

## GRAPH THEORY AND SIMPLE HUECKEL THEORY APPLIED TO BENZENE

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*Recibido 7 de marzo, 2011; Aceptado: 10 de diciembre, 2011*

### Abstract

We compare the results of application of graph theory and of simple Hückel theory in its traditional form to benzene, as an instance of a conjugated molecular system. The identity of the results of solution of eigenvalues of the vertex adjacency matrix and characteristic values of the Hückel determinant prove the isomorphism of these two formalisms. Because of the gross deficiencies of the Hückel theory, we advocate its elimination from the teaching of chemistry in favour of graph theory that has many applications to molecular topology.

### Resumen

Se compararon los resultados de la aplicación de la teoría de gráficos y de la teoría de Hückel tradicional a benceno, como ejemplo de un sistema molecular conjugado. Los resultados idénticos entre los eigenvalores de la matriz de adyacencia de los vértices y los valores característicos del determinante de Hückel verifican el isomorfismo de los dos formalismos. Se recomienda la eliminación de la teoría de Hückel por sus deficiencias y en su lugar utilizar la teoría de gráficos que tiene muchas aplicaciones en topología molecular.

**Key Words:** graph theory, Hückel theory, adjacency matrix, molecular topology, benzene.

**Palabras claves:** teoría de las gráficas, teoría de Hückel, matriz de adyacencia, topología molecular, benceno.

## I. Introduction

Although problems had been previously solved that are now recognised as corresponding to applications of graph theory, Cayley in 1875 attempted to enumerate structural isomers of chemical compounds on the basis of this theory before Sylvester defined the name in 1878 [1]. Of two distinct meanings of a graph, that implying plots of data in, for instance, Cartesian coordinates is separate from that in graph theory, in which an identification of points with specific coordinates is entirely absent; the nature of a graph in a graph-theoretical context is explained below.

In 1928, physicists Hund and Mulliken originated an approximate treatment of the electronic structure of molecules, called the method of molecular orbitals. From 1930 to 1937, another physicist Erich Hückel developed, as an archetype of simple and phenomenological models, this approach that he applied to various molecules of moderate size [2, 3, 4]. This method in essence involves an approximate evaluation of molecular wave functions as a linear combination of atomic functions resembling orbital wave functions of the hydrogen atom; the attendant energies for each electron are hence evaluated for a potential field corresponding to a molecule. This theory treats only the purported  $\pi$  electrons – as if electrons were distinguishable, and the other electrons and atomic nuclei exhibit an influence only as parts of that effective potential field. The energy of the entire molecule is then calculated as a sum of energies of all electrons, with which are associated molecular-orbital wave functions with no more than two electrons per orbital [5]. Despite the gross approximations involved in Hückel's method, it was convenient for manual calculation, having been developed well before the era of the electronic digital computer; for that reason the method became popular, even though its deficiencies were manifest and manifold. Some facets of the method were subsequently made more general by Hoffmann for computations on other than conjugated molecules under a name *extended Hückel theory* [6] that, with gross neglect of electronic correlation like its predecessor, delivers predictions of poor quality. For this reason we distinguish the early formalism as *simple Hückel theory*.

Hückel's original method was particularly suitable for application to benzene and to other so-called *conjugated* molecules. Here we apply both graph theory and simple Hückel theory to benzene, and draw critical conclusions from a comparison of the results.

## II. Graph theory

According to the mathematical theory of graphs [7], a simple graph essentially comprises points in one set and lines in another set. Because each point has no

particular coordinates, a preferable designation is a *vertex*; an undirected line, either single or multiple, that might connect two vertices is accordingly designated an *edge*. A simple graph  $G$  is then defined as an ordered couple, or *duple*,  $[V(G), E(G)]$ , that comprises vertices  $V$  in one non-empty set and edges  $E$  in another; the latter might be an empty set. The number of elements in  $V$  defines the *order* of  $G$ , and the number of elements of  $E$  defines the *size* of  $G$ . A *tree* is a connected graph in which a *path* from any vertex does not lead back to itself, whereas a path that returns to the original vertex is called a *cycle*.

On such a formal basis of a graph, one defines its associated matrices. One such matrix that is particularly useful is a vertex adjacency matrix  $\mathbf{A}$ : matrix element  $A_{jk}$  therein has the value unity if between vertices  $j$  and  $k$  there exist a single edge, or nought otherwise; this matrix of the same order as  $G$  is symmetric, with nil elements along the principal diagonal. Further adjacency matrices  $\mathbf{A}_l$  are analogously constructed with element  $A_{jk}^{(l)} = 1$  when  $l$  is the minimum number of edges between vertices  $j$  and  $k$ , or nought otherwise. Also symmetric, distance matrix  $\mathbf{D}$  has, as element  $D_{jk}$ , the minimum number – a non-negative integer – of edges between two vertices  $j$  and  $k$ . A relation between these matrices is

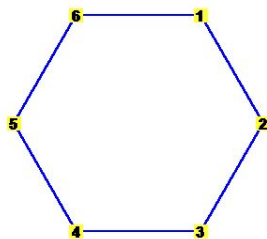
$$\mathbf{D} = \mathbf{A} + \sum_{l=2} l \mathbf{A}_l$$

A characteristic of a matrix is that it might have distinct eigenvalues numbering one or more, such that operating according to multiplication with that matrix on a vector reproduces that vector multiplied by a scalar quantity called an *eigenvalue*; this property is expressed as

$$\mathbf{M} \underline{v} = \lambda \underline{v},$$

containing square matrix  $\mathbf{M}$  of order  $k$ , vector  $\underline{v}$  of dimension  $k$  and eigenvalue  $\lambda$  in a set of maximum number  $k$ . A vector that conforms to this definition becomes an *eigenvector*. The eigenvalues of an adjacency matrix pertaining to a particular graph constitute the *spectrum* of that graph. Because the adjacency matrix is symmetric, all its eigenvalues are real numbers. The  $k$  eigenvectors of vertex adjacency matrix  $\mathbf{A}$  of graph  $G$  of order  $k$  are linearly independent, but multiple eigenvectors might have the same eigenvalue.

For instance, we form a cyclic graph  $C$  of order 6, hence with six vertices and six edges, of which we represent pictorially a diagram of that graph, also just called a graph.



The lengths between adjacent vertices and the angles between adjacent edges therein convey no significance; the only property that this diagram implies is an order of connexion, or topology. In vertex adjacency matrix  $A$  of that graph,

$$\begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 0 & 1 & 0 \end{bmatrix}$$

the first row indicates that edges connect vertex 1 to both vertices 2 and 6; the second row shows that edges connect vertex 2 to vertices 1 and 3, and so forth. We assume that the vertices of the displayed cycle are numbered consecutively from 1 to 6 around the hexagon.

The eigenvalues and eigenvectors of that adjacency matrix are readily calculated to yield the following results. The spectrum of that adjacency matrix comprises eigenvalues 2, 1, -1 and -2. Eigenvalue 2 corresponds to a single eigenvector,  $\langle 1, 1, 1, 1, 1, 1 \rangle$ , and eigenvalue -2 corresponds to a single eigenvector,  $\langle 1, -1, 1, -1, 1, -1 \rangle$ ; in contrast eigenvalue 1 corresponds to two eigenvectors  $\langle 1, 0, -1, -1, 0, 1 \rangle$  and  $\langle -1, -1, 0, 1, 1, 0 \rangle$ , and eigenvalue -1 corresponds to two eigenvectors  $\langle -1, 0, 1, -1, 0, 1 \rangle$  and  $\langle -1, 1, 0, -1, 1, 0 \rangle$ . Eigenvalues 2 and -2 are thus each singly degenerate, and eigenvalues 1 and -1 each doubly degenerate. These results are derived in a purely abstract mathematical manner.

In a chemical context, one might associate a vertex with an atomic centre, and an edge between two vertices as a putative chemical bond between two such atomic centres; the vertex adjacency matrix is hence known in a chemical context as a topological matrix. If one ignore the hydrogenic atomic centres bound one to each

carbon atomic centre in benzene, the graph above might represent that isolated molecule with one vertex to denote each such carbon centre. On the same basis of ignoring all hydrogenic atomic centres, that same graph might, however, represent also cyclohexane  $C_6H_{12}$ , or an hypothetical cyclohexacarbon  $C_6$ , because a mathematical model of a molecule as a simple graph takes account of the nature of neither what might be represented as an edge or a vertex, nor of a geometric structure that one might attribute to a stable molecule in its equilibrium conformation. A review of graph theory applied to aromatic molecules lists more than 1000 references [8], and an article on manual Hückel calculations of acyclic polyenes involves simplifying the root of the secular equation with graph theory [9].

### III. Simple Hückel Theory

Simple Hückel theory is based on several restrictive premises, which reduce the description of an organic molecule to a minimal model [10], as follows.

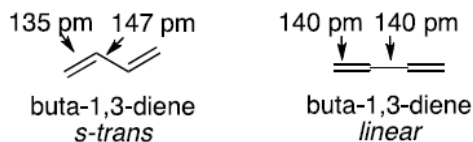
- 1) This method was originally developed to describe planar conjugated hydrocarbons. The  $\pi$  framework includes C–C covalent bonds but not hydrogen atoms. The  $\sigma$  electrons are considered as separate entities and treated as a *frozen core*, without interaction between  $\sigma$  and  $\pi$  electrons. The number of  $\pi$  orbital wave functions – the sum of bonding  $\pi$  and anti-bonding  $\pi^*$  – is equal to the number,  $N$ , of carbon atomic centres within the conjugated system.
- 2) The Hückel approximation is considered a one-electron theory, in which all interactions between electrons are ignored. The total Hückel electronic energy  $E_H$  is the sum of the energies of molecular-orbital wave functions times their occupation number.

$$E_H = 2 \sum_{j=1}^{N/2} n_j \epsilon_j$$

- 3) The overlap of  $\pi$  orbital wave functions at short range dominates, and coulombic interactions at long range are neglected. Overlap only between nearest neighbours is considered; all other interactions are set equal to zero.
- 4) All carbon atoms are considered to have an equivalent core, and any variation of interatomic distances is neglected.

These premises consequently restrict the use of simple Hückel theory to applications that exclude ionic bonds, charge-transfer systems or weak interactions. More importantly for organic molecules, Hückel calculations on simple  $\pi$  systems are independent of structure. The Hückel determinant is topological, unaffected by

twisting or bending or distortion from planarity. For instance, buta-1,3-diene is a planar conjugated hydrocarbon with a stable conformation described as *s-transoid*. As a model buta-1,3-diene, Hückel calculations use effectively a linear molecule with all C–C bonds of equal length. These two models are evidently inconsistent.



According to Hückel's treatment of benzene [11], electrons in the  $\pi$  system are described with molecular orbitals  $\psi_j$  that are formed as linear combinations of carbon  $2p\pi$  orbitals  $\phi_k$ , each associated with atomic centre  $k$ ; these  $2p_z$   $\pi$  orbitals are aligned parallel with axis  $C_6$  of symmetry perpendicular to the molecular plane. Hence,

$$\psi_j = \sum_{k=1}^6 c_{jk} \phi_k$$

such that each such molecular orbital extends around the entire hexagon of carbon atomic centres. In further simplification, the only electronic interactions great enough to require inclusion in the effective hamiltonian are those between an electron near a particular carbon nucleus and the other electrons and that nucleus, and between that electron and other electrons and nuclei of adjacent atomic centres to which a putative chemical bond exists. As for benzene in which all carbon atoms are equivalent, we define a Coulomb integral,

$$\alpha \equiv \int \phi_k^* \mathfrak{H}_{\text{eff}} \phi_k \, d\tau, \quad \text{for all } k,$$

and a bond or resonance integral,

$$\beta \equiv \int \phi_k^* \mathfrak{H}_{\text{eff}} \phi_l \, d\tau, \quad \text{for atoms } k, l \text{ adjacent,}$$

in which  $\mathfrak{H}_{\text{eff}}$  denotes an effective hamiltonian for one  $\pi$  electron. Hückel quantity  $\alpha$ , assumed to have the same value for all carbons, corresponds to the energy of an electron in a  $2p$  orbital, perpendicular to the carbon frame. Hückel quantity  $\beta$  corresponds to the energy of interaction of two  $2p$  orbitals of separate C atoms that are directly connected to each other with a  $\sigma$  bond. To generate this hamiltonian as a matrix, we set element  $H_{kl}$  equal to  $\alpha$  for  $l = k$ , and to  $\beta$  for adjacent carbon atomic centres  $j$  and  $k$ . Overlap integrals,

$$S_{jk} \equiv \int \phi_k^* \phi_l \, d\tau,$$

are set equal to unity for  $l = k$  and to nought otherwise. The condition according to

which coefficients  $c_{jk}$ , calculated to minimize energy  $\epsilon_j$  of each molecular orbital  $\psi_j$ ,

$$\sum_{k=1}^6 c_{jk} (H_{kl} - \epsilon_j S_{kl}) = 0,$$

become evaluated is that this determinant vanishes for each energy  $\epsilon$ ,

$$\| H_{kl} - \epsilon S_{kl} \| = 0,$$

which, with the definitions above, yields this Hückel matrix.

$$\begin{bmatrix} \alpha - \epsilon & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha - \epsilon & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - \epsilon & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - \epsilon & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - \epsilon & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha - \epsilon \end{bmatrix}$$

If we replace  $\epsilon$  by  $\alpha - \beta x$ , and divide through by  $\beta$ , which is legitimate because for a solution of this system the determinant of this matrix must equal zero, we obtain another matrix of similar form.

$$\begin{bmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{bmatrix}$$

The determinant, equal to zero, of this matrix yields this characteristic polynomial of order six,

$$-4 + 9x^2 - 6x^4 + x^6 = 0$$

of which the roots  $-2, -1, 1, 2$  are eigenvalues of the latter matrix; these values become the values of  $x$  that we might convert to energies according to the relation above. Values  $\pm 1$  each occur twice, implying a double degeneracy, but values  $\pm 2$  occur only once. We can alternatively find directly the eigenvalues  $\epsilon$  of the Hückel matrix, presented as this unsorted column vector.

$$\begin{bmatrix} \alpha + 2\beta \\ \alpha - 2\beta \\ \alpha - \beta \\ \alpha + \beta \\ \alpha - \beta \\ \alpha + \beta \end{bmatrix}$$

The components of this vector are exactly equivalent to the roots of the polynomial above. The corresponding eigenvectors, which are produced directly in the same calculation as the eigenvalues, are exactly equivalent to those produced from graph theory above. These eigenvalues and eigenvectors in sets from the matrix of adjacency of vertices and from the Hückel matrix are identical; this identity proves the isomorphism of graph spectral theory and simple Hückel theory.

#### IV. Discussion

The treatment with graph theory of both trees that might represent acyclic molecules and cycles that analogously represent cyclic molecules yields exactly the same eigenvalues and eigenvectors of the vertex adjacency matrix as result from the Hückel matrix generated for all corresponding conjugated molecules – benzene is by no means an exceptional case.

According to the phenomenological Hückel approach, parameters  $\alpha$  and  $\beta$  become either empirically evaluated, i.e. from experimental data, or ignored. For instance,  $\beta$  might be evaluated from the wavenumber of onset of strong absorption in the ultraviolet spectral region: thereby  $\beta$  adopts disparate values for *s*-transoid and putative *s*-cisoid isomers of buta-1,3-diene, despite the electronic structures of these conformational isomers being almost the same. Parameter  $\alpha$  would differ between C and N atomic centres, as for instance might be evaluated on comparison of spectra of benzene and pyridine, or of buta-1,3-diene and methanal azine. Because such values of  $\alpha$  and  $\beta$  are, however, poorly transferable between molecular systems, these values are practically worthless.

The major deficiency of this simple Hückel theory is its lack of theoretical basis. Each and every condition described above as a simplification is a gross oversimplification; the approximations are crude, and the results of a calculation reflect those conditions. Although there might have been some justification or utility of this theory in the years directly following its development, the present availability of both hardware and programs for quantum chemistry run on electronic digital computers that enable rapid calculations including all electrons, taking quantitative account of conformations within an approximate separation of electronic and nuclear motions, makes this approach entirely obsolete and superseded. Its primary postulate of



differentiation between  $\pi$  and other electrons, which is physically unsupportable, should be excised from the description of molecular electronic structure in the teaching of chemistry and any applications thereof.

In its conventional sense, which corresponds to what might be deduced from xray diffraction of an appropriate crystalline sample, molecular structure is a classical concept that is absolutely foreign to rigorous quantum mechanics [12, 13]. For that reason, any attempt to explain non-observable features of molecular structure with quantum-mechanical concepts is fallacious. That condition in no way precludes a useful, and generally moderately accurate, calculation of conformations, and their internuclear distances and angles, in molecules and their aggregates with programs for molecular electronic structure, based on and requiring an empirical separation of electronic and nuclear motions, just as one might apply for the same purpose methods of molecular mechanics [14] that might have no quantum-mechanical component or justification whatsoever.

Chemical applications of graph theory are highly useful, for instance, for the enumeration and depiction of constitutional isomers, such as for regioisomeric derivatives of benzene or for branched hydrocarbons. The calculations of graph theory involve combinatorial procedures, to generate graphs as topological depictions, and linear algebra – the formation of matrices and vectors, the extraction of eigenvalues and eigenvectors and related operations, as we have applied above. All these procedures are efficiently and rapidly implemented with programs for symbolic computation; for instance, in *Maple* [15] that we applied for all calculations described herein, a repository of procedures and commands contains 160 items that enable a comprehensive generation of graphs and analysis of their properties. Mathematical software is so valuable for not only the teaching of mathematics to, and learning by, students of chemistry but also the implementation of all mathematical calculations [16] that every practitioner of chemistry should become familiar with its capabilities; much misunderstanding of quantum-mechanical concepts that are purely mathematical, with neither physical nor chemical basis, is readily resolved with an expanded understanding of the mathematical principles in algebra, calculus, linear algebra and differential equations. We recommend that graph theory in a chemical context should be taught in appropriate undergraduate courses, preferably to replace obsolete methods and quantum mechanics that are poorly understood and of which the value for most chemical practice is overvalued.

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