

On Degeneracy of \mathcal{A} -Eigenvalue-Based Molecular Descriptors and r -Equienergetic Chemical Trees

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Abstract

Among more than two hundreds of eigenvalue-based topological indices only a couple of them are defined using the eigenvalues devised from the adjacency matrix of a graph. The resolvent energy is probably the most recent-one such an index. In this article, the degeneracy of the energy, Estrada index, and the resolvent energy is presented. The specious degeneracy of the resolvent energy in the case of chemical trees is discussed. Then, the data on searching for resolvent equienergetic chemical trees is given.

1 Introduction

A need for the quantification of a molecular structure can be traced back to the very beginnings of the structural and theoretical chemistry. Numerous counting, topological, geometric, and quantum-based molecular descriptors have been devised for this purpose [36]. A prominent and probably the largest group among them is the topological indices. They can be assorted into two major classes of degree- and distance-based descriptors [10–12]. However, there are existing topological indices that cannot be fitted into any

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of these two classes, such as degree–distance and eigenvalue–based topological molecular descriptors. While there are just a few degree–distance topological indices, the number of eigenvalue–based descriptors has been largely increasing these days [13–15, 18, 19, 25]. Currently, about 200 such indices were introduced, creating a novel class of eigenvalue–based topological molecular descriptors [15, 19].

The first, oldest and the most investigated member of a class of the eigenvalue–based topological molecular descriptors is the *graph energy*. It was introduced in 1978 as a simplification and, at the same time, the generalization of the formula for calculating the total π -energy of conjugated molecules at the HMO-level of theory [9, 25]. The graph energy is defined as

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

where λ_i is the i -th eigenvalue of a graph G , obtained from its adjacency matrix.

For more than twenty years, research of this quantity was scarce and random. However, in the last twenty years, scientists from all around the globe embraced it, and the properties of the graph energy have been heavily investigated. The popularity of this topological invariant has been growing rapidly. Its definition is being used as a template for introducing dozens of other descriptors [15, 19]. These indices are based on the eigenvalues derived from graph matrices other than the adjacency matrix of a graph G . This paper is focused on the topological descriptors that are calculated using the eigenvalues devised from the adjacency matrix of a graph. In the rest of the text such eigenvalues will be denoted as *\mathcal{A} -eigenvalues*.

The second most popular eigenvalue–based topological index is the *Estrada index*. It was introduced in 2000 as a descriptor that harvests information on folding in proteins and other biomolecules [6]. The Estrada index is defined as

$$EE(G) = \sum_{i=1}^n e^{\lambda_i} \quad (2)$$

where λ_i is the i -th \mathcal{A} -eigenvalue of a graph G .

Since its introduction, the Estrada index attracted the attention of researchers. Countless papers are dealing with its properties and possible applications (see [20, 32] and references cited therein). Similarly as in the case of the graph energy, the definition (2) is being frequently used as a template for making novel topological descriptors [1, 4, 21, 24, 27, 28, 33, 34, 37].

The *resolvent energy* is one of the latest topological descriptors based on the \mathcal{A} -eigenvalue of graphs. It was defined in 2016 [16, 17] as

$$ER(G) = \sum_{i=1}^n \frac{1}{n - \lambda_i} \quad (3)$$

where λ_i is the i -th \mathcal{A} -eigenvalue of a graph G .

The resolvent energy attracted the attention of the predominantly mathematicians, resulting in more than a few papers [3, 5, 7, 8, 38, 39]. The definition of the resolvent energy was already used as a mold for the introduction of a few novel molecular descriptors (see [35] and references cited therein).

The relations among the energy, Estrada index and the resolvent energy were elaborated in [30]. The prediction potential of these indices and their comparative analysis were performed in [31]. In the next section the degeneracy (a.k.a. sensitivity) of these indices in the case of chemical trees is discussed. Then, the problem of resolvent equienergetic chemical trees will be tackled.

2 On discriminating ability of \mathcal{A} -eigenvalue-based molecular descriptors

One of the main qualities of a “proper” molecular descriptor is its possible ability to discriminate among the isomers [29]. Nowadays, there are thousands of topological descriptors, but none of them succeeded to completely fulfill this property. Therefore, it is purposeful to rank the molecular descriptors according to their discriminating ability. For such task a measure is needed, which would be able to properly quantify the level of degeneracy (a.k.a. sensitivity) of a molecular descriptor.

Although there were earlier attempts to assess the discriminating power of topological indices, a measure that is now in use was proposed by Konstantinova [23]. She named it as the sensitivity of the topological descriptor. It is defined as

$$S(G) = \frac{N - N_{TI}}{N}$$

where N is the total number of isomers, and N_{TI} is number of isomers that cannot be distinguished by the topological index TI .

The value of the sensitivity of topological indices varies in the range between 0 and 1. Therefore, it is usually reported as the percentage of sensitivity, or more frequently as the percentage of degeneracy of a topological index (calculated as $[1 - S(G)] * 100\%$).

We have examined here the discrimination ability of the graph energy, Estrada index, and the resolvent energy on chemical trees having from 9 to 20 vertices. For this purpose, an in-house Python program was developed. Two chemical trees A and B are considered to have the same value of above-mentioned topological indices if $|TI(A) - TI(B)| < 10^{-13}$. This threshold is taken because of the limit in precision of common numerical computations in Python, which is 10^{-15} . The results are presented in the Table 1 and Figure 1.

Table 1. The percentage of degeneracy of the graph energy, Estrada index, and resolvent energy.

n	# chemical trees	E	EE	ER
9	35	17.14 %	14.29 %	14.29 %
10	75	2.67 %	2.67 %	2.65 %
11	159	14.47 %	14.47 %	14.48 %
12	355	13.52 %	13.52 %	13.52 %
13	802	18.70 %	18.70 %	21.45 %
14	1858	15.02 %	14.96 %	25.78 %
15	4347	19.88 %	19.85 %	37.87 %
16	10359	17.26 %	17.24 %	48.34 %
17	24894	20.52 %	20.52 %	61.22 %
18	60523	16.83 %	16.83 %	71.49 %
19	148284	17.43 %	17.48 %	88.69 %
20	366319	14.43 %	14.89 %	92.90 %

From data given in the Table 1 and Figure 1, it can be seen that all three lines are nearly overlapping upon 13 vertices. After that, the behavior of the degeneracy of the graph energy and the Estrada index is practically the same, showing the level of degeneracy around 20%. Moreover, it is noticeable the mediocre rise in the discrimination ability of these descriptors for chemical trees with the large number vertices. On the other hand, the flow of the degeneracy of the resolvent energy are showing an unexpected steep rise. It is astonishing that the level of sensitivity of the resolvent energy for chemical trees with 20 vertices is only around 7%.

Obtained results on discrimination ability of the resolvent energy suggest that there are many resolvent equienergetic chemical trees. However, the definition (3) and an elementary knowledge on the equality of rational numbers indicate much larger sensitivity

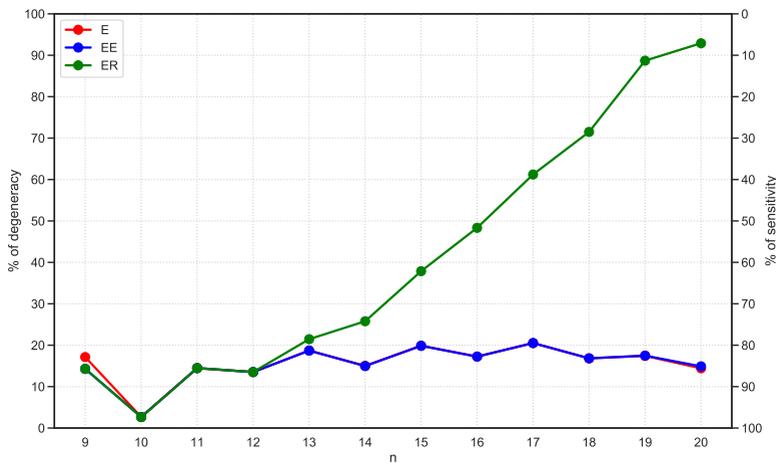


Figure 1. A flow of percentage of the degeneracy of the graph energy, Estrada index, and resolvent energy with the number of vertices.

of ER . This will be discussed in the next section.

3 On r -equienergetic chemical trees

The \mathcal{A} -eigenvalue-based topological descriptors cannot completely discriminate among molecules in most of the classes of isomers because of the presence of so-called isospectral molecular graphs [2]. This fact was long-time known, but discovering non-isospectral isomers that share the same graph energy value was rather surprising. Such graphs are being called equienergetic. The search for the families of such graphs was particularly actual in the first decade of the 21st century. In [26], the screening of trees for equienergetic-ones revealed that there are trees with nearly the same values of the graph energy. Such trees are being called *almost-equienergetic*.

The assessment of the degeneracy of resolvent energy, shown in the Section 2, imply that as the size of chemical trees is increasing, almost all of them belong to some of resolvent equienergetic families. In the rest of the text, the chemical trees with the same resolvent energy will be named as r -equienergetic chemical trees. Having in mind the condition of equality of rational numbers, such tendency of resolvent energy is rather surprising.

We performed systematic search for r -equienergetic graphs on databases consisting

of chemical trees from 9 to 19 vertices. Two chemical trees A and B are considered as r -equienergetic if $|ER(A) - ER(B)| < 10^{-20}$. A reason for decreasing the threshold to 10^{-20} lays in the fact that at least 5 digits in the value of resolvent energy of chemical trees are constant for all n -vertex isomers. Also, it was expected that many almost- r -equienergetic chemical trees will be eliminated from the screening results by using smaller threshold. In order to be able to calculate the resolvent energy with such precision, an in-house Python program has been developed, which is using *mpmath* module [22] for performing arbitrary-precision float-point arithmetic. Results are collected and presented in the Table 2.

Table 2. Families of the n -vertex chemical trees whose resolvent energies differ by less than 10^{-20} . # families is the number of families of a given size and a given type. The type $a + b + \dots$ means that family consists of a isospectral members, b isospectral members that are not isospectral with the members of a , and so on.

n	# families	size	type
9	5	2	2 + 0
10	2	2	2 + 0
11	19	2	2 + 0
	2	3	3 + 0
12	38	2	2 + 0
	5	3	3 + 0
13	98	2	2 + 0
	26	3	3 + 0
14	232	2	2 + 0
	20	3	3 + 0
	2	4	4 + 0
15	597	2	2 + 0
	99	3	3 + 0
	16	4	4 + 0
	5	5	5 + 0
16	1245	2	2 + 0
	207	3	3 + 0
	34	4	4 + 0

n	# families	size	type
	5	5	5 + 0
	1	6	6 + 0
17	3144	2	2 + 0
	645	3	3 + 0
	144	4	4 + 0
	40	5	5 + 0
	14	6	6 + 0
	2	7	7 + 0
18	6605	2	2 + 0
	1147	3	3 + 0
	236	4	4 + 0
	49	5	5 + 0
	11	6	6 + 0
	2	7	7 + 0
	1	8	8 + 0
	497	2	1 + 1
	199	3	2 + 1
	19	3	1 + 1 + 1
	24	4	3 + 1
	20	4	2 + 2
	9	4	2 + 1 + 1
	5	5	4 + 1
	6	5	3 + 2
	4	5	3 + 1 + 1
	1	5	2 + 2 + 1
	2	6	4 + 2
	1	6	3 + 2 + 1
	1	8	4 + 4
19	15819	2	2 + 0
	2601	3	3 + 0
	633	4	4 + 0
	193	5	5 + 0
	58	6	6 + 0
	14	7	7 + 0

n	# families	size	type
	5	8	8 + 0
	2	9	9 + 0
2680	2		1 + 1
1080	3		2 + 1
176	3		1 + 1 + 1
241	4		3 + 1
145	4		2 + 2
129	4		2 + 1 + 1
15	4		1 + 1 + 1 + 1
56	5		4 + 1
57	5		3 + 2
25	5		3 + 1 + 1
39	5		2 + 2 + 1
15	5		2 + 1 + 1 + 1
2	5		1 + 1 + 1 + 1 + 1
18	6		5 + 1
8	6		4 + 2
5	6		3 + 3
2	6		4 + 1 + 1
14	6		3 + 2 + 1
3	6		2 + 2 + 2
10	6		2 + 2 + 1 + 1
1	6		2 + 1 + 1 + 1 + 1
1	7		6 + 1
7	7		5 + 2
8	7		4 + 3
1	7		5 + 1 + 1
2	7		4 + 2 + 1
1	7		3 + 3 + 1
2	7		3 + 2 + 2
1	7		2 + 2 + 2 + 1
1	7		2 + 2 + 1 + 1 + 1
1	8		6 + 2
1	8		5 + 3
1	8		3 + 2 + 2 + 1

n	# families	size	type
1	9		5 + 4
1	9		5 + 2 + 2
1	10		7 + 3
1	11		4 + 4 + 3

It is evident that up to 17 vertices there are no r -equiresolvent chemical trees other than isospectral-ones. Chemical trees with 18 vertices have many families of non-isomorphic graphs whose resolvent energies differs by less than 10^{-20} . The number of such families in the case of chemical trees with 19 vertices is even larger. For example, five non-isospectral chemical trees with 19 vertices, having $ER = 1.0052992142869941494$, are presented on Figure 2.

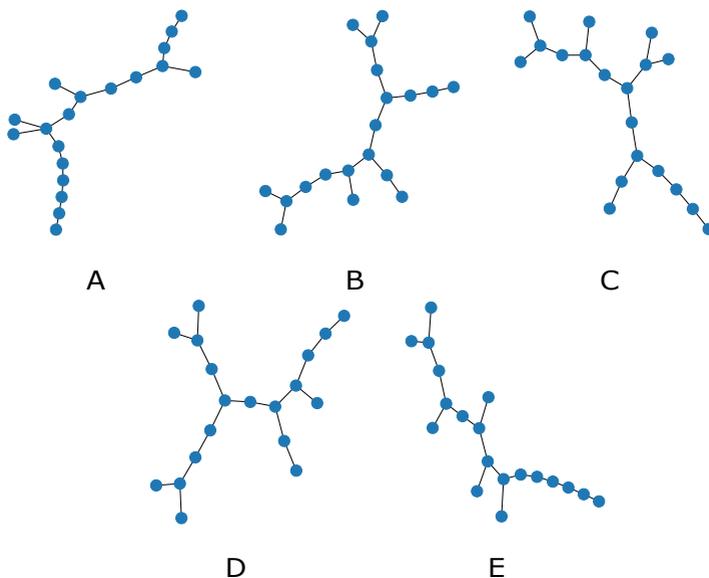


Figure 2. Non-isospectral chemical trees having the same resolvent energy up to 20 decimal digits.

The spectra of the chemical trees, depicted on Figure 2 are given below:

$$\text{Spec(A)} = \{-2.2404, -2.0064, -1.7806, -1.6064, -1.2162, -1.1216, -0.5564, -0.3969, \\ 0, 0, 0, 0.3969, 0.5564, 1.1216, 1.2162, 1.6064, 1.7806, 2.0064, 2.2404\}$$

$$\text{Spec(B)} = \{-2.2406, -2.0043, -1.7907, -1.5877, -1.2656, -1.0705, -0.5966, -0.3625, \\ 0, 0, 0, 0.3625, 0.5966, 1.0705, 1.2656, 1.5877, 1.7907, 2.0043, 2.2406\}$$

$$\text{Spec(C)} = \{-2.2412, -1.9953, -1.8236, -1.4820, -1.4142, -0.9268, -0.7357, -0.2713, \\ 0, 0, 0, 0.2713, 0.7357, 0.9268, 1.4142, 1.4820, 1.8236, 1.9953, 2.2412\}$$

$$\text{Spec(D)} = \{-2.2409, -2, -1.8082, -1.5473, -1.3331, -1, -0.6631, -0.3125, 0, 0, 0, \\ 0.3125, 0.6631, 1, 1.3331, 1.5473, 1.8082, 2, 2.2409\}$$

$$\text{Spec(E)} = \{-2.2407, -2.0022, -1.7998, -1.5684, -1.3008, -1.0336, -0.6307, -0.3357 \\ 0, 0, 0, 0.3357, 0.6307, 1.0336, 1.3008, 1.5684, 1.7998, 2.0022, 2.2407\}$$

Since it would be astonishing if there is existing a pair of non-isomorphic chemical trees with the same resolvent energy, we collected trees obtained for 18 and 19 vertices in previous in-silico experiment and recalculated their resolvent energies with the higher precision. We got that if the resolvent energies of chemical trees with 18 vertices are calculated with the precision of 23 decimal digits, only isospectral-ones are r -equienergetic. The same was obtained for chemical trees with 19 vertices and the precision of 24 decimal digits.

4 Conclusions

The discrimination ability of the graph energy and the Estrada index in the case of chemical trees are nearly the same and do not exceed 21 %. However, the sensitivity of the resolvent energy is significantly decreasing with the number of vertices. This implies that there are many r -equiresolvent chemical trees. Conducted screening shows that, although the threshold was set to less than 10^{-20} , there are indeed a lot of r -equienergetic chemical trees with higher number of vertices. Additional investigation demonstrated that the increasing of precision lowers the number of families of non-isospectral r -equienergetic chemical trees. We dare to claim that there is not existing a single pair of r -equienergetic

chemical trees other than isospectral-ones. In other words, all obtained non-isospectral families with the same resolvent energy were almost- r -equienergetic. This also means that obtained degeneracy of the resolvent energy is illusive, and that its sensitivity outperforms other \mathcal{A} -eigenvalue-based topological indices. However, the computational cost and high precision calculations are preventing its practical use and possible application in discriminating isomeric molecules.

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