BioChem Press

Inter*net* Electronic Journal of
Molecular Design

Topological Aspects Beyond the Hückel Theory

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Citation of the article:
   I. László, Topological Aspects Beyond the Hückel Theory, *Internet Electron. J. Mol. Des.* **2004**, *3*, 0–0, http://www.biochempress.com.

Topological Aspects Beyond the Hückel Theory[#]

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Abstract

Motivation. Starting from a problem of the density of states of carbon atoms, the extension of Sachs theorem to tight–binding methods, containing atoms of several atomic orbitals, is presented. The concept of topologically determined electronic energy levels will be reviewed. Necessary and sufficient conditions for non–existence of Sachs graphs is given and connection between Sachs graphs and matching problems will be studied.

Method. The methods of graph theory and linear algebra are used.

Results. It was demonstrated that the topological arrangement of atoms can guarantee the existence of stable electronic energy levels. These levels are stable in the presence of off–diagonal disorder of the Hamiltonian matrix.

Conclusions. Graph theoretical methods can be extended beyond the Hückel theory to more sophisticated tight–binding methods.

Keywords. Chemical graph theory; Hückel theory; tight–binding methods; matching theory.

1 INTRODUCTION

The first time I have ever heard about chemical graph theory was a lecture presented by Nenad Trinajstić at a quadrangle conference in Hungary in 1976. This was a conference of quantum chemists from Austria, Czechoslovakia, Hungary and Yugoslavia. I have just graduated the year before in physics at the Eötvös Loránd University. My supervisor in quantum chemistry was Ede Kapuy and Gábor Náray–Szabó and I've attended graph theory courses delivered by Vera T. Sós, but I could not understand chemical graph theory. I had the same problems with the other lectures presented by Ante Graovac, Ivan Gutman and Tomislav Živković. I liked this theory very much but unfortunately I could not use it in my calculations. It was more than 10 years later when Sándor Kugler suggested that we could try our three–dimensional PPP method [1] in the study of amorphous carbon. We developed this method for the study of C_{60} UV spectrum.

Amorphous carbon contains fourfold–coordinated diamond–like and threefold–coordinated graphite–like carbon atoms. Each threefold–coordinated atom gives one electron to the π–electron network. As the density of electronic states at the Fermi level is determined by the threefold–coordinated carbon atoms we tried to apply our PPP method for graphite–like carbon clusters. In one cases we obtained peaks and in other cases we obtained gaps at the Fermi level. In many cases, however, the geometrical structures were very similar. We simplified the method and we could produce the same behavior by Hückel Theory as well. The question was, which way could we describe the structures having or not having peaks at the Fermi level. It seemed to be a veritable problem of chemical graph theory. Fortunately I had a reprint of the "Workshop on Quantum Chemistry, May 6–9, 1974, Mátrafüred, Hungary". It was dedicated to me by Gábor Náray–Szabó and it contained an article from N. Trinajstić and T. Živković with the title: A gráfelmélet az elméleti kémiában (The graph theory in the theoretical chemistry) [2]. This article was written in Hungarian, and it was a very good introduction to the chemical graph theory. It contained the Sachs theorem [3] that became the basic tool in the solution of our problem.

2 Sachs theorem and the density of states in amorphous carbon

In the study of the π–electron network first we applied the Hückel theory. For the Hückel Hamiltonian **H** we have:

$$H_{ij} = \begin{cases} \alpha, & \text{if } i = j \\ \beta, & \text{if } j \text{ is the first neighbor of } i \\ 0, & \text{otherwise} \end{cases} \tag{1}$$

where α and β are the interaction parameters. A given carbon cluster of threefold–coordinated atoms can be represented by the graph $G = (V, E)$ where each atom is a vertex and each bond represents an edge of the graph. In this notation V is the set of vertices and E is the set of edges. By introducing the **I** unit matrix and the **A** adjacency matrix of G with:

$$A_{ij} = \begin{cases} 1, & \text{if the vertices } i \text{ and } j \text{ are adjacent} \\ 0, & \text{otherwise} \end{cases} \tag{2}$$

the relation $\mathbf{H} = \alpha\mathbf{I} + \beta\mathbf{A}$ changes the secular equation $\det|\mathbf{H} - \varepsilon\mathbf{I}| = 0$ into $\det|x\mathbf{I} - \mathbf{A}| = 0$, where $\varepsilon = \alpha + x\beta$. The $P_G(x)$ characteristic polynomial of matrix **A** is:

$$P_G(x) = \det|x\mathbf{I} - \mathbf{A}| = \sum_{n=0}^{N} a_n x^{N-n} \tag{3}$$

where $N = |V|$ is the umber of vertices in graph $G = (V, E)$. According to Sachs theorem [3,4,5] the a_n coefficients are:

$$a_n = \begin{cases} \sum_{s \in S_n} (-1)^{p(s)} 2^{c(s)}, & \text{if } 0 < n < N \text{ and } S_n \neq 0 \\ 0, & \text{if } 0 < n \leq N \text{ and } S_n = 0 \\ 1, & \text{if } n = 0. \end{cases} \tag{4}$$

where s is a Sachs graph, S_n is the set of all Sachs graphs with n vertices, while $p(s)$ and $c(s)$ denote, respectively, the total number of components and the total number of cycles in s. A Sachs graph s is defined as such a sub graph of G whose components are the complete graphs K_2 and/or cycles C_m $(m = 3,4,...,n)$.

If $a_N = a_{N-1} = a_{N-2} = ... = a_{N-\nu+1} = 0$, then x=0 is a ν–fold degenerated eigenvalue of **A** and $\varepsilon = \alpha$ is the ν–fold degenerated eigenvalue of **H**. As in amorphous carbon structures usually the Fermi level is around the value α we can characterize the clusters of threefold–coordinated carbon atoms according to their topological graphs. Thus if a given graph of N vertices does not have Sachs graph with $N, N-1, …, N-1+\nu$ vertices, the corresponding carbon cluster has a peak at the Fermi level corresponding to the ν–fold degeneracy of the eigenvalue $\varepsilon = \alpha$. We published our results in Physical Review B [6] and further *ab initio* calculations confirmed these results [7,8]. I am grateful to Lajos Jakab who organized me a three day visit in 1989 to the Ruđer Bošković Institute and I could have very useful discussions with Nenad Trinajstić.

3 Topologically determined electronic energy levels USSION

When we tested our theory we found very interesting results. Although Sachs theorem is based on Hückel theory or on the adjacency matrices of graphs, we obtained in some cases degenerated $\varepsilon = x$ eigenvalues even if the first neighbor off–diagonal matrix element H_{ij} had any non–zero values. That is these electronic energy levels were stable in the presence of vibration and off–diagonal disorder. Thus we have found that the $\varepsilon = x$ eigenvalue was ν–fold degenerated if the graph G of the Hamiltonian matrix $\mathbf{H} - \alpha\mathbf{I}$ did not have Sachs graph with $N, N-1, …, N-1+\nu$ vertices. Let the Hamiltonian **H** is represented by an $N \times N$ matrix. The graph G of $\mathbf{H} - \alpha\mathbf{I}$ is then a loop free graph of N vertices and the vertices i and j are joined by an edge if and only if $H_{ij} \neq 0$. In the followings we define the graph G of an $n \times n$ symmetrical square matrix $M = [M_{ij}]$ by a graph of n vertices where the vertices i and j are connected by an edge if and only if $M_{ij} = M_{ji} \neq 0$.

Let us see the eigenvalue problem of symmetrical square matrix $H = [H_{ij}]$ of size $N \times N$. The corresponding Hamiltonian has the form:

$$\mathbf{H} = \sum_{i,j=1}^{N} |i\rangle H_{ij} \langle j| \tag{5}$$

For this Hamiltonian matrix the characteristic polynomial $D(\varepsilon)$ is the following[9,10]:

$$D(\varepsilon) = \det\left| \varepsilon\, \mathbf{I} - \mathbf{H} \right| = \sum_{n=0}^{N} a_n \varepsilon^{N-n} \qquad (6)$$

Here the coefficients a_n are given by

$$a_n = (-1)^n \sum H(i_1 i_2 ... i_n) \qquad (7)$$

where the summation runs over all $\begin{pmatrix} N \\ n \end{pmatrix}$ principal minors of $\mathbf{H}$ of order n. The determinants $H(i_1 i_2 ... i_n)$ are calculated as,

$$H(i_1 i_2 ... i_n) = \sum_p (-1)^{t(p)} H_{i_1 j_1} H_{i_2 j_2} ... H_{i_n j_n} \qquad (8)$$

and t(p) is the parity of the p permutation $j_1 j_2 ... j_n$ of numbers $i_1 i_2 ... i_n$.

If $H_{i_1 j_1} H_{i_2 j_2} ... H_{i_n j_n} \neq 0$ than the graph of the matrix elements of this product is a Sachs graph with n vertices. Namely every permutation can be described by a product of disjoint cycles. Thus if a graph G of a symmetrical $N \times N$ matrix does not have Sachs graph with $N, N - 1, …, N - 1 + \nu$ vertices then the $\varepsilon = 0$ eigenvalue is a ν–fold degenerated eigenvalue of $\mathbf{H}$. Or if the graph of the matrix $\mathbf{H}$- $H_{kk}\mathbf{I}$ does not have Sachs graph with $N, N - 1, …, N - 1 + \nu$ vertices then the $\varepsilon = H_{kk}$ eigenvalue is a ν–fold degenerated eigenvalue of $\mathbf{H}$.

If E_s and E_p are the $s-$ and p–orbital tight–binding diagonal matrix elements, then Sachs graphs can be used for study of the $\varepsilon = E_s$ and/or $\varepsilon = E_p$ eigenvalue multiplicities. Thus application of Sachs graphs is not restricted to the Hückel theory. We published these results as a Rapid Communication in Physical Review [11] and applications were presented for fullerenes [12] and Bethe lattices (trees) [13].

Thus there are Hamiltonian matrices which have such kind of eigenvalues that do not depend on the actual values of the off–diagonal non–zero matrix elements. They are called topologically determined electronic energy levels as they are determined only by the appropriate distribution of the off diagonal zero matrix elements and their actual value is equal to some diagonal matrix element.

4 Necessary and sufficient conditions for non–existence of Sachs graphs

The existence of topologically determined energy level is guaranteed by the non–existence of certain Sachs graphs. In practical applications, however, the demonstration of the existence of special graph structure is much easier than the demonstration of non–existence of Sachs graphs. Thus we turned to the study of necessary and sufficient conditions for non–existence of Sachs graphs.

It is trivial that the 2–star graph $G_1 = (V_1, E_1) = (\{1,2,3\}, \{(1,2),(1,3)\})$ does not have Sachs graph

with n=3 vertices. Namely if we suppose that such a Sachs graph exists, the edge (1,2) must belong to it, and the vertex 3 turns to be an isolated vertex. This is contradicting to the supposition that G_1 has a Sachs graph with n=3 vertices. Using this indirect proof one can see very easily, that also the $(N-1)$–star graph $G_2 = (V_2, E_2) = (\{1,2,...,i,...,j,...,N\}, \{(1,2),(1,3),...,(1,i),...,(1,j),...,(1,N)\})$ with N vertices and $N-1$ edges does not have Sachs graph with n=3,…,N vertices. Now let us see the case of N identical atoms arranged at the vertices of an $N-1$–star graph and we suppose further that each atom has one s orbital and three p orbitals. Now the diagonal matrix elements of the corresponding first neighbor tight–binding Hamiltonian **H** equal to E_s or E_p and we can obtain non–zero off–diagonal matrix elements only between orbitals that are centered on different neighboring atoms.

Namely in tight binding approximations it is supposed usually that the off–diagonal matrix elements between orbitals belonging to the same atom are equals to zero. The graph G_3 of the $\mathbf{H} - E_p\mathbf{I}$ shifted Hamiltonian has the following properties. The vertices corresponding to the p orbitals on the atoms 2, 3, …, N are loop–free vertices and they are connected only to the s and p orbitals of the first atom. We call a set of vertices independent if no two elements of it are adjacent Let the set of vertices of the p orbitals on the atoms 2, 3, … N be V_1 and the set of s and p orbitals of the first atom be V_2. If $|V|$ is the number of vertices in the set V and $\Gamma(V)$ marks the neighboring vertices of V, than $|V_1| = (N-1)*3$, $|V_2| = 4$ and $\Gamma(V_1) = V_2$. It can be proved that G_3 does not have Sachs graph with $N, N-1, …, N-1+\nu$ vertices if $\nu = |V_1| - |V_2| > 0$ [14,15].

It turned out that by the graph G_3 we found the special graph structure we were looking for in our search for sufficient and necessary conditions for the non–existence of Sachs graphs. In Ref. [14] we proved that if the N vertices of a graph G_4 can be partitioned in sets V_1, V_2 and V_3 in such a way that the vertices in V_1 are loop–free independent vertices, and $V_2 = \Gamma(V_1)$ with $|V_1| - |V_2| = \nu > 0$ then the graph G_4 does not have Sachs graph with $N, N-1, …, N-1+\nu$ vertices. The necessity of this vertex partitioning for non–existence of Sachs graphs was proved in ref. [15].

Our results concerning the topologically determined energy levels can be summarized in the following Theorem.

Theorem [14,15]. Suppose that the N basis functions of the symmetrical Hamiltonian

$$\mathbf{H} = \sum_{i,j=1}^{N} |i\rangle H_{ij} \langle j| \tag{9}$$

can be partitioned into three disjoint sets V_1 , V_2 and V_3 with the following properties:

1   Set V_1: If $\langle i| \in V_1$ and $\langle j| \in V_1$ then $H_{ij} = H_{ji} = 0$ and $H_{ii} = H_{jj} = \alpha$, where α is the same value for each basis functions of set V_1. The number of basis functions in set V_1 is $m > 0$.

2   Set V_2: V_2 contains all the $\langle i|$ basis functions for which there is at least one $\langle j| \in V_1$ with $H_{ij} = H_{ji} \neq 0$. The number of basis functions in set V_2 is $n \geq 0$.

3   Set V_3: $\langle i| \in V_3$ if $\langle i| \notin V_1$ and $\langle i| \notin V_2$

Thus if we can construct the above defined sets V_1, V_2 and V_3 with $m > n$ then the value $\varepsilon = \alpha$ is an eigenvalue of the Hamiltonian matrix **H** and this eigenvalue is at least $(m-1)$–fold degenerated. These eigenvalues are called topologically determined levels and the corresponding eigenfunctions are localized on the basis functions of set V_1.

The relation of this theorem with the Coulson–Rushbrooke theorem is presented in [13].

As an example let us see the graph

$$G_5 = \left(\{1,2,3,4,5,6,7,8,9,10,11\}, \{(1,2),(2,3),(3,4),(4,5),(5,1),(5,6),(6,7),(7,8),(8,9),(9,10),(10,1),(10,11)\} \right)$$

In this graph the $(1,2,3,4,5)$ pentagonal and $(1,5,6,7,8,9,10)$ heptagonal cycles are connected by the common edge $(1,5)$, and the vertex 11 is joined to the vertex 10. The graph G_5 has a Sachs graph having the components $(1,2,3,4,5)$, $(6,7)$, $(8,9)$ and $(10,11)$, that is one C_5 cycle and three complete graphs K_2.

Now let us see the graph

$$G_6 = \left(\{1,2,3,4,5,6,7,8,9,10,11\}, \{(1,2),(2,3),(3,4),(4,5),(5,1),(5,6),(6,7),(7,8),(8,9),(9,10),(10,1),(9,11)\} \right)$$

It is obtained from the graph G_5 by replacing the edge $(10,11)$ with $(9,11)$. This small changing in the structure yields that G_6 does not have Sachs graph. Namely here the set of vertices $V_1 = \{11,10,2,4,6,8\}$ is a set of independent loop–free vertices and the set $\Gamma(V_1) = V_2 = \{9,1,3,5,7\}$ is the set of neighboring vertices for V_1. The graph G_6 does not have Sachs graph as $|V_1| = 6 > |V_2| = 5$. Let us construct the matrix $M = [M_{ij}]$ of graph G_6 with:

$$M_{11,11} = M_{10,10} = M_{2,2} = M_{4,4} = M_{6,6} = M_{8,8} = \alpha_0$$

In that case $\varepsilon = \alpha_0$ is an eigenvalue of matrix M independent of the actual values of the non zero matrix elements and the corresponding eigenvector is localized on the set of vertices $V_1 = \{11,10,2,4,6,8\}$.

5 Sachs graphs and matching problems

Now we shall present that the topologically determined electronic energy levels can be described with the help of the matching theory [16] as well, where the existence of perfect 2–matching in a graph G means that it contains a system of vertex–disjoint cycles and edges, that is a Sachs–graph. The other name of perfect 2–matching is q–factor [16].

Let G be an undirected simple graph. Multiple edges and loops are not allowed. A set of edges in

a graph G is called matching if no two edges have a vertex in common. The size of any largest matching in G is called the matching number of G and is denoted by $v(G)$. A 2–matching of a graph G is an assignment of weights 0, 1 or 2 to the edges of G such that the sum of weights of edges incident with any given vertex is at most 2 [16]. The size of a 2–matching is the sum of weights and the maximum size is denoted by $v_2(G)$. A 2–matching is called perfect if the sum of weights of edges incident with any vertex is exactly 2. It can be seen that in a perfect 2–matching the edges of weights 1 and 2 compose a system of vertex–disjoint cycles and edges which cover all vertices of graph G [16].

A perfect 2–matching of graph G is the same sub graph that that we called previously Sachs–graph, and it was called *q*–factor by Tutte [17], who proved the following theorem which is presented also by Lovász and Plummer in Corollary 6.1.5 of ref. [16].

Theorem (Tutte [17, 16]). A graph G has a perfect 2–matching (*i.e.* a q–factor) if and only if $\left|\Gamma(A)\right| \ge \left|A\right|$ for every independent set of A vertices.

Tutte's Theorem is in agreement with our statement about the existence and non–existence of Sachs–graphs. We said above namely that a graph G has a Sachs–graph (2–matching) or its vertices can be partitioned into the disjoint sets V_1, V_2 and V_3 where for the independent set of loop–free vertices V_1 we have the relation $\left|\Gamma(V_1)\right| = \left|V_2\right| < \left|V_1\right|$. The perfect agreement holds only if we do not allow loops in G as it is usually supposed in matching theory [16]. There is however, no contradiction between the two phrasing even if there are loops in graph G of a Hamiltonian matrix H. At this time in the definition of 2–matching the weight of a loop must be taken twice and Tutte's Theorem rest valid if we replace the words " … independent set A of vertices" by "…independent set A of loop–free vertices" [18].

6 CONCLUSIONS

The topological aspect of the Hückel theory can be extended to more sophisticated Hamiltonians, to the tight binding Hamiltonians, where the applied graphs describe the distribution of the non–zero matrix elements of the Hamiltonian matrix. Applying only graph theoretical methods, the existence of non–trivial electronic energy levels can be found and their localization properties can be described without solving the eigenvalue problem.

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