Mathematical Chemistry Works
of Dragoš Cvetković

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Abstract

In addition to his countless contributions to spectral graph theory, some works of Dragoš Cvetković are concerned with chemical problems. These are briefly outlined, with emphasis on his collaboration with the present author.
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1. Introduction

As well known, Dragoš Cvetković is world-wide recognized as a leading expert and promoter of spectral graph theory. He discovered many important results on spectra of graphs and is author of numerous seminal monographs and textbooks, of which we mention here only [2] and [3]. He mainly studied the spectrum of the 0-1 adjacency matrix (which traditionally is called "graph spectrum"), but also of the Laplacian and signless Laplacian matrices. He may be considered as the founder of the theory of signless Laplacian spectra.

It may be less well known that Cvetković participated in researches in theoretical chemistry and gave several valuable contributions also in an area of science which nowadays is usually referred to as mathematical chemistry. The present paper is an attempt to survey these works and to comment them from an our-time point of view. In some detail we are outlining the relation and collaboration which Cvetković had (and hopefully still has) with the present author.

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2. Cvetković Meets Gutman
Gutman Meets Cvetković

The year is 1971.

Dragoš Cvetković is Assistant in the Mathematics Department of the Faculty of Electrical Engineering of the Belgrade University, working for his Ph.D. thesis on spectral graph theory.

Ivan Gutman is graduate student of chemistry. For some time he is interested in quantum chemistry, and learned in due detail the Hückel molecular orbital (HMO) theory.

In 1971 in the Mathematical Institute in Belgrade, a series of lectures was organized entitled "Finite Mathematics". (Nowadays, this would be "Discrete Mathematics".) Cvetković delivered two lectures within this series, one on graph theory, and another on graph spectra. Gutman attended these lectures and immediately recognized that graph spectra are exactly what is used within HMO theory. He decided to take part in the discussion after Cvetković's lectures, but being shy remained silent.

Some time later, Cvetković defended his Ph.D. thesis, and this event was announced in the newspapers. Gutman attended the defense and then he contacted Dragoś, informing him that graph theory has applications in chemistry (in HMO theory). Cvetković was (pleasantly) surprised, but postponed any further discussion for some later moment.

Unfortunately, in the next days, Gutman was leaving Belgrade for good, to move first to his native town Sombor, and then to Zagreb, Croatia. Therefore, his contacts with Cvetković had to be made by mail and later by mutual visits. Anyway, in late 1971 they produced their first joint paper [4].

The paper [4] is of outstanding importance for mathematical chemistry. In it, for the first time, the analogies between graph–theoretical concepts (graph, vertex, edge, degree, cycle, . . .) and chemical concepts (structural formula, atom, bond, valency, ring, . . .) is made clear. There it is mentioned (but not for the first time, see [32]) that graph spectral theory and HMO theory are directly related. A standard notion in HMO theory, the concept of alternant hydrocarbons is recognized to coincide with the bipartiteness of the underlying molecular graph.

3. Nullity

The first application of graph spectral theory to HMO theory was in the determination of the nullity n_0 (algebraic multiplicity of number zero in the spectrum) of a graph. Namely, this quantity corresponds to the number of non-bonding molecular orbitals in HMO theory. If the molecular graph is bipartite, then the existence of non-bonding molecular orbitals, i.e., $n_0 > 0$, implies that the respective molecule is unstable and cannot exist.

Several simple recursive methods for calculating n_0 were put forward in [4] and the later articles [5–7]. Of these we mention here the relation

$$n_0(G) = n_0(G - u - v) \tag{1}$$

which applies to any graph in which u and v are adjacent vertices, and either u or v are of degree one. By means of Equation (1) the nullity of any tree can be determined, as well as that of numerous other molecular graphs.

The results of [4,5,7] attracted much attention and were quoted in several later papers and books, for instance in [26].

It is worth mentioning that the problem of nullity of general graphs (in particular, of graphs without pendent vertices) is unsolved until these very days.

4. Sachs Theorem

Let $\phi(G, \lambda)$ be the characteristic polynomial of the graph G [2, 3]. If G has n vertices, and

$$\phi(G) = \sum_{k=0}^{n} a_k \, \lambda^{n-k}$$

then

$$a_k = \sum_{s \in \mathbf{S}_k(G)} (-1)^{p(s)} \, 2^{c(s)} \tag{2}$$

where the summation goes over the set $\mathbf{S}_k(G)$ of all k-vertex subgraphs s of G whose components are regular of degree either one or two. By $p(s)$ and $c(s)$ are denoted the number of components and cyclic components, respectively, of the subgraph s.

Formula (2) was discovered by the German mathematician Horst Sachs in 1964. Because he published his result in German language in a Hungarian mathematical journal [37] it did not attract much attention, and was not noticed by scholars working on HMO theory.

Cvetković stated formula (2) in his Ph.D. thesis (which eventually was published as [12]). Gutman learned it from Cvetković's thesis. Other colleagues in Zagreb learned it from Gutman.

The chemical importance of Sachs theorem, Equation (2), was enormous. Namely, it provided a direct and complete connection between molecular structure (i.e. structure of the molecular graph) and the secular determinant in HMO theory (which happens to be identical to the characteristic polynomial of the underlying graph [4, 32]). This connection was searched over decades, but without success (see, for instance, [24]).

The chemical community learned about Sachs theorem from the paper [27]. The response was outstanding: the Sachs theorem was commented and re-stated by dozens of other authors, and found chemical applications in countless papers,

whose number is of order 10^3, see [28]. Although Cvetković's name does not appear on any of these works, there is no doubt that he played a crucial role in the chemical application of Sachs theorem.

5. Kekulé Structures – Perfect Matchings

From a present-day's point of view, the claim that a Kekulé structure (in chemistry) corresponds to a perfect matching (of the underlying molecular graph) is obvious and trivial. Yet, in the 1970s, this was an important observation, worth publishing [9]. It enabled chemists to apply the mathematical techniques pertaining to perfect matching and their counts. In particular, the number K of Kekulé structures could be recursively evaluated by means of the simple formula

$$K(G) = K(G - e) + K(G - u - v) \tag{3}$$

where e is any edge of the (molecular) graph G, whose end-points are the vertices u and v.

An application of (3) was reported in [8]. Further applications resulted in combinatorial expressions for the Kekulé structure count of a great variety of classes of molecular graphs, see [25].

Perfect matchings play an important role also in spectral graph theory, in connection with the coefficient a_n of the characteristic polynomial, which is just the determinant of the adjacency matrix. For instance, in the case of benzenoid systems, this coefficient is equal to $(-1)^{n/2} K(G)^2$. Various aspects of this problem were studied in the paper [10].

6. The Largest Eigenvalue

The largest eigenvalue λ_1 is certainly the most detailed studied graph spectral property [2, 3, 11]. Lovász and Pelikán [34] showed that among trees (with a fixed number of vertices), the path and the star have minimal and maximal λ_1-values. Motivated by this, it was proposed that λ_1 be used as a topological index for measuring branching (of trees) [13].

It is interesting that the paper [13] was often quoted by other authors, but none of them tried to check whether λ_1 is anyhow related with other existing measures of molecular branching. This, finally, was done only in 2002, when the details of the correlation between λ_1 and other branching indices were established [29].

Later developments showed that the largest eigenvalue is not particularly suitable for modeling molecular branching and nowadays λ_1 is no more used for this purpose.

7. Graph Energy

Graph energy $E(G)$ is equal to the sum of absolute values of the graph eigenvalues, a definition motivated by results earlier established within the HMO theory. This quantity was introduced by Gutman in 1978 on a conference in Stift Rein, Austria [30], on which Cvetković was also present. The new concept did not attract the attention of colleagues, including Cvetković. Only much later, graph energy became popular among mathematicians and is nowadays much studied [31, 35].

Cvetković became involved in the study of graph energy via his computer system "GRAPH" [14]. One of the applications of this system was a search for graphs with greatest energy [15]. What only could be established in [15] was that the greatest–energy graph differs from the complete graph K_n. This research was continued in [23], when the greatest–energy n-vertex graphs where determined for $n \leq 10$. However, the general form of these graphs could not be envisaged. Another result of the work [23] is the nowadays much used

$$E(G) \geq 2\sqrt{n-1}$$

which holds for all connected n-vertex graphs, with equality if and only if $G \cong K_{1,n-1}$.

Cvetković's next paper concerned with greatest-energy graphs in [19], where he showed that such graphs must have only a limited number of distinct eigenvalues.

It should be mentioned that the characterization of graphs with greatest energy (and with a fixed number of vertices) is unsolved until these very days. Only some special cases have been solved until now [33].

At this point it is worth noting that a graph–energy–like quantity is mentioned in a recent paper [20], concerned with the traveling salesman problem.

8. Miscellaneous

There are several more works of Dragoš Cvetković which could not be included in the above sections, but which are relevant for mathematical chemistry. We briefly mention them here.

An early work [21] is concerned with a property of the eigenvalues of bipartite graphs, which in chemistry is known under the name "Pairing Theorem", see [36].

In the paper [22] are characterized all molecular graphs, relevant for HMO theory, whose spectra consist of integers. This research has been further extended in [1].

In papers [16, 17] spectral properties of fullerenes are studied.

A somewhat unrelated direction of chemically motivated research is found in the paper [18], which deals with properties of some graph invariants related to electron charges in the HMO theory.

Conflicts of Interest. The author declares that there are no conflicts of interest regarding the publication of this article.

References

[1] K. Balińska, D. Cvetković, M. Lepović and S. Simić, There are exactly 150 connected integral graphs up to 10 vertices, *Univ. Beograd. Publ. Elektrotehn. Fak. Ser. Mat.* **10** (1999) 95–105.

[2] D. Cvetković, M. Doob and H. Sachs, *Spectra of Graphs – Theory and Applications*, Third Edition, Johann Ambrosius Barth, Heidelberg, 1995.

[3] D. Cvetković, P. Rowlinson and S. Simić, *An Introduction to the Theory of Graph Spectra*, London Mathematical Society Student Texts, 75, Cambridge Univ. Press, Cambridge, 2010.

[4] D. M. Cvetković and I. Gutman, The algebraic multiplicity of the number zero in the spectrum of a bipartite graph, *Mat. Vesnik* **9** (1972) 141–150.

[5] D. Cvetković, I. Gutman and N. Trinajstić, Graph theory and molecular orbitals. II, *Croat. Chem. Acta* **44** (1972) 365–374.

[6] D. Cvetković, I. Gutman and N. Trinajstić, Graph theory and molecular orbitals. IX. On the stability of cata-condensed hydrocarbons, *Theor. Chim. Acta* **34** (1974) 129–136.

[7] D. Cvetković, I. Gutman and N. Trinajstić, Graphical studies on the relations between the structure and reactivity of conjugated systems: The role of non-bonding molecular orbitals, *J. Mol. Struct.* **28** (1975) 289–303.

[8] D. Cvetković and I. Gutman, Kekulé structures and topology. II. Cata-condensed systems, *Croat. Chem. Acta* **46** (1974) 15–23.

[9] D. Cvetković, I. Gutman and N. Trinajstić, Kekulé structures and topology, *Chem. Phys. Lett.* **16** (1972) 614–616.

[10] D. Cvetković, I. Gutman and N. Trinajstić, Graph theory and molecular orbitals. VII. The role of resonance structures, *J. Chem. Phys.* **61** (1974) 2700–2706.

[11] D. Cvetković and P. Rowlinson, The largest eigenvalue of a graph: A survey, *Linear and Multilinear Algebra* **28** (1990) 3–33.

[12] D. Cvetković, Graphs and their spectra, *Publ. Elektrotehn. Fak. (Ser. Mat. Fiz.)* **354** (1971) 1–50.

[13] D. Cvetković and I. Gutman, Note on branching, *Croat. Chem. Acta* **49** (1977) 115–121.

[14] D. Cvetković and S. Simić, Graph theoretic results obtained by the support of the expert system "graph", *Bull. Cl. Sci. Math. Nat. Sci. Math.* **19** (1994) 19–41.

[15] D. Cvetković and I. Gutman, The computer system GRAPH: A useful tool in chemical graph theory, *J. Comput. Chem.* **7** (1986) 640–644.

[16] D. Cvetković, P. W. Fowler, P. Rowlinson and D. Stevanović, Constructing fullerene graphs from their eigenvalues and angles, *Linear Algebra Appl.* **356** (2002) 37–56.

[17] D. Cvetković and D. Stevanović, Spectral moments of fullerene graphs, *MATCH Commun. Math. Comput. Chem.* **50** (2004) 63–72.

[18] D. Cvetković, Characterizing properties of some graph invariants related to electron charges in the Hückel molecular orbital theory, in: P. Hansen, P. Fowler, M. Zheng (Eds.), *Discrete Mathematical Chemistry*, American Mathematical Society, Providence, RI, 2000, pp. 79–84.

[19] D. Cvetković and J. Grout, Graphs with extremal energy should have a small number of distinct eigenvalues, *Bull. Cl. Sci. Math. Nat. Sci. Math.* **32** (2007) 43–57.

[20] D. Cvetković, Z. Dražić, V. Kovačević–Vujčić and M. Čangalović, The traveling salesman problem: the spectral radius and the length of an optimal tour, *Bull. Cl. Sci. Math. Nat. Sci. Math.* **43** (2018) 17–26.

[21] D. Cvetković, Bichromaticity and graph spectrum, *Matematička Biblioteka*, (in Serbian) **41** (1969) 193–194.

[22] D. Cvetković, I. Gutman and N. Trinajstić, Conjugated molecules having integral graph spectra, *Chem. Phys. Lett.* **29** (1974) 65–68.

[23] G. Caporossi, D. Cvetković, I. Gutman and P. Hansen, Variable neighborhood search for extremal graphs. 2. Finding graphs with extremal energy, *J. Chem. Inf. Comput. Sci.* **39** (1999) 984–996.

[24] C. A. Coulson, Notes on the secular determinant in molecular orbital theory, *Proc. Cambridge Phil. Soc.* **46** (1950) 202–205.

[25] S. J. Cyvin and I. Gutman, *Kekulé Structures in Benzenoid Hydrocarbons*, Springer, Berlin, 1988.

[26] I. S. Dmitriev, *Molecules without Chemical Bonds?*, Himiya, Leningrad (in Russian) 1980, Mir, Moscow (in English) 1981, Deutscher Verlag der Grundstoffindustrie, Leipzig (in German) 1982.

[27] A. Graovac, I. Gutman, N. Trinajstić and T. Živković, Graph theory and molecular orbitals. Application of Sachs theorem, *Theor. Chim. Acta* **26** (1972) 67–78.

[28] I. Gutman, Impact of the Sachs theorem on theoretical chemistry: A participant's testimony, *MATCH Commun. Math. Comput. Chem.* **48** (2003) 17–34.

[29] I. Gutman and D. Vidović, Two early branching indices and the relation between them, *Theor. Chem. Acc.* **108** (2002) 98–102.

[30] I. Gutman, The energy of a graph, *Ber. Math.-Statist. Sekt. Forsch. Graz* **103** (1978) 1–22.

[31] I. Gutman and B. Furtula, Survey of graph energies, *Math. Interdisc. Res.* **2** (2017) 85–129.

[32] Hs. H. Günthard and H. Primas, Zusammenhang von Graphentheorie und MOâĂŘTheorie von Molekeln mit Systemen konjugierter Bindungen, *Helv. Chim. Acta* **39** (1956) 1645–1653.

[33] W. H. Haemers and Q. Xiang, Strongly regular graphs with parameters $(4m^4, 2m^4 + m^2, m^4 + m^2, m^4 + m^2)$ exist for all $m > 1$, *European J. Combin.* **31** (2010) 1553–1559.

[34] L. Lovász and J. Pelikán, On the eigenvalues of trees, *Period. Math. Hungar.* **3** (1973) 175–182.

[35] X. Li, Y. Shi and I. Gutman, *Graph Energy*, Springer, New York, 2012.

[36] R. B. Mallion and D. H. Rouvray, The golden jubilee of the Coulson–Rushbrooke pairing theorem, *J. Math. Chem.* **5** (1990) 1–21.

[37] H. Sachs, Beziehungen zwischen den in einem Graphen enthaltenen Kreisen und seinem charakteristischen Polynom, *Publ. Math. Debrecen* **11** (1964) 119–134.

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