Graph Theory in Chemistry

II. Graph-Theoretical Description of Heteroconjugated Molecules

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The Sachs' formula which relates the structure of a (vertex- and edge)-weighted graph and its characteristic polynomial is given. Weighted graphs are used to represent conjugated molecules containing the variety of heteroatoms and heterobonds. Vertices and edges in such molecular graphs have different weights following the deviation of the corresponding (Hückel) Coulomb and resonance integrals from the standard (benzene) values.

Until very recently [1–7] graph theory, in the case of conjugated systems, has been applied (in the framework of HMO theory) to hydrocarbons only [8]. In HMO theory graphs may be interpreted in two different ways: a) as the structural graph of the conjugated system considered [9–11] or b) as a graph in which vertices correspond to the basis functions used for the construction of the HMO's (basis graph) [12]. The concept of basis graphs may be extended to quantum chemical methods other than HMO theory. However, under the approximations of the simple HMO theory, the basis graph is the same as the structural graph. A molecular (carbon)-graph (or C-graph) G_N related to a conjugated molecule with N carbon atoms corresponds to its π-network. After labelling the vertices of G_N the adjacency matrix, $\boldsymbol{A}$, of G_N may be constructed following the definition [13]:

$$A_{rs} = \begin{cases} 1 & \text{if vertices } r \text{ and } s \text{ are connected,} \\ 0 & \text{otherwise.} \end{cases} \qquad (1)$$

The topological matrix of a conjugated molecule appearing in Hückel theory has been shown to be equivalent to the adjacency matrix of a corresponding molecular graph [9, 14]. Thus, using an appropriate scaling, the Hückel secular determinant may be expressed as follows:

$$P(G_N; x) = \det | x\boldsymbol{I} - \boldsymbol{A} | = \sum_{n=0}^{N} a_n x^{N-n} \qquad (2)$$

and the Hückel problem is completely reduced to the adjacency matrix eigenvalue problem. According to the scale used the eigenvalues x_i $(i = 1, 2, \ldots, N)$ are given by,

$$x_i = (E_i - \alpha_C)/\beta_{CC} \qquad (3)$$

where E_i $(i = 1, 2, \ldots, N)$ is the Hückel molecular orbital energy, α_C the Coulomb integral of a carbon atom, and β_{CC} is the standard carbon-carbon bond resonance integral [15].

The coefficients a_n of the characteristic polynomial $P(G_N; x)$ may be found without going through the procedure of solving determinant but solely from the topology of the molecular graph. Such a procedure has been suggested first by Coulson [16] and has been put in the concise mathematical form by several mathematicians [17], but a form given by Sachs [18] is very convenient for our discussion. The Sachs' formula which covers molecular graphs corresponding to conjugated hydrocarbons, is given by,

$$a_n = \sum_{s \in S_n} (-)^{c(s)} 2^{r(s)}; \quad 0 \leqq n \leqq N. \qquad (4)$$

Here s is a Sachs graph [19] [that is such a graph which has no other components [8] but complete graphs of valency one and cycles (rings)], S_n is the set of all Sachs graphs with n vertices, $c(s)$ and $r(s)$ are, respectively, the total number of components and the number of ring components in s. Summation is over all Sachs graphs (with n vertices). N is the number of vertices in the graph G_N. The Sachs' formula as defined above may be very conveniently used for the evaluation of individual polynomial coefficients of the interest (e.g. a_N) and the structure-reactivity relationships are developed on this basis [19–22].

Recently, the Sachs' formula was extended to vertex-weighted ** graphs, that is to say to those graphs which may be used to represent some heteroconjugated molecules [1, 4, 5]. A vertex-weighted graph is a graph which has one (or more) of its vertices distinguished from others. These vertices of a different "type" are weigthed and the weight is related

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** Originally [1, 4, 5] these graphs were named "rooted" graphs, a name which is not quite appropriately used there, because this type of graphs belong to trees [23, 24].

to the value of α_X. α_X is the Coulomb integral of a heteroatom X and it is defined as follows:

$$\alpha_X = \alpha_C + a\,\beta_{CC}\,. \tag{5}$$

A non-zero value of a describes the difference between the heteroatom (weighted vertex) and carbon atom (ordinary vertex). This is reflected on diagonal elements of the "adjacency" matrix. In order to avoid any confusion we call [12] this type of "adjacency" matrix the weight matrix, $\boldsymbol{W}$. The same term will be used also in the case of vertex- and edge-weighted graphs.

In the case where only ordinary vertices are present, the diagonal elements of adjacency matrix, $\boldsymbol{A}$, of a graph G_N are all zero [see Eq. (1)], that is $\mathrm{Tr}\,\boldsymbol{A}(G_N) = 0$. However, in the case of vertex-weighted graphs $G_{N,vw}$, $\mathrm{Tr}\,\boldsymbol{W}(G_{N,vw}) = \sum_i a_i$, where the sum is over all weighted vertices in $G_{N,vw}$. The characteristic polynomial $P(G_{N,vw}; x)$ of a vertex-weighted graph $G_{N,vw}$ (for the case of vertices being all of the same weight, a) is given by [5],

$$P(G_{N,vw}; x) = \sum_{n=0}^{N} \sum_{s \in S_n} (-)^{c(s)}\, 2^{r(s)}\, (x-a)^{t(G_N - s)} \cdot x^{N-n-t(G_N-s)} \tag{6}$$

where the symbols already mentioned in Eq. (4) have their previous meaning. Graph $(G_N - s)$ is obtained by deletion of (Sachs') graph s from graph G_N and $t(G_N - s)$ is the number of weighted vertices in (particular) vertex-weighted graph $(G_N - s)$. The use of formula (6) has been extensively described in our earlier work [4]. However, it is limited to a class of hetero-conjugated molecules with the same type of heteroatom and the differences in the resonance integrals β_{CC} and β_{CX} are not considered.

Now, we have extended the Sachs' formula to cover the vertex- and edge-weighted graphs $G_{N,vew}$, that is to graphs which represent heteroconjugated molecules containing bonds with the values of resonance integrals different from β_{CC}, and which contain several different heteroatoms. These graphs contain one (or more) edges which differ in some way from others. The resonance integral β_{XY} of an edge X-Y connecting two differently weighted verticles X and Y may be written as:

$$\beta_{XY} = b_{XY}\,\beta_{CC} \tag{7}$$

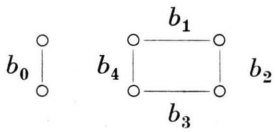
where $b_{XY}(\neq 1)$ describes the difference between the standard (benzene) carbon-carbon resonance integral, β_{CC}, and the resonance integral of X-Y bond, β_{XY}. This means that values other than 1 (denoted as b) have been introduced to the off-diagonal elements of the weight matrix.

The characteristic polynomial $P(G_{N,vew}; x)$ of a vertex- and edge-weighted graph $G_{N,vew}$ is given by,

$$P(G_{N,vew}; x) = \sum_{n=0}^{N} \sum_{s \in S_n} (-)^{c(s)}\, 2^{r(s)} \cdot \prod_{(s)} b_i \prod_{(G-s)} (x - a_j)\; x^{N-n-t(G_N-s)} \tag{8}$$

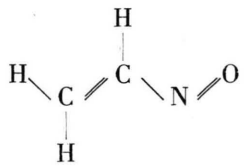
where the symbols already mentioned in Eqs. (4) and (6) have their previous meaning. Here we wish to point out that Eq. (8) is similiar to Coates' topological formula [25] which is used in circuit theory. The produkt $\prod_{(s)} b_i$, which corresponds to (vertex- and edge-) weighted Sachs graph s, is obtained by multiplication of b's in the following way. For a Γ component of a Sachs graph s, b is squared, and for a ring component of s, b's are multiplied "around" the ring. As an example consider the product $\prod_{(s)} b_i$ for hte following (vertex- and edge-) weighted Sachs graph s

$$\prod_{(s)} b_i = b_0^2 (b_1\, b_2\, b_3\, b_4)\,.$$



The product $\prod_{(G-s)} (x - a_j)$ may be obtained as follows. The factor $(x - a_j)$ must be taken into account as many times as there are (weighted) vertices with the weight a_j in the graph $(G_N - s)$, and it needs to be done for every "type" of heteroatom present in the graph $(G_N - s)$. In the case that there is only one type of (weighted) vertex (with the weight a) present in $G_{N,vew}$, the product $\prod_{(G_N-s)} (x - a_j)$ reduces to $(x-a)^{t(G_N-s)}$, as in Equation (6).

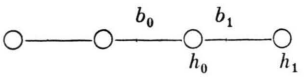
As an example, the characteristic polynomial of I is evaluated below.



(*I*)

In the corresponding molecular graph, $G_{N,vew}(I)$, there are three different "types" of vertices and

Table 1. The characteristic polynomial of a molecular graph representing *I*.

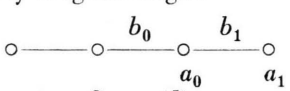


$G_{N,vew}(I)$

n	S_n	$P(S_n;\ x)$
0	∅	$x^2(x-h_0)\,(x-h_1)=x^4-x^3(h_0+h_1)+x^2\,h_0\,h_1$
2	$t(s)=0$, $t(s)=1$, $t(s)=2$	$(-)^1 2^0(x-h_0)\,(x-h_1)\,x^0+\ (-)^1 2^0\,b_0^2(x-h_1)\,x^1+$ $+\,(-)^1 2^0\,b_1^2\,x^2=-x^2(1+b_0^2+b_1^2)+x(h_0+h_1+b_0^2\,h_1)-h_0\,h_1$
4	$t(s)=2$	$(-)^2 0^0\,b_1^2\,x^0=b_1^2$

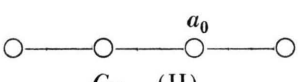
$$P(G_{vew}(I)\,;\,x)=\sum_{\pi}P(S_n;\,x)=x^4-x^3(h_0+h_1)-\ x^2(1+b_0^2+b_1^2-h_0\,h_1)+x(h_0+h_1+b_0^2\,h_1)+b_1^2-h_0\,h_1$$

three differently weighted edges.



$G_{N,vew}(I)$

Nitrogen and oxygen atoms are weighted differently (a_0 and a_1) than carbon atoms ($a=0$). Similarly, bonds C – N and N – O are indicated with weight b_0 and b_1, respectively. Using β_{CC} as the unity, the C – C bond, of course, has a weight of unity [8]. The evaluation of $P(G_{N,vew}(I)\,;x)$ is demonstrated in Table 1. The characteristic polynomial of $G_{N,vew}(I)$ for $a_1=0$ and $b_0=b_1=1$ reduces to the polynomial which corresponds to a system $G_{N,vw}(II)$:



$G_{N,vw}(II)$

with a single weighted vertex (a_0):

$$P[G_{N,vw}(II)\,;x]=x^4-a_0\,x^3-3\,x^2+a_0\,x+1$$

and for $a_0=0$ reduces, of course, to the polynomial which corresponds to butadiene system:

$$P(G_N;\,x)=x^4-3\,x^2+1\,.$$

The whole procedure exposed here may be rather complicated when applied to larger "weighted" systems. However, a real virtue of the method is in providing a *single* coefficient which may be only one needed. In particular, the value of a_N is very often required, because the structure-reactivity relationships show that this particular coefficient may be of value in predicting the stability of investigated species [8, 19].

The study of molecules by use of quantum chemical methods other than HMO theory, as in the studies on the energy spectrum of substituted polyenes [26, 27], lead also to the use of (vertex- and edge-) weighted *(complete)* graphs [12] (but in that case they are interpreted as basis graphs). The formula for the characteristic polynomial of uniformly weighted complete graph (all vertices and all edges have the same weight) is derived [12], in the manner different than the present one, as in the formula for the case of regularly and irregularly weighted complete graphs [12] (i.e. vertex- and edge-weighted complete graphs). The latter graphs can be interpreted as a joint [28] of (some number of) uniformly weighted subgraphs. The formula for the characteristic polynomial is derived only for the case when the weights of all edges, connecting any pair of such subgraphs, have the same value (depending on the pair under consideration). Although, all these formulas [12] can be understood as the special case of formula (8), they are more convenient in treatment of the removal of degeneracy under substitution, under inclusion of enlarged basis set, under inclusion of those molecular integrals which are usually neglected in the simple MO theories, and so on.

The special case of formula (8) is arising [6, 7] when the off-diagonal elements can take values: +1, −1 or 0, which is the case in the so called Möbius or anti-Hückel systems [6, 7, 29, 30]. The similar graphs appear also in our attempts to estimate the energy gap of hydrocarbon polymers [31].

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