

# Two Mathematical Papers Relevant for the Hückel Molecular Orbital Theory<sup>1</sup>

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## Abstract

We present and comment mathematical papers [5] and [9]. The first one is related to the Pairing Theorem of the Hückel molecular orbital theory and the second one establishes the equivalence of the Hückel molecular orbital theory and mathematical spectral graph theory.

## 1 Introduction

Spectral graph theory is a mathematical theory in which linear algebra and graph theory meet. For any graph matrix  $M$  we can build a spectral graph theory in which graphs are studied by means of eigenvalues of the matrix  $M$ . This theory is called  $M$ -theory. The most frequently used graph matrix is the adjacency matrix  $A$ . The spectral graph theory includes all particular  $M$ -theories together with interaction tools.

Originally,  $A$ -theory was developed and we shall consider here only this theory.

The adjacency matrix  $A$  of a graph  $G$ , with  $n$  vertices, is the matrix whose element  $a_{ij}$  is equal to the number of the edges, which lead from the vertex  $i$  to the vertex  $j$ . The spectrum of the graph  $G$  is the family of solutions  $\lambda_i$  ( $i = 1, \dots, n$ ) of the characteristic equation  $\det(\lambda I - A) = 0$  of the matrix  $A$ , i. e. the family of eigenvalues of  $A$ .

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<sup>1</sup>Recently W. So and W. Haemers asked who was first to observe that bipartite graphs are characterized by their spectra (Theorem 2 below). That inspired me to prepare [7] and this paper.

We present and comment the mathematical papers [5] and [9]. The first one is related to the Pairing Theorem of the Hückel molecular orbital theory and the second one establishes that the Hückel molecular orbital theory from Chemistry and mathematical theory of graph spectra are essentially the same.

Surveys of related results appeared in my thesis [6] and in the monograph [8].

I defended my thesis [6] on May 27, 1971. The thesis, originally prepared in Serbian, has been published in English in a condensed form [6]. It attracted attention of American mathematician Richard Bellman who suggested to me to extend these results and collect them in book form. This led after some time to publication of the book [8]. The book has been widely used and cited a few thousand times in the literature.

The next two sections treat the Pairing Theorem and the Hückel molecular orbital theory.

## 2 The Pairing Theorem

I realized that the well established Perron–Frobenius theory of non-negative matrices is relevant for the theory of graph spectra. In the thesis [6] and in the monograph [8] I have collected all useful theorems from the Perron–Frobenius theory and classified basic implications of them.

Spectral properties of irreducible non-negative matrices are described by the following theorem of *Frobenius* and this has several immediate corollaries for graph spectra.

**Theorem 1.** *An irreducible non-negative matrix  $A$  always has a positive eigenvalue  $r$  that is a simple root of the characteristic polynomial. The modulus of any other eigenvalue does not exceed  $r$ . To the “maximal” eigenvalue  $r$  there corresponds a positive eigenvector. Moreover, if  $A$  has  $h$  eigenvalues of modulus  $r$ , then these numbers are all distinct and are roots of the equation  $\lambda^h - r^h = 0$ . More generally: the whole spectrum  $[\lambda_1 = r, \lambda_2, \dots, \lambda_n]$  of  $A$ , regarded as a system of points in the complex  $\lambda$ -plane, is mapped onto itself under a rotation of the plane by the angle  $\frac{2\pi}{h}$ . If  $h > 1$ , then by a permutation of rows and the same permutation of columns  $A$  can be put into the following “cyclic” form*

$$A = \left\| \begin{array}{cccccc} O & A_{12} & O & \dots & O & \\ O & O & A_{12} & \dots & O & \\ \vdots & & & \ddots & & \\ O & O & O & \dots & A_{h-1,h} & \\ A_{h1} & O & O & \dots & O & \end{array} \right\| ,$$

where there are square blocks along the main diagonal.

The adjacency matrix of an undirected multigraph  $G$  is symmetric (and, therefore, Hermitian) and the spectrum of  $G$ , containing only real numbers, according to Theorem 1 lies in the segment  $[-r, r]$ .

We consider now the bipartiteness of graphs.

It is proved in [1] that a bipartite graph has a symmetric spectrum. This fact was known even earlier in chemical literature under the name the *Pairing Theorem* [2, 4]. It is interesting that in [2] a very simple proof of this theorem is given. In [5] a new proof of this theorem and the proof of the inverse theorem are given:

**Theorem 2.**<sup>2</sup> *Connected, finite, undirected graph, without loops and with at least two vertices, is bipartite if and only if, its spectrum, considered as a set of points on the number axis, is symmetric with respect to the point zero.*

This characterization of bipartite graphs appeared for the first time in my paper [5]. The theorem appears also in my book "Spectra of Graphs" as Theorem 3.11 on p. 87, where other related references can be found. The paper [5] appears in the book as reference [Cve1].

The proof in [5] uses the Frobenius theorem (Theorem 1) what nowadays can be considered as shooting with cannons on small birds. In a recent book [11], the proof uses the fact that in the case of a symmetric spectrum all the odd spectral moments are zero and the graph has no cycles of odd length.

Actually, from the proof in [5] it is clear that only bipartite graphs, from the considered class of graphs, have in the spectrum the number  $-r$ , where,  $r$  is the largest number from the spectrum.

Hence, for connected graphs we have a substantially stronger result:

**Theorem 3.** *A connected graph  $G$  is bipartite if and only if  $\lambda_1 = -\lambda_n$ .*

This important characterization of connected bipartite graphs is proved in [6] (Theorem 4.3) using the Frobenius theorem. Again this can be done with simpler tools (see [11], Theorem 3.2.4).

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<sup>2</sup>The theorem is formulated in [11] in a more condensed form: *A graph  $G$  is bipartite if and only if its spectrum is symmetric with respect to the origin.*

### 3 The Hückel molecular orbital theory

In order to solve the Schrödinger equations for complicated many-electron molecular systems, various approximations are used. In the pioneering days of quantum chemistry (in the 1930s and 1940s) an approximate method for describing the state of single electrons in conjugated hydrocarbons was developed [15], known under the name *Hückel molecular orbital theory*. For more information on Hückel theory the interested reader can consult, for example, [3, 8, 12].

Within the framework of the Hückel method [15], the Hamiltonian matrix  $H = [h_{ij}]$  is a square matrix of order  $n$ , where  $n$  is the number of carbon atoms in the molecule. Let these carbon atoms be labelled by  $1, 2, \dots, n$ . Then the matrix elements  $h_{rs}$  are given by

$$h_{rs} = \begin{cases} \alpha & \text{if } r = s = 1, 2, \dots, n \\ \beta & \text{if } r \neq s \text{ and the atoms } r \text{ and } s \text{ are chemically bonded} \\ 0 & \text{if } r \neq s \text{ and no chemical bond between the atoms } r \text{ and } s \text{ exists.} \end{cases} \quad (1)$$

The parameters  $\alpha$  and  $\beta$  are called the *Coulomb* and the *resonance integral*; in Hückel theory these are assumed to be constants.

Having in mind relations (1), we see that the Hückel Hamiltonian matrix can be presented as

$$H = \alpha I_n + \beta A, \quad (2)$$

where  $A$  is a symmetric matrix whose diagonal elements equal 0 and whose off-diagonal elements equal 1 or 0, depending on whether the corresponding atoms are connected or not. In fact  $A$  is just the adjacency matrix of the Hückel graph<sup>3</sup>. Equation (2) immediately gives the following result.

**Theorem 4.** *If  $\lambda$  is an eigenvalue and  $z$  an eigenvector of the matrix  $A$ , then  $\alpha + \beta\lambda$  is an eigenvalue and  $z$  is an eigenvector of the matrix  $H$ .*

From this theorem it follows that the Hückel molecular orbitals coincide with the eigenvectors  $z_j$  of eigenvalues  $\lambda_j$ ,  $j = 1, 2, \dots, n$ , of the adjacency matrix of the Hückel graph. The eigenvalues  $\lambda_j$  of the matrix  $A$  and the energies  $E_j$  of the corresponding electrons are

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<sup>3</sup>The *Hückel graph* is used for an abbreviated representation of conjugated hydrocarbons. Its vertices represent only the carbon atoms, and all its edges are simple (irrespective of whether the corresponding chemical bonds are single or double). The vertices of a Hückel graph may be of degree 1, 2, or 3.

related simply as

$$E_j = \alpha + \beta\lambda_j.$$

There are exactly  $n$  different molecular orbitals, namely the  $z_j$  for  $j = 1, 2, \dots, n$ .

This important conclusion shows that there is a deep and far-reaching relation between the Hückel molecular orbital theory and graph spectral theory. The Hückel theory provides an important field of application of the graph spectra.

The main contribution of [9] was to establish that the Hückel theory and theory of graph spectra are essentially the same. It was Ivan Gutman who realized this fact during some contacts with me<sup>4</sup> in 1971. The relation between Hückel's theory and theory of graph spectra was noticed earlier in [14], but was poorly used later (see, for example, [17]). However, since [9] was published in a mathematical journal, it has not been cited very much in the chemical literature. The chemical community has realized the connection between the two theories after [13] has been published<sup>5</sup> but the fact remains that [9] was the first paper to establish clearly this connection. Note that the paper was presented on December 10, 1971, in Mathematical Institute, Belgrade.

In Chemistry the problem of determining the algebraic multiplicity of the number 0 in the spectra of bipartite graphs is of interest. It can easily be proved that if the spectrum of the corresponding graph contains at least one number zero, then the molecule cannot have the total electron spin equal to zero, which implies its instability in chemical sense. The wave functions for which  $\lambda = 0$  are called "non-bonding molecular orbitals".

Let  $\eta(G)$  be the algebraic multiplicity of the eigenvalue 0 in the spectrum of the bipartite graph  $G$ . The problem is to find out the connection between the graph structure and the number  $\eta(G)$ . This connection can be, perhaps, expressed by a set of rules by which we can, after a finite number of steps, determine  $\eta(G)$ , the spectrum in total being thus left undetermined. (This problem for an arbitrary graph was posed in [1]).

The following theorem appears in [9].

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<sup>4</sup>My recollection is that I. Gutman told me this fact during the public defence of my thesis on May 27, 1971, in Belgrade. However, I. Gutman claims that he realized the connection between the two theories even earlier when he was attending a talk of mine on graph spectra in Mathematical Institute, Belgrade. That might have been even in 1970; we were not able to establish the exact date.

<sup>5</sup>Relations between the coefficients of the characteristic polynomial and the structure of a graph from [16] were denoted here as the *Sachs theorem*, a name which was used widely afterwards in the chemical literature.

**Theorem 5.** *If  $q$  is the maximal number of mutually non-adjacent edges in a tree  $G$  having  $n$  vertices, then  $\eta(G) = n - 2q$ .*

This theorem is an immediate consequence of a statement about the coefficients of the characteristic polynomial of the adjacency matrix of a tree from [16]. It has been generalized in [10] in the following way.

**Theorem 6.** *If a bipartite graph  $G$  with  $n$  vertices does not contain any cycle of length  $4s$  ( $s = 1, 2, \dots$ ), then  $\eta(G) = n - 2q$ , where  $q$  is the maximal number of mutually non-adjacent edges in  $G$ .*

A general solution of the problem of finding the multiplicity of 0 in the spectrum of a graph is not known, but a variety of partial results have been obtained. As an illustration we present the following statement from [9] (see also [8], Section 8.1).

**Theorem 7.** *Assume the graph  $G$  has a vertex  $x$  of degree 1 where  $x$  is adjacent to the vertex  $y$ . Then the graphs  $G$  and  $G - x - y$  have equal multiplicity of the number 0 in their spectra, i.e.  $\eta(G) = \eta(G - x - y)$ .*

A short list of respective terms from graph theory and from Chemistry has been given in [9]:

graph	conjugated hydrocarbon, conjugated polyene, polyene, aromatic hydrocarbon (i.e., skeleton of their $\sigma$ -electron bonds)
vertex	atom (of carbon)
edge	bond
vertex degree	valency
adjacency matrix	topological matrix, Hückel matrix
characteristic equation	secular equation
bipartite graph	alternant hydrocarbon
cycle with $N$ vertices	$[N]$ -annulene
chain	linear polyene

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