and no two quaternary carbons (Type 3 vertices) are adjacent, then $E = 3I_r$, which is a positive definite matrix with inertia $(r, 0, 0)$. More generally, the $r \times r$ matrix E is the direct sum of submatrices S corresponding to the quaternary segments of the forest R, and the vector $\mathrm{in}(E)$ is the sum of the inertias of these submatrices. Therefore, to complete the proof, we must show that each of these matrices is positive definite.

By hypothesis, the quaternary segments are trees on at most 6 vertices. Because there are 14 nonisomorphic trees on 6 or fewer vertices, in order to complete the proof we are obliged to verify that all 14 possibilities for S are positive definite. For instance, for the tree depicted in Fig. 3, S is permutation similar to the matrix

$$\begin{bmatrix} 3 & -1 & 0 & 0 & 0 \\ -1 & 3 & -1 & 0 & 0 \\ 0 & -1 & 3 & -1 & -1 \\ 0 & 0 & -1 & 3 & 0 \\ 0 & 0 & -1 & 0 & 3 \end{bmatrix}$$

whose eigenvalues (to four decimal places) are 4.8478, 3.7654, 3.0000, 2.2345, and 1.1522. Thus the above matrix is positive definite.

Analogous checking shows that the same holds for all 14 trees with 6 or fewer vertices. In particular, ranging over the 14 possibilities for S, the smallest eigenvalue encountered is 0.7639 (and the largest is 5.2361, both arising from the star on 6 vertices). Note that, because congruence does not generally preserve the spectrum, none of these numbers need be eigenvalues of $L(G) - I$.

Discussion

Based on the proof of Theorem 1 and the difficulty of constructing a counterexample for Rule 1, the authors are confident that the rule is a valid guide for any alkanes presently existing or likely to be discovered or synthesized in the foreseen future.

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