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On HOMO–LUMO Separation of Acyclic Molecules*

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Abstract

Let G be a simple, connected graph with n vertices and eigenvalues $\lambda_1 > \lambda_2 \geq \cdots \geq \lambda_n$. Let $H = \lfloor \frac{n+1}{2} \rfloor$ and $L = \lceil \frac{n+1}{2} \rceil$, then the HOMO–LUMO separation of G is defined to be

$$\Delta(G) = \lambda_H - \lambda_L.$$

It is well known that HOMO–LUMO separation plays an important role in chemistry and physics. In this paper, limit points of HOMO–LUMO separation for acyclic molecular graphs (or trees) are studied. It is shown that the set of limit points is

$$\{\beta_1, \beta_2, \cdots, \beta_n, \cdots,\} \bigcup \left[0, \sqrt{6+\sqrt{5}} - \sqrt{2+\sqrt{5}}\right],$$

where $\beta_1 = 2(\sqrt{2}-1)$ and (β_n) is monotone decreasing and approaches $\sqrt{6+\sqrt{5}} - \sqrt{2+\sqrt{5}}$. Moreover, we show that, except the combs, for each tree T with maximum degree at most 3 (the molecular graph of alkenes) and order not less than 11,

$$\Delta(T) \leq \sqrt{6+\sqrt{5}} - \sqrt{2+\sqrt{5}} \approx 0.8116.$$

1 Introduction

In 1952, Fukui et al. proposed Frontier Molecular Orbital Theory (FMO Theory) [6], which is concerned with the frontier orbitals, and in particular the effects of the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital

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(LUMO) on reaction mechanisms. For example, it was found that the reactivity of a molecule is reciprocally proportional to the energy gap between the HOMO and LUMO levels [11]. In the Hückel molecule orbital model [12], the energies of these orbits are in linear relationship with eigenvalues of the corresponding molecular graph, and therefore, Fukui defined the HOMO–LUMO separation of a molecule as follows [7]. Let G be a (molecular) graph of order n, and let $\lambda_1 \geq \lambda_2 \geq \cdots \geq \lambda_n$ be the eigenvalues of its adjacency matrix. The HOMO–LUMO separation of G is

$$\Delta(G) = \lambda_H - \lambda_L,$$

where

$$H = \left\lfloor \frac{n+1}{2} \right\rfloor \quad \text{and} \quad L = \left\lceil \frac{n+1}{2} \right\rceil.$$

Motivated by the problem about HOMO–LUMO separation, related quantities, such as the eigenvalues λ_H, λ_L (called the median eigenvalues of G) themselves and $\max\{|\lambda_H|, |\lambda_L|\}$ (the HL-index introduced by Fowler and Pisanski [8, 9], see also Jaklič et al. [15]) attracted much attention of researchers from both chemical and mathematical literatures. For more recent papers, see Li, et al. [17] and [2,16,18-20].

In this paper, we shall study limit points of HOMO–LUMO separation of acyclic molecular graphs. Note that, for an acyclic molecular graph (or a tree), say T, the eigenvalues of T are symmetric with respect to 0 and T has either a Kekulé structure (or perfect matching) or none. In the latter case the HOMO–LUMO separation is zero and the molecule has extremely high chemical reactivity, so it is very unstable. In the former case the HOMO–LUMO separation is non-zero. In practice, we are normally interested only in this case. An acyclic molecule with a Kekulé structure is called an acyclic Kekulean molecule. Let $\mathfrak{T}_{2k}$ denote the set of all acyclic Kekulean molecular graphs with $2k$ vertices, then for any $T \in \mathfrak{T}_{2k}$, $\Delta(T) = 2\lambda_k > 0$. In [10], Godsil proved that among all acyclic Kekulan molecular graphs in $\mathfrak{T}_{2k}$, the path P_{2k} has the minimum HOMO–LUMO separation. On the other hand, Shao and Hong proved in [21] that the comb C_{2k} has the maximum HOMO–LUMO separation. Since the HOMO–LUMO separation of C_{2k} is decreasing monotonically from 2 to $2(\sqrt{2}-1)$ as k runs from 1 to ∞, we have $\Delta(T) \leq 2$ for any tree T. More recently, Zhang and Chang [25] determined all trees T in $\mathfrak{T}_{2k}$ with $\Delta(T) > 2(\sqrt{2}-1)$. In [26], Zhang and Chen further determined all trees T in $\mathfrak{T}_{2k}$ with

$\Delta(T) > \sqrt{6+\sqrt{5}} - \sqrt{2+\sqrt{5}} \approx 0.8116$. They also gave an asymptotic ordering of trees in $\mathfrak{T}_{2k}$ with respect to the HOMO–LUMO separation.

Recalling that a real number ξ is said to be a limit point of real number set $\mathcal{C}$ if there is an infinite sequence of distinct real numbers $\xi_n \in \mathcal{C}$ such that $\xi = \lim_{n\to\infty} \xi_n$. Let $\triangle = \{\Delta(T) |\ T \in \mathfrak{T}_{2k}, k = 1, 2, \cdots\}$, in this paper, we shall consider limit points of the set $\triangle$. The study of limit points of graph eigenvalues was initiated by Hoffman [13] in 1972. Since then, many interesting results have been obtained on this topic. For example, the set of limit points of the largest eigenvalues of all graphs (or all trees)[13,22] is

$$\{a_1, a_2, \ldots\} \bigcup \left[\sqrt{2+\sqrt{5}}, +\infty\right),$$

where (a_n) is an increasing sequence with $a_1 = 2$ and $\lim_{n\to\infty} a_n = \sqrt{2+\sqrt{5}}$. And every real number is a limit point of eigenvalues of graphs [23]. For other miscellaneous results on limit points of eigenvalues, see [1,4,5,14,24].

The rest of the paper is arranged as follows. In Section 2, we shall give some lemmas we need. Then in Section 3, we shall completely determine the set of limit points of the HOMO–LUMO separations of acyclic Kekulean molecular graphs. As a by product, we also show that, except the combs, for each acyclic Kekulean molecule with maximum degree at most 3 (the molecular graph of alkenes) and order not less than 11, its HOMO–LUMO separation is not larger than $\sqrt{6+\sqrt{5}} - \sqrt{2+\sqrt{5}} \approx 0.8116$.

2 Preliminaries

For simplicity, we use tree instead of acyclic molecular graph in the following. For any tree T of order k, the new tree of order $2k$ obtained by attaching a new pendant edge to each vertex of T is called the *expanded tree* of T and denoted as $\breve{T}$ [26]. Clearly $\breve{T} \in \mathfrak{T}_{2k}$, furthermore, we have the following result.

Lemma 2.1.[25] For any tree T of order k, the HOMO–LUMO separation of $\breve{T}$ is

$$2\lambda_k(\breve{T}) = \sqrt{\lambda_1(T)^2 + 4} - \lambda_1(T),$$

where $\lambda_1(T)$ is the largest eigenvalue of T. ■

Now we define two families of trees. Let $P_n(n \geq 1); Z_n(n \geq 3); W_n(n \geq 5)$; and $T_i(i = 1; 2; \cdots; 6)$ be trees depicted in Figure 1, the set of these trees is denoted by Ω_1, which includes the Dynkin graphs P_n, Z_n, T_1, T_2, T_3, $(\lambda_1(G) < 2)$ and the Euclid graphs $(\lambda_1(G) = 2)$ except the cycles [3].

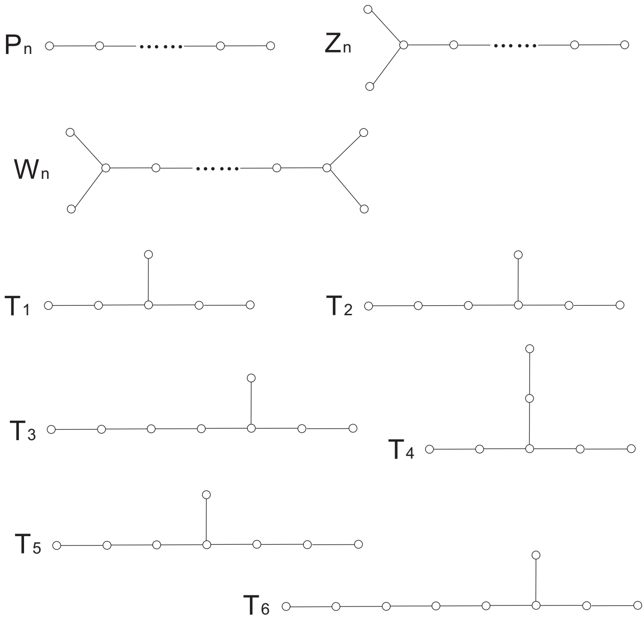

Figure 1. Trees in Ω_1.

Let $T(a; b; c)$ denote the tree with a vertex v of degree 3 such that $T(a; b; c) - v = P_a \cup P_b \cup P_c$ and $Q(a; b; c)$ denote the tree obtained from the path with vertices $1; 2; \cdots ; a + b + c - 1$ (in order) by attaching a pendant edge at each of the vertices a and $a + b$, respectively (see Figure 2).

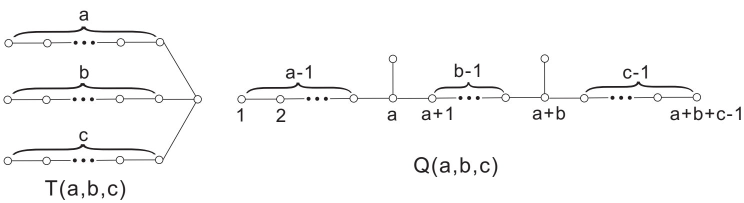

Figure 2. $T(a; b; c)$ and $Q(a; b; c)$.

The set of trees of the following types is denoted by Ω_2:

(a) $T(a;b;c)$ for

$a = 1; b = 2; c > 5$ or

$a = 1; b > 2; c > 3$ or

$a = 2; b = 2; c > 2$ or

$a = 2; b = 3; c = 3.$

(b) $Q(a;b;c)$ for $(a;b;c) \in \{(2;1;3); (3;4;3); (3;5;4); (4;7;4); (4;8;5)\}$

or $a > 1; b > b^*(a;c); c > 1$ where $(a;c) \neq (2;2)$ and

$$b^*(a;c) = \begin{cases} a + c, & \text{for } a > 3; \\ 2 + c, & \text{for } a = 3; \\ -1 + c, & \text{for } a = 2. \end{cases}$$

Lemma 2.2.[26] For $k \geq 6$, let

$$\mathfrak{V}_{2k} = \left\{ T : T \in \mathfrak{T}_{2k}, \Delta(T) > \sqrt{6 + \sqrt{5}} - \sqrt{2 + \sqrt{5}} \right\}.$$

Then $\mathfrak{V}_{2k} = \{\breve{T} : T \in \Omega_1 \cup \Omega_2\}$. ■

Lemma 2.3.[13] Let $\Lambda = \{\lambda_1(T) : T \in \Omega_1 \cup \Omega_2\}$, then limit points of Λ are

$$2 = \alpha_2 < \alpha_3 < \cdots < \alpha_n < \alpha_{n+1} < \cdots < \alpha_\infty = \sqrt{2 + \sqrt{5}},$$

where $\alpha_n = \upsilon_n^{1/2} + \upsilon_n^{-1/2}$ with υ_n as the largest real root of the polynomial

$$f_n(\upsilon) = \upsilon^n - (\upsilon^{n-2} + \cdots + \upsilon + 1).$$ ■

Lemma 2.4.[22] Every real number not less than $\sqrt{2 + \sqrt{5}}$ is a limit point of the largest eigenvalues of trees. ■

3 Main results

Theorem 3.1. Let $\triangle = \{\Delta(T) | \ T \in \mathfrak{T}_{2k}, k = 1, 2, \cdots\}$ denote the set of HOMO–LUMO separations of trees with a Kekulé structure. Then the set of limit points of $\triangle$ is

$$\{f(\alpha_2), f(\alpha_3), \cdots, f(\alpha_n), \cdots, f(\alpha_\infty)\} \bigcup \left[0, \sqrt{6 + \sqrt{5}} - \sqrt{2 + \sqrt{5}}\right],$$

where $f(x) = \sqrt{x^2 + 4} - x$. Moreover $2(\sqrt{2} - 1) = f(\alpha_2) > f(\alpha_3) > \cdots > f(\alpha_n) > \cdots > f(\alpha_\infty) = \sqrt{6 + \sqrt{5}} - \sqrt{2 + \sqrt{5}}$.

Proof. Note that $f(x) = \sqrt{x^2+4} - x$ is a strictly decreasing and continuous function of the variable x. So, first by Lemma 2.1-3, the only limit points of $\triangle$ not less than $\sqrt{6+\sqrt{5}} - \sqrt{2+\sqrt{5}}$ are $f(\alpha_2), f(\alpha_3), \cdots, f(\alpha_n), \cdots, f(\alpha_\infty)$, which is decreasing in this order and approaches $f(\alpha_\infty)$. Second, for any real number $r \in \left(0, \sqrt{6+\sqrt{5}} - \sqrt{2+\sqrt{5}}\,\right]$, $f^{-1}(r) \in [\sqrt{2+\sqrt{5}}, +\infty)$. Thus by Lemma 2.4, there exists a tree sequence (T_k) such that $\lim_{k\to\infty} \lambda_1(T_k) = f^{-1}(r)$, then by Lemma 2.1, $\lim_{k\to\infty} \Delta(\breve{T}_k) = f(f^{-1}(r)) = r$. Finally, it is known that $\Delta(P_{2k}) = 4\cos\frac{k\pi}{2k+1}$, which approaches 0 as $k \to \infty$. Now the proof is complete. ■

Since for a tree $T \notin \bigcup_{k=1}^{\infty} \mathfrak{T}_{2k}$, $\Delta(T) = 0$, we immediately deduce the following results.

Theorem 3.2. The set of limit points of HOMO–LUMO separation for all trees is

$$\{f(\alpha_2), f(\alpha_3), \cdots, f(\alpha_n), \cdots, f(\alpha_\infty)\} \bigcup \left[0, \sqrt{6+\sqrt{5}} - \sqrt{2+\sqrt{5}}\right]. \qquad ■$$

Now we turn our attention to trees with maximum degree at most 3 (the molecular graph of alkenes). For this special class of trees, we can give a more precise result about its HOMO–LUMO separation.

Theorem 3.3. Except the combs, for each tree T with maximum degree at most 3 and order not less than 11, we have

$$\Delta(T) \leq \sqrt{6+\sqrt{5}} - \sqrt{2+\sqrt{5}} \approx 0.8116.$$

Proof. By Lemma 2.2, the only trees with HOMO–LUMO separation not less than $\sqrt{6+\sqrt{5}} - \sqrt{2+\sqrt{5}}$ are $\breve{T}, T \in \Omega_1 \cup \Omega_2$. But these trees, except $\breve{P}_k = C_{2k}$ (the comb), have maximum degree larger than 3. So the result follows. ■

From the above Theorem, we immediately deduce the following result since it is known that, for the comb C_{2k} [25],

$$\Delta(C_{2k}) = 2\left(\sqrt{\cos^2\frac{\pi}{k+1} + 1} - \cos\frac{\pi}{k+1}\right).$$

Corollary 3.1. The limit points of HOMO–LUMO separation of all trees with maximum degree at most 3 lie in

$$\left[0, \sqrt{6+\sqrt{5}} - \sqrt{2+\sqrt{5}}\right] \cup \left\{2(\sqrt{2}-1)\right\}. \qquad ■$$

Then a natural problem pops up.

Problem 1. Is the HOMO–LUMO separation of all trees with maximum degree at most 3 (the molecular graph of alkenes) dense in $\left[0, \sqrt{6+\sqrt{5}} - \sqrt{2+\sqrt{5}}\right]$? ■

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