

IMPACT OF THE SACHS THEOREM ON THEORETICAL CHEMISTRY: A PARTICIPANT'S TESTIMONY

Ivan Gutman

*Faculty of Science, University of Kragujevac, P. O. Box 60,
YU-34000 Kragujevac, Yugoslavia,
e-mail: gutman@knez.uis.kg.ac.yu*

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Dedicated to Professor
Horst Sachs
teacher and friend
on the occasion of his 75th birthday

Abstract

An outline is given of the role which the coefficient theorem, discovered in 1964 by Horst Sachs, played in the theoretical chemistry of conjugated molecules.

INTRODUCTION

In this article we are not going to describe and exemplify the chemical applications of the Sachs theorem – which has already been done in several books and in a plethora of reviews – but rather we shall tell *the story* of the chemical applications of the Sachs theorem, from the perspective of someone who actively participated in

their elaboration. We intend to reduce the mathematical formalism to a necessary minimum and to direct the interested reader to pertinent literature sources. The terminology and notation used throughout this article are outlined at the end of this text, in the *Appendix*.

The article is divided into three parts: *History*, *Chemical Applications of the Sachs Theorem* and *Chemical Theories Based on the Sachs Theorem*. In the first part we describe the situation in the relevant area of theoretical chemistry before the Sachs coefficient theorem became known, as well as the discovery, naming and dissemination of the Sachs theorem. In the second part we are concerned with the routine and less-routine chemical applications of the Sachs theorem, pertaining to the computation of the coefficients of the characteristic polynomial. In the third part we briefly present those chemical theories which were built on concepts encountered in the Sachs theorem, and which are capable of quantifying various effects of cyclic conjugation.

The references quoted are numerous, but far from being exhaustive. We cite all chemical review articles and books known to us in which the Sachs theorem is explicitly discussed. To produce a list of all original scientific papers (occurring in the chemical literature) in which there is a direct use of the Sachs theorem would now be very difficult. Such a list would contain several hundreds of bibliographic units; here we quote only a few dozen of them. There may be thousands of chemical papers in which the considerations are based, often implicitly, on results coming from the Sachs theorem. Creating such a bibliography would nowadays be an almost impossible task.

HISTORY

Before

In the 1930s Erich Hückel put forward an approximate molecular orbital model, aimed at providing a description of the behaviour of the π -electrons in unsaturated conjugated organic molecules [1–3]. It was a quarter of century before Günthard and

Primas recognized that the Hamiltonian matrix \hat{H} of the Hückel molecular orbital (HMO) theory is a linear function of the adjacency matrix of a pertinently constructed “molecular graph” [4]:

$$\hat{H} = \alpha I + \beta A(G) \quad (1)$$

with α and β being the standard HMO parameters [5, 6]. (The meaning of the other symbols in Eq. (1) is explained in the Appendix.) From this finding follows that the energy levels of the π -electron molecular orbitals, as calculated within the framework of the HMO approximation, are linear functions of the graph eigenvalues (cf. the Appendix):

$$E_j = \alpha + \beta \lambda_j \quad , \quad j = 1, 2, \dots, n \quad (2)$$

This, in turn, means that the characteristic polynomial of the graph G , via its zeros, plays an important role in the theory of conjugated molecules.

However, the paper [4] did not trigger any noteworthy activity among theoretical chemists. In its time it was just an interesting, yet ostensibly useless, observation. An important step between Eq. (1) and its chemical applications was missing.

What theoretical chemists needed was some method of determining the π -electron energy levels E_j , Eq. (2), directly from molecular structure. In the absence of such a method, they would be satisfied with the knowledge of the coefficients of the characteristic polynomial (the “secular determinant” [5, 6]), since these coefficients carry much information about the energy levels.

Another important motive for being interested in the structure-dependency of the coefficients of the characteristic polynomial was the existence of the integral formulae, discovered by Coulson – alone [7] and with Longuet-Higgins [8–10] – enabling the main HMO π -electron characteristics of a conjugated molecule (total π -electron energy, charges and bond orders) to be expressed via the characteristic polynomial of the molecular graph and of some of its subgraphs. For instance, the Coulson integral formulae for the total π -electron energy (E) and the π -electron charge density q_r on atom r read

$$E = \frac{1}{\pi} \int_{-\infty}^{+\infty} \left[n - i \lambda \frac{\phi'(G, i \lambda)}{\phi(G, i \lambda)} \right] d\lambda \quad (3)$$

and

$$q_r = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\phi(G - v_r, i \lambda)}{\phi(G, i \lambda)} d\lambda \quad (4)$$

where $i = \sqrt{-1}$ and where ϕ denotes the characteristic polynomial and ϕ' its first derivative of ϕ ; for more details on ϕ see the Appendix.

Samuel, in 1949 [11] (see also [12]), seems to have been the first to communicate an attempt to compute the coefficients of the secular determinant from molecular structure. (This, of course, is tantamount to computing the coefficients of the characteristic polynomial from the structure of the molecular graph.) In 1950 Coulson published another work along the same lines [13]. Although (as we see now) these authors were quite close to the discovery of the “Sachs theorem”, they did not manage properly to formulate it and were far from its formal proof.

In the following 20 years no noteworthy progress was achieved in this direction of research.

The Discovery and Another Discovery

Horst Sachs published his famous theorem in 1964 in a Hungarian mathematical journal [14], in the German language (see also [15]). It is no surprise that not a single chemist noticed this paper.

Before and after 1964 several mathematicians arrived at similar (weaker) or equivalent results. These complicated historical details are analysed in [16, p. 36] and [17], and will not be our concern here. Yet, as a curiosity, we mention that in the same year 1964 Mirko Milić [18] (an electrical engineer) and Leonard Spialter [19] (a chemist, doing research in chemical documentation and having no connection with quantum chemistry) published results identical to those of Sachs. None of the papers [14, 18, 19] seems to have had any impact on theoretical chemistry before the appearance of the article [20].

In 1971 a fortunate encounter occurred. The present author, then a graduate student of chemistry at the Faculty of Science in Belgrade (who knew some HMO theory), met Dragoš Cvetković, then an Assistant in the Mathematics Department of the Faculty of Electrical Engineering in Belgrade (who was just finishing his Ph. D. thesis on graph spectral theory, eventually published as [21]). As a result of this

encounter the paper [22] was produced, dealing with chemical applications of graph spectral theory, but only sporadically mentioning the Sachs theorem.

From Cvetković the present author learned about a theorem, earlier discovered by Sachs. He immediately recognised that this implies a fundamental, long sought, result in quantum chemistry.

In the same year the present author moved to Zagreb, to continue his studies at the “Ruder Bošković” Institute. There he joined a group of young theoretical chemists, lead by (also young) Nenad Trinajstić. He told them what he learned from Cvetković. They too realised both the importance of this result and the fact that it was completely unknown to the chemical community. Eventually, a paper was written, using language and formalism understandable to theoretical chemists, and illustrating the theorem by pertinently chosen examples. *Theoretica Chimica Acta*, a prestigious journal available worldwide in science libraries, agreed to publish the paper [20]. Needless to say that in [20] due credit is given to Sachs, whose authorship of the theorem is clearly indicated.

While writing the paper [20] it became necessary to give the theorem a name. The present author is the one who conceived and first used the name “*Sachs theorem*”. The name “*Sachs graph*” (cf. the Appendix) emerged in a discussion between Tomislav Živković and the present author. After being launched in the paper [20] the names “Sachs theorem” and “Sachs graph” were accepted by the entire chemical community and will, probably, remain in theoretical chemistry for ever.

In summary, we may say that the Sachs theorem was discovered twice. First by Sachs himself in 1964 (or 1963) [14, 15] and then by the present author in 1971/72. The second “discovery” entailed just finding the respective result in the literature and then communicating it to the “rest of the chemical world”. However, as explained in the following subsection, this second discovery is responsible for the meteoric chemical success of the Sachs theorem.

One may wonder how the history of this part of theoretical chemistry would look had the present author not met Dragoš Cvetković in Spring 1971 and had he not moved to Zagreb in the Summer of that year.

After

Once the theoretical-chemical community became aware of the powerful coefficient theorem, a large number of scientists started to apply it in their researches. Many of them deemed it to be purposeful to repeat and additionally exemplify the use of the Sachs theorem [23–40]. In addition to these reviews, there are numerous books in which, among other things, the Sachs theorem is discussed [41–51]. Some of these works are in Bulgarian [34, 35], Chinese [42], Hungarian [26], Japanese [28], Rumanian [50], Russian [36, 48] and Serbo-Croatian [38].

As already mentioned, the scientific papers dealing with chemical applications of the Sachs theorem are too numerous to allow the creation of a complete bibliography. It should, nevertheless, be mentioned that the vast majority of these papers appeared in the 1970s and 1980s, and their number significantly decreased in the 1990s and later.

CHEMICAL APPLICATIONS OF THE SACHS THEOREM

The Sachs theorem, Eq. (6) in the Appendix, was originally stated for simple graphs (without weighted edges and self-loops) and is, as such, applicable only to the molecular graphs of conjugated hydrocarbons. An obvious task was then to extend it to heteroconjugated species [27, 52–55]. Another easy-to-solve problem was the formulation of the analogy of the Sachs theorem for the permanent polynomial [56] (see also [57]).

Any Sachs graph S , appearing in the Sachs formula, Eqs. (6) and (7), may be viewed as a structural feature, contained in the respective graph G . If G is a molecular graph, then S may be interpreted as a structural detail of the respective molecule. Some of these structural details have obvious chemical meanings and were considered in chemistry long before the discovery of the Sachs theorem. In particular,

if $n(S) = 2$, $p(S) = 1$, $c(S) = 0$, then S represents a chemical bond;

if $n(S) = k$, $p(S) = 1$, $c(S) = 1$, then S represents a k -membered ring;

if $n(S) = n$, $p(S) = n/2$, $c(S) = 0$, then S represents a Kekulé structure.

The definitions of the quantities $n(S)$, $p(S)$ and $c(S)$ are found in the Appendix.

Other types of Sachs graphs have less obvious chemical interpretations. In order to overcome this “difficulty” efforts have been made to express the coefficients of the characteristic polynomial in terms of structural details to which chemists are more accustomed. Some limited success along these lines was achieved for the first few coefficients [33, 49, 58, 59].

Much attention was given to the fact that in the expression for the last coefficient a_n of the characteristic polynomial, and for the closely related determinant of the adjacency matrix, there occur Sachs graphs representing Kekulé structures [20, 60–64]. For chemical applications it is important to know when $\det A(G)$ is zero, because then the graph G has zero eigenvalues and the respective conjugated system possesses non-bonding molecular orbitals. This, in turn, implies lack of stability. The use of the Sachs theorem for establishing the existence of zero eigenvalues was elaborated in [65, 66]. Some closely related works are also [67–69].

Combining the Sachs formula (7) with the Coulson integral formula, Eq. (3), one gains insight about the structure-dependency of total π -electron energy [38, 70–75]. By means of such a Coulson–Sachs expression it was, for the first time, possible to approach the Hückel $(4m + 2)$ -rule for polycyclic conjugated hydrocarbons [70, 71, 73].

An analogous combination of the Sachs formula with Eq. (4) enabled conclusions to be drawn about the structural factors influencing the π -electron charge distribution in conjugated hydrocarbons [76].

More-sophisticated applications of the Sachs theorem are discussed in the subsequent section.

CHEMICAL THEORIES BASED ON THE SACHS THEOREM

A long time ago chemists observed that a cyclic arrangement of π -electrons may have dramatic effects on the chemical properties of the respective conjugated molecule, and may sometimes bring about a significant thermodynamic stabilization (referred

to as “aromaticity”) or destabilization (referred to as “antiaromaticity”). In polycyclic conjugated molecules several such cyclic-conjugation effects are simultaneously present, interfering with each other in a complicated manner that is difficult to understand. Before the appearance of the Sachs theorem there was no satisfactory approach to rationalize the π -electron effects of cycles in polycyclic conjugated molecules.

The fortunate fact is that (some) Sachs graphs consist of cycles. Via the Sachs graphs we may infer about the effect of these cycles on total π -electron energy, charge distribution etc. This makes it possible to design a formalism capable of quantitatively distinguishing the effects of individual cycles as well as the collective effects of several or all cycles. Especially important are the energy effects.

The combination of the Coulson integral formula (3) for total π -electron energy E and of the Sachs formula (7) may be written as

$$E = f(\mathcal{S}(G))$$

where f is a complicated, but known and analytically well-defined, function. Each element of the set $\mathcal{S}(G)$, i. e., every structural detail represented by a Sachs graph, has a precisely defined contribution to E .

Let $\mathcal{S}_{ac}(G)$ be the subset of $\mathcal{S}(G)$ containing only those elements of $\mathcal{S}(G)$ for which $c(S) = 0$, i. e., only acyclic Sachs graphs. Then $f(\mathcal{S}_{ac}(G))$ can be viewed as the part of the total π -electron energy of G , caused by effects other than cyclic conjugation. Consequently, $f(\mathcal{S}(G)) - f(\mathcal{S}_{ac}(G))$ may be thought of as the energy effect caused by the simultaneous action of cycles in a polycyclic conjugated system. This quantity, independently invented by Aihara [77] and the Zagreb group [78, 79], is known by the name “topological resonance energy”, TRE . A conjugated system is classified as “aromatic” if its TRE value is positive. If $TRE < 0$ or $TRE \approx 0$ then one speaks of “antiaromatic” and “nonaromatic” species, respectively. TRE has been successfully employed in the study of a variety of conjugated compounds. Scores of papers have been published on TRE and its applications; here we quote just two typical examples [80, 81].

Let Z be a cycle of G and let $\mathcal{S}_Z(G)$ be the set of all those elements of $\mathcal{S}(G)$ which do not contain Z . Then a reasoning analogous to what was outlined above leads to

the conclusion that $f(\mathcal{S}(G)) - f(\mathcal{S}_Z(G))$ is the individual energy effect of the cycle Z [82] (see also [83]). This approach to cyclic conjugation also resulted in numerous publications, of which we quote only three recent works [84–86].

In Eq. (7) the summation on the right-hand side goes over the elements of the set $\mathcal{S}(G)$. If, however, the summation is limited only to the elements of the subset $\mathcal{S}_{ac}(G)$, then a new polynomial is obtained – the matching polynomial $\alpha(G)$:

$$\begin{aligned}\alpha(G) = \alpha(G, \lambda) &= \sum_{S \in \mathcal{S}_{ac}(G)} (-1)^{p(S)} 2^{c(S)} \lambda^{n-n(S)} \\ &= \sum_{k \geq 0} (-1)^k m(G, k) \lambda^{n-2k}\end{aligned}$$

where $m(G, k)$ is the number of k -matchings (= selections of k independent edges) of G . Recall that in the case of acyclic graphs, $\mathcal{S}_{ac}(G) = \mathcal{S}(G)$ and, consequently, $\alpha(G) = \phi(G)$.

The matching polynomial has remarkable algebraic properties; e. g. all its zeros are real-valued numbers [87]. This observation was independently conceived in quantum chemistry (via the Sachs theorem, as described above) [79], as well as in statistical physics [88] and mathematics [89] (without reference to the Sachs theorem, but see [90]). For details of the well-developed theory of the matching polynomial and for further references see [91, Chapter 4].

A far-reaching generalisation of the above-outlined approaches to the theory of cyclic conjugation was elaborated in [92, 93]. The crucial mathematical entity introduced in [92] is the μ -polynomial.

Let Z_1, Z_2, \dots, Z_t be the cycles contained in the graph G . With each cycle Z_i we associate a weight w_i , $i = 1, 2, \dots, t$. To a Sachs graph $S \in \mathcal{S}(G)$ we assign the weight $w(S)$, equal to the product of the weights of the cycles contained in S . If S is acyclic, then $w(S) = 1$. The μ -polynomial is defined as [92]

$$\mu(G) = \mu(\vec{w}, G) = \mu(G, \vec{w}, \lambda) = \sum_{S \in \mathcal{S}(G)} (-1)^{p(S)} 2^{c(S)} \lambda^{n-n(S)} w(S) \quad (5)$$

where \vec{w} is an abbreviation for (w_1, w_2, \dots, w_t) . If the graph G is acyclic, then, by definition, $\mu(G) = \phi(G)$.

Eq. (5) should be compared with Eq. (7). For the properties of the μ -polynomial see [39, 51, 91, 92, 94].

The choices $\vec{w} = (1, 1, \dots, 1)$ and $\vec{w} = (0, 0, \dots, 0)$ reduce the μ -polynomial to $\phi(G)$ and $\alpha(G)$. Another interesting choice of the cycle-weights is $w_j = 1$ for some j and $w_i = 0$ for all $i \neq j$. The resulting polynomial is denoted by $\beta(G, Z_j, \lambda)$. It plays a central role in Aihara's method for computing the energy effect of an individual cycle [83].

Numerous examples corroborate the conjecture [95] that for all graphs G that contain cycles, and for all cycles Z_j of G , all zeros of the β -polynomial are real-valued. To date, a complete proof of this assertion is not known. Details of the research done in connection with this conjecture are outlined in a recent article [96].

If in the integral formulae of the type (3), (4) the characteristic polynomial is replaced by the μ -polynomial, then it is possible to express and calculate the effect of any cycle or of any collection of cycles on any HMO π -electron property [92, 93]. Most studies along these lines were done on the total π -electron energy (as outlined above), but the HOMO-LUMO separation [97] and the π -electron charge-distribution [98] have also been analysed.

APPENDIX: GRAPH-THEORETICAL NOTATION AND TERMINOLOGY

The graphs considered are simple (i. e., without multiple and directed edges and self-loops). Let G be such a graph, possessing n vertices, arbitrarily labelled as v_1, v_2, \dots, v_n . Its adjacency matrix $A(G) = ||A_{ij}||$ is determined via

$$A_{ij} = \begin{cases} 1 & \text{if the vertices } v_i \text{ and } v_j \text{ are adjacent} \\ 0 & \text{otherwise} \end{cases}.$$

The characteristic polynomial of G is defined as

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

where I stands for the unit matrix of order n .

The importance of the characteristic polynomial lies in the fact that its zeros, denoted by $\lambda_1, \lambda_2, \dots, \lambda_n$, are just the eigenvalues of $A(G)$; these are said to be the eigenvalues of the graph G , forming the spectrum of G .

The coefficients a_k , $k = 0, 1, 2, \dots, n$, of the polynomial $\phi(G)$ can be computed from the structure of the graph G by means of a formula, referred to as the Sachs theorem.

A Sachs graph S is a graph in which all components are isolated edges and/or triangles and/or quadrangles and/or pentagons and/or hexagons \dots . In other words, a Sachs graph is a graph in which all components are isolated edges and/or polygons. Under “isolated edge” is meant a 2-vertex graph with one edge. Let $\mathcal{S}_k(G)$ be the set of all k -vertex Sachs graphs, that are as subgraphs contained in G . Then the Sachs theorem reads:

$$a_k = \sum_{S \in \mathcal{S}_k(G)} (-1)^{p(S)} 2^{c(S)} \quad (6)$$

where $p(S)$ is the number of components of the Sachs graph S , and $c(S)$ the number of its cyclic components (polygons). If $\mathcal{S}_k(G) = \emptyset$, then $a_k = 0$.

Let

$$\mathcal{S}(G) = \bigcup_{k \geq 0} \mathcal{S}_k(G) .$$

Then the Sachs theorem can also be written as

$$\phi(G, \lambda) = \sum_{S \in \mathcal{S}(G)} (-1)^{p(S)} 2^{c(S)} \lambda^{n-n(S)} \quad (7)$$

where $n(S)$ is the number of vertices of S .

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