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# Total π-electron energy and Laplacian energy: How far the analogy goes?

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*Abstract*: The Laplacian energy *LE* is a newly introduced molecular-graph-based analog of the total π-electron energy *E*. It is shown that *LE* and *E* have a similar structure-dependency only when molecules of different sizes are compared, when a good linear correlation between them exists. Within classes of isomers, *LE* and *E* are either not correlated at all or (as in the case of acyclic systems) are inversely proportional. The acyclic graphs and molecular graphs having the greatest and smallest *LE* values (determined in this work) differ significantly from those (previously known) having the greatest and smallest *E* values.

*Keywords*: Laplacian energy, graph energy, total π-electron energy.

## INTRODUCTION

The total π-electron energy *E*, as calculated within the Hückel molecular orbital (HMO) model, is one of the most thoroughly studied quantum–chemical characteristics of large polycyclic conjugated molecules. Details on the theory and applications of *E* can be found in the literature[1–3] and in the references cited therein. It was recognized a long time ago that the various π-electron descriptors of the HMO model, including *E*, can be calculated from the eigenvalues $\lambda_1$, $\lambda_2$, …, $\lambda_n$ of the underlying molecular graph.[4,5] In particular, in the case of alternant hydrocarbons:

$$E = \sum_{i=1}^{n} |\lambda_i| \qquad (1)$$

where, as usual,[1,2,4,5] *E* is expressed in the units of the HMO carbon–carbon resonance integral $\beta$.

Formula (1) served as a motivation for the definition of the so-called graph energy. Namely, whereas within the HMO model *E* is meaningful only in the case of a restricted class of molecular graphs,[5] the right-hand side of (1) is a well-de-

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fined quantity for all graphs. In view of this, the energy of a graph (also denoted by $E$) is defined as the sum of the absolute values of all eigenvalues of this graph, and this definition extends to all graphs. This seemingly insignificant change in the interpretation of Eq. (1) resulted in a great expansion of research in this area and has advanced the theory of total π-electron energy greatly; for details see the reviews[1,6] and some of the most recent publications dealing with graph energy.[7–14]

By Eq. (1), the graph energy is defined in terms of the graph eigenvalues $\lambda_1$, $\lambda_2$, …, $\lambda_n$. Recall that these are just the eigenvalues of the adjacency matrix.[15] In graph spectral theory, the eigenvalues of several other matrices have been studied, of which the Laplacian matrix attracted the greatest attention in both mathematics[15] and chemistry.[16–21] In view of this, a Laplacian analog of $E$ has recently been conceived,[22] defined as:

$$LE = \sum_{i=1}^{n} \left| \mu_i - \frac{2m}{n} \right| \qquad (2)$$

where $\mu_1$, $\mu_2$, …, $\mu_n$ are the Laplacian eigenvalues, $m$ is the number of edges and $n$ the number of vertices of the underlying graph. At the first glance, the forms of the right-hand sides of Eqs. (1) and (2) are different. However, both are special cases of the general expression:

$$\sum_{i=1}^{n} \left| x_i - \bar{x} \right|$$

where $\bar{x}$ is the average value of the eigenvalues $x_1$, $x_2$, …, $x_n$. Indeed,[1–18] $\lambda = 0$ whereas $\mu = 2m/n$.

Both in the first paper[22] on the Laplacian energy and in two consecutive papers[23,24] it could be shown that several mathematical properties of $LE$ are fully analogous (or even identical) to properties of $E$. However, with regard to some other properties, $LE$ and $E$ differ significantly. Hitherto, no detailed numerical testing of the relation between $LE$ and $E$ has been reported. The aim of this work is to contribute towards filling this gap.

## RELATION BETWEEN ENERGY AND LAPLACIAN ENERGY IN BENZENOID AND ACYCLIC SYSTEMS

It is known that the main parameters determining the value of the total π-electron energy $E$ are $n$ (= the number of carbon atoms, *i.e.*, the number of vertices of the molecular graph) and $m$ (= the number of carbon–carbon bonds, *i.e.*, the number of edges of the molecular graph).[1,2,25,26] In order to test if, in the case of molecular graphs, the same parameters also influence the value of the Laplacian energy, $E$ and $LE$ have been correlated for benzenoid molecules (Fig. 1) and acyclic systems (Fig. 2). In Fig. 1, the standard set[1,26] of 106 Kekuléan benzenoids from the book[27] is employed. Figure 2 shows the correlation between $E$ and $LE$ for the set consisting of all $n$-vertex trees with $n$ between 2 and 14, for which

$n_0 = 0$. Here $n_0$ stands for the number of zero eigenvalues, which in the HMO model are equal to the number of non-bonding molecular orbitals. The choice $n_0 = 0$ was made because earlier studies[28–30] revealed that the energy of trees is significantly influenced by the value of $n_0$, whereas *LE* was found to be practically independent of this value.

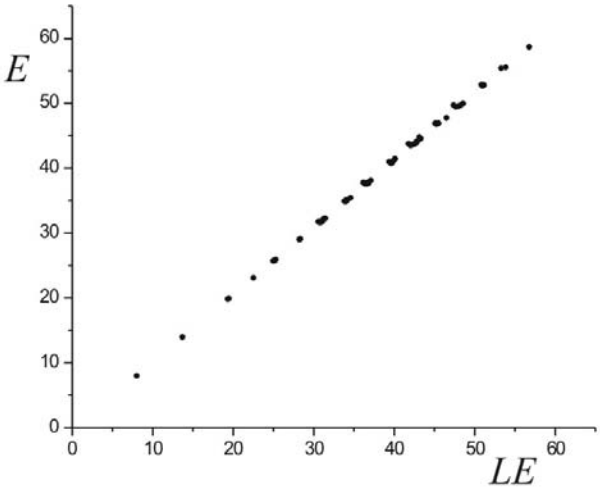


Fig. 1. The Laplacian energy (*LE*) of Kekuléan benzenoid molecules *versus* the respective total π-electron energy (*E*). The data set is taken from the book[27] and consists of 106 benzenoids of various sizes. The regression line reads $LE = (1.043\pm0.002)E - (0.42\pm0.08)$ and the correlation coefficient is 0.9998. For details, see the text.

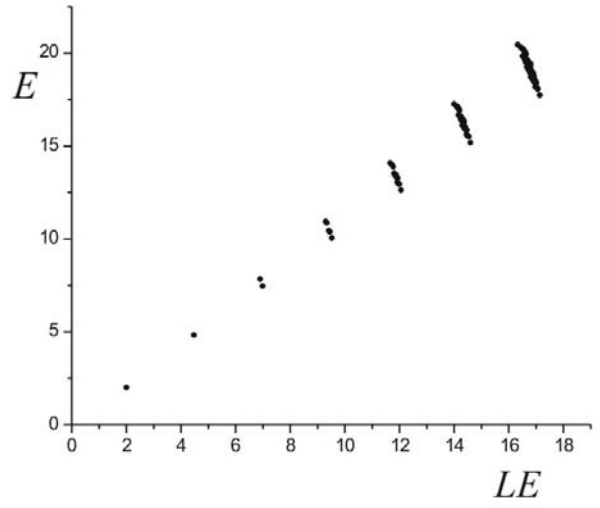


Fig. 2. The Laplacian energy (*LE*) of trees without zero eigenvalues ($n_0 = 0$) *versus* the respective *E* value. The data set consists of all 253 such systems with *n* vertices, $2 \leq n \leq 14$. Recall that from the requirement $n_0 = 0$ follows that *n* must be even.[15] The regression line reads $LE = (1.14\pm0.02)E - (0.0\pm0.3)$ and the correlation coefficient is 0.969. For details, see the text.

From Figs. 1 and 2, it can be seen that a very good linear correlation exists between *LE* and *E*, which means that the gross part of both the total π-electron energy and the Laplacian energy are determined by the parameters *n* and *m*. Furthermore, both *LE* and *E* depend on *n* and *m* in essentially the same way. As the (*n*,*m*)-dependence of *E* is well understood,[1,2,31] it may be said that the (*n*,*m*)-dependence of the Laplacian energy is also known.

RELATION BETWEEN ENERGY AND LAPLACIAN ENERGY IN SETS OF ISOMERS

Many graph-based molecular structure descriptors have the property that their value is mainly determined by the parameters *n* and *m.* In order to envisage the finer details of their structure-dependence, the standard procedure is to examine their behavior within sets of molecular graphs with equal *n* and *m*, *i.e.*, within sets of isomers.

In Figs. 1 and 2, isomers correspond to points that lie very near to each other. In Fig. 1, the spread of these points cannot be seen at all, implying that in the case of benzenoid molecules, structural details other than *n* and *m* have a very small influence on the values of *E* and *LE*. In the case of acyclic systems, this influence is somewhat stronger and the deviation of the data-points from the regression line is easily recognized.

Various sets of benzenoid isomers were examined and in all cases it was found that their Laplacian energies and total π-electron energies are completely unrelated. A characteristic example is shown in Fig. 3.

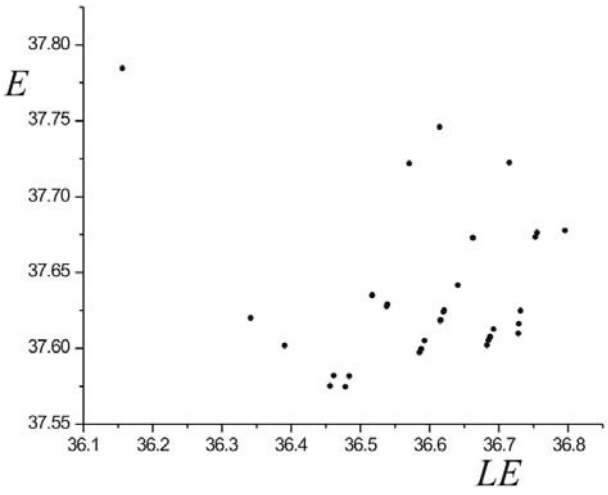


Fig. 3. The Laplacian energy *versus* the total π-electron energy for the set of all 36 (isomeric) catacondensed benzenoids with 6 hexagons, all having the formula $C_{26}H_{16}$. There is no correlation.

The fact that in the case of trees an inverse correlation between *LE* and *E* exists has already seen from Fig. 2. In Fig. 2, the group of near-lying data-points corresponds to a fixed value of *n* and, since for trees $m = n–1$, also to a fixed value of *m*. Note that all trees with odd number of vertices have the property $n_0 > 0$, and therefore for all acyclic systems shown in Fig. 2, the parameter *n* is even.

A detailed examination showed that for acyclic isomers with a fixed value of $n_0$, the (*LE*,*E*) data-points are linearly correlated. A characteristic example is shown in Fig. 4.

The finding that the slopes of the (*LE*,*E*) regression lines are negative is remarkable and (for the authors of this paper) was fully unexpected. It implies that within sets of acyclic isomers, the structural factors which increase the total π-ele-

ctron energy decrease the Laplacian energy, and *vice versa*. It has been known for a long time[32,33] that the extent of branching is the main such structural factor which decreases *E*. As a consequence of this, the more branched an acyclic system is, the greater will be its Laplacian energy. Thus, as far as the effect of branching is concerned, *E* and *LE* exhibit a different and opposite structure-dependence. Further consequences of this finding are outlined in the subsequent section.

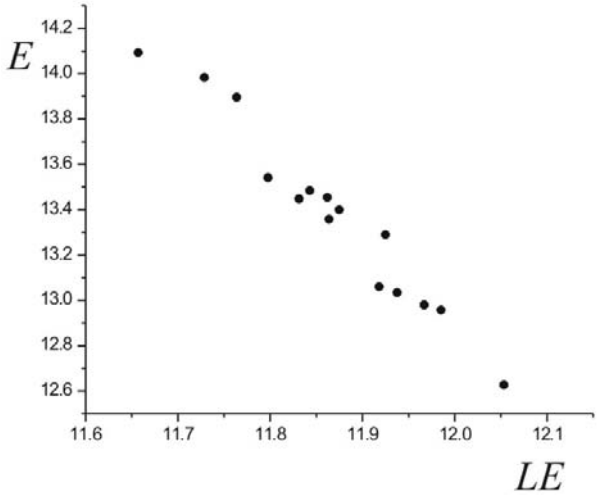


Fig. 4. The Laplacian energy *versus E* for the set consisting of all 10-vertex trees without zero eigenvalues (a total of 15); these graphs pertain to (isomeric) acyclic conjugated hydrocarbons with formula $C_{10}H_{12}$. As a kind of surprise, there is a decreasing linear correlation between *LE* and *E*, implying that acyclic isomers with large *E* have small *LE* and *vice versa*. The correlation coefficient is −0.980.

## TREES AND CHEMICAL TREES WITH GREATEST AND SMALLEST LAPLACIAN ENERGY

In graph theory, a connected acyclic graph is called a "tree". A "chemical tree" is a tree in which no vertex has degree greater than 4. A "path" is a tree in which no vertex has degree greater than 2. A "star" is a tree in which all but one of the vertices are of degree 1. An *n*-vertex path and an *n*-vertex star will be denoted by $P_n$ and $S_n$, respectively, see Fig. 5.

It is known[34] that among all *n*-vertex trees, $P_n$ and $S_n$ have, respectively, the greatest and smallest energy, that is:

$$E(P_n) < E(T_n) < E(S_n) \tag{3}$$

where $T_n$ is any *n*-vertex tree different from $P_n$ and $S_n$.

It was found now (by means of a computer-aided systematic search of all trees with *n* up to 17) that a relation opposite to (3) holds for the Laplacian energy, *viz.*:

$$LE(P_n) > LE(T_n) > LE(S_n) \tag{4}$$

In view of the Relations (3) and (4), one arrives at:

*Rule 1*. Among the *n*-vertex trees, the star $S_n$ has the greatest Laplacian energy. In contrast with this, the star has the smallest energy.[34] Rule 1 holds for all $n \geq 4$, and in a trivial manner also for $n = 1,2,3$.

*Rule 2.* Among the $n$-vertex trees, the path $P_n$ has the smallest Laplacian energy. In contrast with this, the path has the greatest energy.[34] Rule 2 holds for all $n \geq 4$, and in a trivial manner also for $n = 1,2,3$.

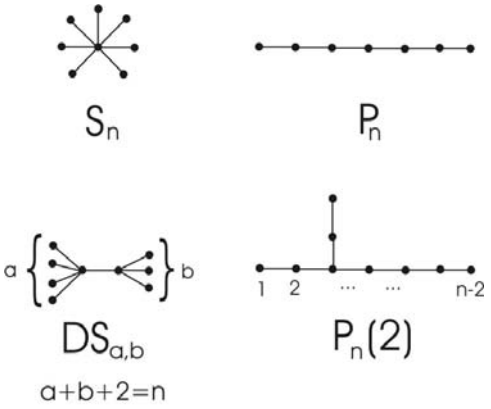


Fig. 5. Trees with extreme Laplacian energy; for details, see the text.

The trees with the second-maximal, third-maximal, and fourth-maximal Laplacian energy have also been determined. Let $DS_{a,b}$ be a "double star" with $a+b+2$ vertices, depicted in Fig. 5. Then one obtains:

*Rule 3.* If $n$ is even, $n \geq 4$, then among the $n$-vertex trees, the double star $DS_{a,b}$ with parameters $a = (n-2)/2$, $b = (n-2)/2$ has the second-greatest Laplacian energy. If $n$ is odd, $n \geq 5$, then among the $n$-vertex trees, the double star $DS_{a,b}$ with parameters $a = (n-1)/2$, $b = (n-3)/2$ has the second-greatest Laplacian energy.

*Rule 4.* If $n$ is even, $n \geq 6$, then among the $n$-vertex trees, the double star $DS_{a,b}$ with parameters $a = n/2$, $b = (n-4)/2$ has the third-greatest Laplacian energy. If $n$ is odd, $n \geq 7$, then among the $n$-vertex trees, the double star $DS_{a,b}$ with parameters $a = (n+1)/2$, $b = (n-5)/2$ has the third-greatest Laplacian energy.

*Rule 5.* If $n$ is even, $n \geq 8$, then among the $n$-vertex trees, the double star $DS_{a,b}$ with parameters $a = (n+2)/2$, $b = (n-6)/2$ has the fourth-greatest Laplacian energy. If $n$ is odd, $n \geq 9$, then among the $n$-vertex trees, the double star $DS_{a,b}$ with parameters $a = (n+3)/2$, $b = (n-7)/2$ has the fourth-greatest Laplacian energy.

Note that the trees described in Rules 3–5 are different from those with the second-minimal, third-minimal, and fourth-minimal energy.[34] On the other hand, the tree with the second-minimal Laplacian energy coincides with the tree with the second-maximal energy:

*Rule 6.* Among the $n$-vertex trees, the graph $P_n(2)$, the structure of which is depicted in Fig. 5, has the second-smallest Laplacian energy. In contrast with this, the same tree has the second-greatest energy.[34] Rule 6 holds for $n \geq 13$.

The trees specified in Rules 2 and 6 are molecular graphs. Therefore, these rules also automatically determine the chemical trees with the minimal and second-minimal Laplacian energy. A search for chemical trees with maximal Laplacian energy lead to another unexpected finding:

*Rule 7.* Among the $n$-vertex chemical trees, the trees the structure of which is depicted in Fig. 6 have the greatest Laplacian energy. Rule 7 holds for all $k \geq 2$, that is for $n \geq 6$ if $n = 3k$, for $n \geq 7$ if $n = 3k+1$ and for $n \geq 8$ if $n = 3k+2$.

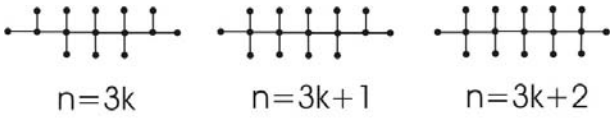


Fig. 6. Chemical trees with the greatest Laplacian energy; for details, see the text.

One should note that the chemical trees shown in Fig.6 with the maximal-Laplacian-energy are different from those having minimal energy.[35]

## CONCLUDING REMARKS

The results outlined in the preceding sections reveal some quite unusual features of the relation between the Laplacian energy *LE* and the total π-electron energy (or graph energy) *E*. Whereas both *LE* and *E* have the same (*n*,*m*)-dependence (as seen from the good linear correlations shown in Figs. 1 and 2), this analogy breaks down when classes of isomers are considered, having equal (*n*,*m*). Then the correlation between *LE* and *E* may be completely lost (*cf.* Fig. 3) or an inverse correlation is found (*cf.* Fig. 4). In the case of trees, this inverse behavior of *LE* and *E* is best manifested in Rules 1 and 2 (and also in Rule 6). However, such an inverse analogy between *LE* and *E* is not generally obeyed, as seen in Rules 3, 4, 5, and 7.

In summary, the Laplacian energy and the total π-electron energy were found to be only weakly related. In other words: the analogy between *LE* and *E* does not go very far. This implies that the Laplacian energy depends on molecular structure in a manner that is different, but not completely different, from the (nowadays well understood[1,2]) structure-dependence of the total π-electron energy. Elucidation of the details of these differences remains a task for the future.

## И З В О Д

## УКУПНА π-ЕЛЕКТРОНСКА ЕНЕРГИЈА И ЛАПЛАСОВА ЕНЕРГИЈА: ДОКЛЕ ИДЕ АНАЛОГИЈА?

СЛАВКО РАДЕНКОВИЋ и ИВАН ГУТМАН

*Природно-математички факултет Универзитета у Крагујевцу*

Лапласова енергија *LE* је недавно уведен, на молекулском графу заснован, аналог укупне π-електронске енергије *E*. У раду је показано да *LE* и *E* имају сличне особине само када се упоређују молекули различитих величина, када међу њима постоји добра линеарна корелација. Унутар класа изомера, *LE* и *E* или уопште нису корелирани или су (као што је случај код ацикличних система) инверзно пропорционални. Ациклични графови и молекулски графови са највећим и најмањим *LE* вредностима (одређени у овом раду) битно се разликују од (раније познатих) ацикличних графова са највећим и најмањим *E* вредностима.

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