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Note on the HOMO–LUMO Index of Graphs*

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Abstract

Let G be a simple, connected graph of order n with eigenvalues $\lambda_1 \geq \lambda_2 \geq \cdots \geq \lambda_n$. The median eigenvalues λ_H, λ_L, for $H = \lfloor (n+1)/2 \rfloor$ and $L = \lceil (n+1)/2 \rceil$ are considered. These play an important role in the Hückel molecular orbital model of π-electron systems. The HL–index is defined as $R(G) := \max\{|\lambda_H|, |\lambda_L|\}$. In this paper, bounds on $R(G)$ are obtained. We also prove that for almost all trees, $R(G)$ is zero.

1 Introduction

Let G be a simple, connected graph of order n and $\mathbf{A}(G)$ its adjacency matrix. The collection of eigenvalues of $\mathbf{A}(G)$ is called the spectrum of G. Let $\lambda_1 \geq \lambda_2 \geq \cdots \geq \lambda_n$ be the eigenvalues of $\mathbf{A}(G)$. In linear algebra and in spectral graph theory, particular attention is paid to the principal eigenvalue λ_1, referred to as the spectral radius of the graph. The minimal eigenvalue λ_n and the second maximal eigenvalue λ_2 have also been studied. Apart from some classical bounds, not much is known in general about the remaining eigenvalues. For more results on graph theory and spectral graph theory, we refer the readers to [5] and [7, 9], respectively.

One of the most spectacular applications of graph spectra is in the Hückel molecular orbital (HMO) theory. The fact that the HMO π-electron energy levels are in a simple linear manner

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related to the graph eigenvalues was discovered by Günthard and Primas in the 1950s [18] and rediscovered by Cvetković and one of the present authors in the 1970s [8]. Since then, graph spectral theory became a standard mathematical tool of HMO theory [6, 10, 17, 27, 30].

Within the HMO model. the π-electron energy levels E_i , $i = 1, 2, \ldots, n$, obey the relation

$$E_i = \alpha + \beta \lambda_i$$

where α and β are constants and $\beta < 0$. It is usual to express the energies in so-called β-units, in which case $E_i = \lambda_i$.

An additional important relation between graph spectral and HMO theory is that the eigenvectors of **A** coincide with the molecular orbitals.

Of the various π-electron properties that can be directly expressed by means of graph eigenvalues, the most significant are the so-called *total π-electron energy*, the energy of HOMO, the energy of LUMO and the *HOMO–LUMO separation* or *HOMO–LUMO gap*.

Recall that HOMO and LUMO are acronyms derived from "**H**ighest **O**ccupied **M**olecular **O**rbital" and "**L**owest **U**noccupied **M**olecular **O**rbital".

For conjugated hydrocarbons possessing n conjugated carbon atoms, the total π-electron energy (in the ground state) is expressed in terms of graph eigenvalues as

$$E = \begin{cases} 2 \displaystyle\sum_{i=1}^{n/2} \lambda_i & \text{if } n \text{ is even} \\ \\ 2 \displaystyle\sum_{i=1}^{(n-1)/2} \lambda_i + \lambda_{(n+1)/2} & \text{if } n \text{ is odd} . \end{cases} \tag{1}$$

If n is even, then the $(n/2)$-th graph eigenvector represents the highest (doubly) occupied molecular orbital (the HOMO), whose energy is $\lambda_{n/2}$. The next eigenvector pertains to the lowest unoccupied molecular orbital (the LUMO), whose energy is $\lambda_{n/2+1}$. Then the HOMO–LUMO separation is

$$\Delta_{HL} = \lambda_{n/2} - \lambda_{n/2+1} .$$

In the case of odd n, the situation is more complex, and the usual concept of HOMO–LUMO separation is physically meaningless. The molecular orbital corresponding to $\lambda_{(n-1)/2}$ is doubly occupied, the next, corresponding to $\lambda_{(n+1)/2}$, is singly occupied, whereas the one corresponding to $\lambda_{(n+3)/2}$ is the lowest unoccupied.

The energies of the HOMO and LUMO, as well as their difference (the HOMO–LUMO gap) are responsible to the kinetic stability and reactivity of conjugated molecules. In particular, if

$\Delta_{HL} = 0$, then the underlying π-electron system is predicted to be extremely reactive and is usually not capable of existence.

The graph–spectrum–based study of the structure–dependency of the HMO total π-electron energy became one of the most prolific topics of mathematical chemistry, with scores of exact or approximate results obtained, and hundreds of published papers (for details see the books [17,27,40] and surveys [21,23,24]). Eventually, the concept of total π-electron energy was slightly modified, resulting in the *graph energy*, defined as [20]:

$$\mathcal{E} = \mathcal{E}(G) = \sum_{i=1}^{n} |\lambda_i| \ . \tag{2}$$

More details on $\mathcal{E}$ can be found in the review [26] and book [40]. Note that E in Eq. (1) and $\mathcal{E}$ in Eq. (2) coincide in the case of almost all chemically relevant (molecular) graphs.

In the same time (in the 1970s and early 1980s), graph–spectrum–based studies were initiated also on the structure–dependency of the HOMO and LUMO energies, as well as the HOMO–LUMO separation [16, 22, 25, 28, 29, 31, 38]. In contrast to total π-electron energy, progress was slow and the results obtained were disappointing. In that time George G. Hall expressed the following pessimistic opinion [31]: *The variation in $\lambda_{n/2}$ from molecule to molecule follows too complicated a pattern to be summarized in general rules.*

Indeed, in the next 20 years graph–theory–based research on HOMO and LUMO energies has almost completely stopped, with only a few sporadic publications [1, 12, 45, 46, 49].

As a kind of pleasant surprise, in the newest times activities in the HOMO–LUMO domain got a new impetus, thanks to the appearance of a few works created by mathematicians [13, 14, 37, 41, 42]. The present paper is aimed at being a further contribution along the same lines.

* * * * *

For the vast majority of molecular graphs that are used in HMO-theoretical considerations, the number n of vertices is even, and the conditions $\lambda_{n/2} \geq 0$ and $\lambda_{n/2+1} \leq 0$ are obeyed. Moreover, most of such graphs are bipratite, in which case the equality $\lambda_{n/2} = -\lambda_{n/2+1}$ holds [6, 10, 17, 27, 30]. For such graphs, $\Delta_{HL} = 2\,\lambda_{n/2}$.

2 Preparations: the HL–index

Bearing in mind that in the HMO model, the median graph eigenvalues play an important role, in [37], the HOMO–LUMO radius or HL–index was defined as

$$R(G) := \max\{|\lambda_H|,\ |\lambda_L|\}$$

where $H = \lfloor \frac{n+1}{2} \rfloor$ and $L = \lceil \frac{n+1}{2} \rceil$. In the following, we list some known results on this index. By the Gerschgorin and Cauchy interlacing theorems, one can easily prove that the HL–index of a graph is bounded by its maximal degree or the average degree [7]. In [37], the authors obtained sharp bounds in terms of the maximum degree, and proved that the HL–index may be arbitrarily large.

Theorem 2.1. *Let G be a graph with maximum degree Δ. Then $0 \leq R(G) \leq \Delta$. Equality in the lower bound is reached for many graphs, whilst the equality in the upper bound is reached only for the complete graph K_2.* □

For bipartite and pseudo-bipartite graphs, tighter bounds were obtained in [13].

Theorem 2.2. *Let G be a bipartite or pseudo-bipartite graph with n vertices and m edges, and let $d(G) = 2m/n$ denote its average degree. Then $0 \leq R(G) \leq \sqrt{d(G)}$. Thus, in particular, if G is a chemical bipartite or pseudo-bipartite graph, then $0 \leq R(G) \leq \sqrt{3}$.* □

A connected graph with maximum degree at most 3 is said to be a *subcubic* graph or a *chemical graph* or a *Hückel graph*. It is an important concept in chemistry [27]. In [13] it was shown that $R(T) \leq 1$ for each chemical tree T. Since for the Heawood graph G, $R(G) = \sqrt{2}$, the upper bound is in general at least $\sqrt{2}$ and less than 3 for chemical graphs: $\sqrt{2} \leq R(G) < 3$. Godsil [15] proved that among all trees on $2k$ vertices with perfect matchings, the path has the minimum smallest positive eigenvalue, i.e., the minimum value of the HL-index. Shao and Hong [46] proved that among all trees on $2k$ vertices with perfect matchings, the comb graph has the maximum HL-index. For more results, we refer to the work of Zhang and Chang [49]. Recently, Mohar [41, 42] proved the following results.

Theorem 2.3. (1) *If G is subcubic, then $R(G) \leq \sqrt{2}$;* (2) *If G is subcubic planar bipartite, then $R(G) \leq 1$;* (3) *There exists a positive constant c such that for each subcubic graph G of order n, G has $\lceil cn \rceil$ median eigenvalues in the interval $[-\sqrt{2}, \sqrt{2}]$.* □

Mohar also conjectured that $R(G) \leq 1$ for every subcubic planar graph.

For general graphs, no such bounds are known. In [37], some interesting problems are proposed. Two of them are listed as follows:

- Determine the graphs G with n vertices and m edges with maximal HL–index.
- Determine the graphs G on n vertices with maximal HL–index.

In this paper, we consider the above two problems and some bounds on the HL–index of graphs are obtained in terms of graph energy. Observe that zero is a trivial lower bound of the

HL–index. Thus, it is interesting to characterize all graphs whose HL–index is zero. We prove that the HL–index of almost all trees is zero.

3 Bounds on the HL–index

By the definitions of HL–index and graph energy, one can easily see that for a simple bipartite graph G of order n, $0 \leq R(G) \leq \mathcal{E}(G)/n$. Actually, this upper bound also holds for general graphs.

Theorem 3.1. *For a simple connected graph G of order n, $0 \leq R(G) \leq \mathcal{E}(G)/n$.*

Proof. Let G be a simple, connected graph of order n with eigenvalues $\lambda_1 \geq \lambda_2 \geq \cdots \geq \lambda_n$. Let $\sum \lambda_i^+$ denote the sum of the positive eigenvalues of G and $\sum \lambda_j^-$ the sum of the negative eigenvalues of G. Then we have

$$\mathcal{E}(G) = 2\sum \lambda_i^+ = 2\sum \lambda_j^-.$$

We distinguish the following cases to show the theorem.

Case 1. $\lambda_{\lfloor \frac{n+1}{2} \rfloor} \geq \lambda_{\lceil \frac{n+1}{2} \rceil} \geq 0$.

Then $R(G) = \lambda_{\lfloor \frac{n+1}{2} \rfloor}$. Note that

$$\begin{aligned} \frac{\mathcal{E}(G)}{n} &= \frac{2\sum \lambda_i^+}{n} \geq \frac{2(\lambda_1 + \cdots + \lambda_{\lfloor \frac{n+1}{2} \rfloor} + \lambda_{\lceil \frac{n+1}{2} \rceil})}{n} \\ &\geq \frac{\lambda_1 + \cdots + \lambda_{\lfloor \frac{n+1}{2} \rfloor}}{\frac{n}{2}} \geq \frac{\lfloor \frac{n+1}{2} \rfloor \lambda_{\lfloor \frac{n+1}{2} \rfloor}}{\frac{n}{2}} \geq \lambda_{\lfloor \frac{n+1}{2} \rfloor}. \end{aligned}$$

So, in this case we have that $R(G) = \lambda_{\lfloor \frac{n+1}{2} \rfloor} \leq \frac{\mathcal{E}(G)}{n}$.

Case 2. $0 \geq \lambda_{\lfloor \frac{n+1}{2} \rfloor} \geq \lambda_{\lceil \frac{n+1}{2} \rceil}$.

Then $R(G) = -\lambda_{\lceil \frac{n+1}{2} \rceil}$. Note that

$$\begin{aligned} \frac{\mathcal{E}(G)}{n} &= \frac{2\sum(-\lambda_j^-)}{n} \geq \frac{-\lambda_{\lceil \frac{n+1}{2} \rceil} - \cdots - \lambda_n}{\frac{n}{2}} \\ &\geq \frac{\left(n - \left(\lceil \frac{n+1}{2} \rceil - 1\right)\right)\left(-\lambda_{\lceil \frac{n+1}{2} \rceil}\right)}{\frac{n}{2}}. \end{aligned}$$

Since $n - \left(\lceil \frac{n+1}{2} \rceil - 1\right) \geq \frac{n}{2}$, we have that $\frac{\mathcal{E}(G)}{n} \geq -\lambda_{\lceil \frac{n+1}{2} \rceil}$. So, $R(G) = -\lambda_{\lceil \frac{n+1}{2} \rceil} \leq \frac{\mathcal{E}(G)}{n}$.

Case 3. $\lambda_{\lfloor \frac{n+1}{2} \rfloor} > 0$, $\lambda_{\lceil \frac{n+1}{2} \rceil} < 0$.

Then $R(G) = \max\{\lambda_{\lfloor \frac{n+1}{2} \rfloor}, -\lambda_{\lceil \frac{n+1}{2} \rceil}\}$. Note that

$$\frac{\mathcal{E}(G)}{n} = \frac{2\sum \lambda_i^+}{n} = \frac{\lambda_1 + \cdots + \lambda_{\lfloor \frac{n+1}{2} \rfloor}}{\frac{n}{2}} \geq \frac{\lfloor \frac{n+1}{2} \rfloor \lambda_{\lfloor \frac{n+1}{2} \rfloor}}{\frac{n}{2}} \geq \lambda_{\lfloor \frac{n+1}{2} \rfloor}$$

and

$$\begin{aligned}\frac{\mathcal{E}(G)}{n} &= \frac{2\sum(-\lambda_j^-)}{n} = \frac{-\lambda_{\lceil\frac{n+1}{2}\rceil} - \cdots - \lambda_n}{\frac{n}{2}} \\ &\geq \frac{\left(n - \left(\lceil\frac{n+1}{2}\rceil - 1\right)\right)\left(-\lambda_{\lceil\frac{n+1}{2}\rceil}\right)}{\frac{n}{2}} \geq -\lambda_{\lceil\frac{n+1}{2}\rceil}.\end{aligned}$$

So, $\frac{\mathcal{E}(G)}{n} \geq \max\{\lambda_{\lfloor\frac{n+1}{2}\rfloor}, -\lambda_{\lceil\frac{n+1}{2}\rceil}\}$. That is, $R(G) = \max\{\lambda_{\lfloor\frac{n+1}{2}\rfloor}, -\lambda_{\lceil\frac{n+1}{2}\rceil}\} \leq \frac{\mathcal{E}(G)}{n}$.

The proof is now complete. □

Therefore, each upper bound for $\mathcal{E}(G)$ implies an upper bound for $R(G)$.

Let G be a graph with n vertices and m edges. Koolen and Moulton [34, 36] obtained the following result: If $2m \geq n$, then

$$\mathcal{E}(G) \leq \frac{2m}{n} + \sqrt{(n-1)\left[2m - \left(\frac{2m}{n}\right)^2\right]}.$$

If, in addition, G is bipartite, then [35, 36]

$$\mathcal{E}(G) \leq \frac{4m}{n} + \sqrt{(n-2)\left[2m - 2\left(\frac{2m}{n}\right)^2\right]}.$$

Let T be a tree of order n. A basic result is that [19] $\mathcal{E}(S_n) \leq \mathcal{E}(T) \leq \mathcal{E}(P_n)$, where S_n and P_n denote the star graph and path graph of order n, respectively. The unicyclic graphs with maximum energy are finally determined in [33] and [2], independently. Huo et al. [32] determined the maximal energy among all bipartite bicyclic graphs. Recently, Wagner [48] showed that the maximum value of the graph energy within the set of all graphs with cyclomatic number k (which includes, for instance, trees or unicyclic graphs as special cases) is at most $4n/\pi + c_k$ for some constant c_k that only depends on k.

From these results, we get appropriate bounds for $R(G)$.

Theorem 3.2. *Let G be a graph with n vertices and m edges. If $2m \geq n$, then*

$$0 \leq R(G) \leq \frac{2m}{n^2} + \frac{1}{n}\sqrt{(n-1)\left[2m - \left(\frac{2m}{n}\right)^2\right]}.$$

If, in addition, G is bipartite, then

$$0 \leq R(G) \leq \frac{4m}{n^2} + \frac{1}{n}\sqrt{(n-2)\left[2m - 2\left(\frac{2m}{n}\right)^2\right]}.$$

If $m = n - 1$, i.e., if G is a tree, then

$$0 \leq R(G) \leq \frac{4}{\pi}.$$

If $m = n - 1 + k$, i.e., the cyclomatic number is k, then

$$0 \le R(G) \le \frac{4}{\pi} + \frac{c_k}{n}$$

where c_k is a constant depending only on k.

Proof. We only consider the third case since the other cases are immediate consequences of Theorem 3.1. Notice that for a tree T, $0 \le R(T) \le \mathcal{E}(P_n)/n$ and

$$\mathcal{E}(P_n) \;=\; \begin{cases} \dfrac{2}{\sin\frac{\pi}{2(n+1)}} - 2 & \text{if } n \equiv 0 \ (mod\ 2) \\ \dfrac{2\cos\frac{\pi}{2(n+1)}}{\sin\frac{\pi}{2(n+1)}} - 2 & \text{if } n \equiv 1 \ (mod\ 2)\ . \end{cases}$$

Since the function $\frac{1}{x}\left(\frac{2}{\sin\frac{\pi}{2(x+1)}} - 2\right)$ is monotonically increasing on x and

$$\lim_{x\to+\infty} \frac{1}{x}\left(\frac{2}{\sin\frac{\pi}{2(x+1)}} - 2\right) = \frac{4}{\pi}$$

and also the function $\frac{1}{x}\left(\frac{2\cos\frac{\pi}{2(n+1)}}{\sin\frac{\pi}{2(n+1)}} - 2\right)$ is monotonically increasing on x and

$$\lim_{x\to+\infty} \frac{1}{x}\left(\frac{2\cos\frac{\pi}{2(n+1)}}{\sin\frac{\pi}{2(n+1)}} - 2\right) = \frac{4}{\pi}$$

we have $0 \le R(T) \le 4/\pi$. □

Let G be a graph of order n. In [34] it was shown that $\mathcal{E}(G) \le \frac{n}{2}(\sqrt{n}+1)$. If in addition G is bipartite, then [35] $\mathcal{E}(G) \le \frac{n}{\sqrt{8}}(\sqrt{n}+\sqrt{2})$. Recently, it was demonstrated [47] that if G is a k-regular graph order n, then $\mathcal{E}(G) \le \frac{k+(k^2-k)\sqrt{k-1}}{k^2-k+1}\,n$. Then from Theorem 3.1, we obtain the following results.

Theorem 3.3. *Let G be a graph of order n. Then*

$$0 \le R(G) \le \frac{\sqrt{n}+1}{2}\ .$$

If G is bipartite, then

$$0 \le R(G) \le \frac{\sqrt{n}+\sqrt{2}}{\sqrt{8}}\ .$$

If G is k-regular, then

$$0 \le R(G) \le \sqrt{k-1} + \frac{1}{k+\sqrt{k-1}}\ .$$

□

4 The HL–index of trees

Note that zero is a trivial lower bound of $R(G)$. Therefore it is interesting to characterize all graphs with $R(G) = 0$. Note that for bipartite graphs with odd number of vertices, the HL–index is zero. In the following, we show that this is the property of almost all trees.

Before our proof, we recall a useful lemma. Let G be a graph. Denote by $N(v)$ the set of first neighbors of the vertex v of G.

Lemma 4.1. [3] *If G has two vertices v_i and v_j, such that $N(v_i) = N(v_j)$, then zero is an eigenvalue of G.* □

Corollary 4.2. *If a bipartite graph G has two vertices v_i and v_j, such that $N(v_i) = N(v_j)$, then $R(G) = 0$.* □

By this corollary, if we know that in a tree there are two leaves attached to the same vertex, then the HL–index of this tree is equal to zero.

We now show that for almost every tree, there exist two leaves connected to the same vertex.

Following the book [4], we say that *almost every* (a.e.) graph in a graph space $\mathcal{G}_n$ has a certain property Q if the probability $\Pr(Q)$ in $\mathcal{G}_n$ converges to 1 as n tends to infinity. Occasionally, we will say *almost all* instead of almost every.

Let $\mathcal{T}_n$ be the set of trees with n vertices. We always suppose that each tree in $\mathcal{T}_n$ is chosen with equal probability. In order to complete our proof, we state the following lemma [43].

Lemma 4.3. [43] *For almost all trees, the number of vertices of degree one approximately equals $(0.438156 + o(1))n$ and the number of vertices of degree 2 approximately equals $(0.293998 + o(1))n$.* □

A *rooted tree* is a tree with one vertex designated to be the root. If we add one new vertex to the root, the new tree is a *planted tree*. This additional vertex is not included into the vertex count of the underlying rooted tree.

The edges with one endpoint of degree one and the other of degree two will play a central role in our proof. For the sake of brevity we refer to these as $(1, 2)$-edges.

Let A_n be the number of planted trees with n vertices, and

$$p(x, u) = \sum_{n \geq 1, k \geq 0} a_{n,k}\, x^n\, u^k$$

be the generating function, in which $a_{n,k}$ represents the number of planted trees with n vertices and k $(1, 2)$-edges. Clearly, $\sum_k a_{n,k} = A_n$. It has been shown that [43]

$$A_n \leq \frac{1}{2}\binom{\frac{1}{2}}{n} \cdot 4^n \ .$$

Direct calculation yields

$$p(x,u) = x + x^2u + x^3(u+1) + x^4(2u+2) + x^5(u^2+4u+4) + \cdots .$$

In [39], it was established that for almost all trees, the number of $(1,2)$-edges is

$$\left(\frac{2}{x_0\, b_0^2}\, w(1,2) + o(1)\right) n$$

where $x_0 \approx 0.3383219$, $b_0 \approx 2.6811266$ [11] and $w(1,2) = \sum_{k\geq 2} p_u(x_0^k, 1)$.

We can now prove the following theorem.

Theorem 4.4. *For almost every tree, there are two leaves attached to the same vertex.*

Proof. By Lemma 4.3, we get that there are less than $0.267847\, n$ vertices with degree at least three for almost all trees in $\mathcal{T}_n$. Suppose that there is no pair of leaves connected to the same vertex of these. Then there would be at least $0.17030\, n$ leaves connected to vertices of degree two. In other words, the number of $(1,2)$-edges would be at least $0.17030\, n$.

We can get that

$$\begin{aligned} p_u(x,1) &= x^2 + x^3 + 2x^4 + 6x^5 + \cdots c_n x^n + \cdots \\ &\leq x^2 + x^3 + 2x^4 + 6x^5 + \sum_{n\geq 6} \frac{n}{2} \cdot A_n \cdot x^n \\ &< x^2 + x^3 + 2x^4 + 6x^5 + \sum_{n\geq 6} \frac{n}{2} 4^{n-1} x^n \ , \end{aligned}$$

where $c_n's$ are some constants. It is easy to see that in a tree, there are at most $n/2$ $(1,2)$-edges. Then, the first inequality holds. And by the fact that $A_n \leq \frac{1}{2}\binom{\frac{1}{2}}{n} \cdot 4^n < 4^{n-1}$, the second inequality holds. Recall that $x_0 \approx 0.33832$. Therefore,

$$\begin{aligned} \sum_{k\geq 2} p_u(x_0^k, 1) &\leq \sum_{k\geq 2} \left(x_0^{2k} + x_0^{3k} + 2\, x_0^{4k} + 6\, x_0^{5k} + \sum_{n\geq 6} \frac{n}{2}\, 4^{n-1}\, x_0^{nk} \right) \\ &= \frac{x_0^4}{1-x_0^2} + \frac{x_0^6}{1-x_0^3} + \frac{2\, x_0^8}{1-x_0^4} + \frac{6\, x_0^{10}}{1-x_0^5} + \sum_{n\geq 6} \frac{n}{2}\, 4^{n-1} \cdot \frac{x_0^{2n}}{1-x_0^n} \\ &< 0.018 + 1.01 \cdot \sum_{n\geq 6} \frac{n}{16} \cdot 0.5^{n-1} < 0.074. \end{aligned}$$

Then, $\dfrac{2}{x_0\, b_0^2}\, w(1,2) < 0.074$. We get that for almost all trees, the number of $(1,2)$-edges is less than $0.074\, n$, which is a contradiction. Hence, there exists at least one pair of leaves connected to the same vertex in almost every tree. □

From Theorem 4.4 and Corollary 4.2, we arrive at our main result.

Theorem 4.5. *For almost every tree, the HL-index is zero.*

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