Graph Theory in Chemistry — Generalisation of Sachs' Formula

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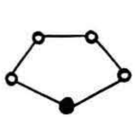
The Sachs' formula is generalised so that it can be applied to those (rooted) graphs which may be used to represent conjugated systems containing a restricted class of hetero-atoms.

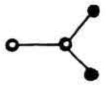
By means of a formula due to Sachs[1], the structure of a non-rooted graph G (for example, a graph representing the topology of the carbon atoms in a conjugated hydrocarbon) may be related to the characteristic polynomial $[P(G;x)]$ of the vertex adjacent matrix of G[2]. Sachs' formula can be expressed as follows:

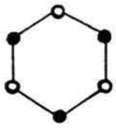
$$P(G;x)=\sum_{n=0}^{N}\ \sum_{s\,\varepsilon\,S_n}(-)^{c(s)}\,2^{r(s)}\,x^{N-n} \qquad (1)$$

where s is a Sachs graph (as defined in[3]), S_n is the set of all Sachs graphs with n vertices, $c(s)$ is the number of components[3] and $r(s)$ is the number of cycles[3], in S. N is the number of vertices in G. This formula may be applied to the graphs associated with conjugated hydrocarbons in a straightforward way, as described by Graovac et al.[3]. There have been several other (ostensibly different) approaches to this problem[4–9], but these have all been shown to be equivalent[10].

We have now extended Sachs' formula in order to make it applicable to rooted graphs[11] – for example, the graphs which can be used to represent heteroconjugated molecules. A rooted graph, G, is a graph which contains one or more vertices which are considered to differ, in some way, from the others; these vertices of a different "type" (called the roots or the rooted vertices) are denoted ●[12] in order to distinguish them from the other vertices (○)[13] present in G. To illustrate this, we give below some example of rooted graphs







which can be considered to represent the sigma-bond topology of the atoms comprising the conjugated systems of, for example, thiophene-like, 1,1-dichloroethylene-like, and *s*-triazine-like molecules.

The generalised Sachs formula which is appropriate for relating the structures of a rooted graph (with set of rooted vertices R) to its characteristic polynomial $(P(G;R;x))$ is *

$$P(G;R;x)=\sum_{n=0}^{N}\ \sum_{s\,\varepsilon\,S_n}(-)^{c(s)}\,2^{r(s)}\cdot(x-h)^{t(G-s)}\,x^{N-n-t(G-s)} \qquad (2)$$

where the symbols already mentioned in (1) have their previous meaning, $t(G)$ is the number of rooted vertices in the rooted graph G, and $t(s)$ is the number of roots in any particular (rooted) Sachs graph. (It is immediately evident that the set of all Sachs graphs (S_n) belonging to a given rooted graph may contain some Sachs graphs which are rooted as well as others which are non-rooted.) The significance of h is as follows; the diagonal elements of the adjacency matrix $\mathbf{A}(G)$[12,13] of a labelled, non-rooted graph G are all zero – i. e. $a_{rr}=0$, $r=1,2,\ldots,N$; in the case of a rooted graph, having root vertices labelled i, j, k, …, the corresponding diagonal elements of the adjacency matrix appropriate to such a graph take the value h,

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* Here, we simply quote Eq. (2) without proof. Readers interested in the mathematical details of its derivation are referred to our article in the forthcoming publication arising from the Second Czechoslovak Symposium on Graph Theory, Prague, June 1974.

rather than zero – i. e. $a_{ii} = a_{jj} = a_{kk} = \ldots = h$, with all a_{rr} $(r \neq i, j, k, \ldots)$ still $= 0$, (and, as in the case of non-rooted graphs[2,13], the off-diagonal elements a_{rs}, $r \neq s$, are 1 if vertices r and s are adjacent, and zero otherwise).

A non-zero value of h is thus seen to be a device by which information concerning this "difference" between the rooted and non-rooted vertices may be transmitted to the vertex adjacency matrix of the labelled, rooted graph in question. If h is zero, then, of course, Eq. (2) reduces to Equation (1). Graph theoretically, h may thus be thought of as some kind of "weighting" of the rooted vertices; an alternative graph-theoretical interpretation of this is being given elsewhere[14]. In that alternative approach, we have related the structure of a given rooted graph to the coefficients of the characteristic polynomial of its adjacency matrix deriving, one by one, the numerical value of *each individual coefficient* a_n (from the structural features of the set of all Sachs graphs on n vertices), for each value of n in turn. In order to do this it was necessary to introduce the concept of *self-loops* on the rooted vertices[14], and to extend the definition of a Sachs graph to include graphs comprising such self-loops (since the null-graph is not considered as a Sachs graph[1]). In the approach being detailed here, such a concept is not necessary; however, although the present formalism is easier to apply if one's aim is simply to relate graph structure to the global, overall form of the corresponding characteristic polynomial (via a summation of characteristic polynomials for each set of Sachs graphs), the alternative procedure[14] does have what is, from a combinatorial point of view, a very attractive feature – namely that, in a straightforward way, it does provide some insight into the relation between the structure of a given graph and the individual coefficients of its characteristic polynomial.

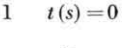
Returning again to the present formulation, we wish to emphasize that the empty graph has been treated as a Sachs graph with no vertices, unlike in Sachs' original definition[1] which makes no provision for Sachs graphs with fewer than two vertices (as was implied above); the contribution to the characteristic polynomial for the case $n = 0$ is, therefore,

$$(x - h)^{t(G)}\, x^{N - t(G)}\,. \tag{3}$$

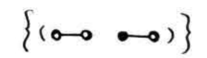
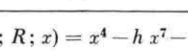
We illustrate the use of the generalised Sachs formula given in Eq. (2), by means of the two example given below.

The reader may care to observe that the Hamiltonian matrices arising when simple Hückel M. O. theory is applied to hetero-conjugated molecules are closely related to the adjacent matrices of the corresponding rooted graphs which reflect the sigma-bond topology of the atoms comprising such hetero-conjugated systems; and that when α_C (the standard carbon Coulomb integral[15]) is taken as the reference zero of energy, and all energies are measured in units of β_{CC}, the standard carbon-carbon resonance integral[15] (i. e. $x_i = (E_i - \alpha_C)/\beta_{CC}$), the two sets of matrices are isomorphic. Evidently, therefore, what we have interpreted graph theoretically as the weighting of a rooted vertex, h, can be identified

Table 1 a. Examples (1): The characteristic polynomial of the graph representing 2-aza butadiene-like systems:

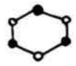


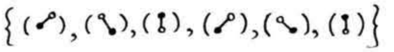
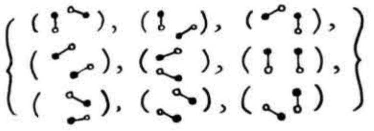
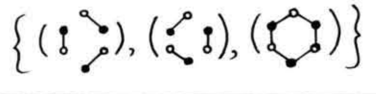
$N = 4;\ t(G) = 1\,.$

n	S_n	$P(S_n; R; x)$
0	ϕ	$x^3(x-h) = x^4 - x^3 h$
2	 $t(s)=1$ $t(s)=1$ $t(s)=0$	$2(-)^1 2^0 (x-h)^{0\,0} x^2 + (-)^1\ 2^0 (x-h)\, x = -3x^2 + x h$
4	 $t(s)=1$	$(-)^2 2^0 (x-h)^0 x^0 = 1$

Thus, $P(G; R; x) = \sum\limits_n P(S_n; R; x) = x^4 - h\, x^7 - 3x^2 + x h + 1\,.$

Table 1 b. Examples (2): The characteristic polynomial of the graph representing *s*-triazine-like systems:

 $N = 6;\ t(G) = 3$.

n	S_n	$P(S_n; R; x)$
0	ϕ	$x^3(x-h)^3 = x^6 - 3x^5h + 3x^4h^2 - {}^3h^3$
2		$6(-)^1 2^0 (x-h)^2 x^2 = -6x^4 + 12x^3h - 6x^2h^2$
4		$9(-)^2 2^0 (x-h)x = 9x^2 - 9xh$
6		$2(-)^3 2^0 (x-h)^0 x^0 + (-)^1 2^1 (x-h)^0 x^0 = \mathbf{-4}$

Thus,

$$P(G; R; x) = \sum_n P(S_n; R; x) = x^6 - 3hx^5 + (3h^2 - 6)x^4 + (-h^3 + 12h)x^3 + (9 - 6h^2)x^2 - 9hx - 4$$

immediately with the usual Hückel parameter[15] in the expression

$$\alpha_X = \alpha_C + h\,\beta_{CC}$$

in which h is alleged to reflect the difference (in units of β_{CC}) between the Coulomb integral (α_C) of a carbon atom in benzene and that (α_X) thought to be appropriate, in HMO theory, for a given type of heteroatom, X. Furthermore, the eigenvalues, $\{x_i\}$, of the adjacency matrix of a rooted graph [being the roots of its characteristic polynomial, $P(G; R; x)$, the expression for which we have given in Eq. (2)] are identical with the HMO energy levels $\{x_i\}$ (as defined above) of the hetero-conjugated system which the given rooted graph is considered to represent.

This 'rooted graphs' formalism thus provides a purely graph-theoretical interpretation of the application of simple HMO theory to a restricted class of heteroconjugated systems – in a way analogous to that in which it was shown previously that application of the simplest HMO method to conjugated hydrocarbons could be rationalised and systematised by means of the theory of non-rooted graphs[3, 13]. We refer, above, to a "restricted class' of heteroconjugated molecules for it will be noted that, in the theory as we have outlined it, there is no provision for making the off-diagonal elements of adjacency matrices anything other than 0 or 1; accordingly, in the theory of rooted graphs as presented in this note, we do not, therefore, have the flexibility to make any changes in the off-diagonal elements of such matrices – changes which could possibly be regarded as being equivalent, in the context of HMO theory, to variation of resonance integrals from the standard (benzene) value. A graph theoretical interpretation of this aspect of simple HMO theory is, therefore, not attempted here.

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