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INVERSE ADJACENCY MATRIX AND SPECTRAL PROPERTIES OF CHEMICAL GRAPHS

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Abstract

The adjacency matrix inversion is shown to be useful for characterization of chemical graphs with zero eigenvalues, as well as for determination of the corresponding ("zero") eigenvectors. Asymptotic zero eigenvalues and eigenvectors of the chemical graphs with the infinite simple chain are used, and the new notions, such as phase and effective length of the end-subgraphs, are introduced. The chemical sense of these notions and their possible applications in the polymethine dye theory are presented in this paper. Three theorems concerning end-subgraph phase are represented.

Notations

$\underline{A}$ = adjacency matrix (AM) of an arbitrary graph

$(\underline{A}^{-1})_p$ = p-th column of an inverse AM (IAM)

a_k = coefficient of a matrix characteristic equation

$\underline{B}$, $\underline{D}$, $\underline{S}$, $\underline{T}$ = AMs of the end-subgraphs of the graph with the infinite chain

C_k = zero eigenvector corresponding to the k-th eigenvalue

$\underline{F}$ = rectangular matrix of a rank 1

$\underline{I}$ and $\underline{O}$ = identity and null matrix respectively

L = end-subgraph effective length

m = order of the matrix $\underline{A}$

N, N_B, N_L = normalization factors of the eigenvector

n = the number of vertices in the infinite chain

$\underline{U}$ = AM of an odd alternant graph

$\underline{u}$ = adjacency vector of a vertex

$\underline{V}_F$ = IAM non-diagonal blocks

$\underline{V}_S$, $\underline{V}_T$ = IAM diagonal blocks

$\underline{X}$ = asymptotic zero eigenvector

Z = infinite simple chain constant

λ_k = the k-th eigenvalue of an end-subgraph AM, approximating a zero one

Φ = end-subgraph phase

Adjacency matrix (AM) of a graph giving a comprehensive information of it is highly profound in chemical aspect [1]. An inverse AM (IAM) however has not yet been paid sufficient attention neither in graph theory nor in its chemical applications. In the present paper we show that IAM proves to be quite effective in the investigation of some graph spectral properties with physico-chemical contents.

Let a degree of a graph with AM $\underline{A}$ be determined in usual way [1], then $\underline{A}^k$ is the AM k-th degree. The IAM $\underline{A}^{-1}$ also corresponds to a graph, generally speaking, to a colored (chemical) one: with loops and multiple edges.

As any matrix satisfies its characteristic equation:

$$\sum_{k=0}^{m} a_k \cdot \underline{A}^k = \underline{0}$$

an inverse matrix can be represented through $\underline{A}$ degrees:

$$\underline{A}^{-1} = \left| A \right|^{-1} \cdot \sum_{k=1}^{m} a_k \cdot \underline{A}^{k-1}$$

where m is the order of the matrix $\underline{A}$, a_k - the integer coefficients (if $\underline{A}$ is integer), both positive and negative, a_0 being equal to $\left| A \right|$.

IAM does not exist if AM is a singular one. It is just in this case that the AM has zero eigenvalues. Evidently, IAM existence can be an effective criterion for the characterization of graphs with zero eigenvalues, i.e. for solving Collatz-Sinogowitz problem [2].

Let us first consider a bipartite graph with a non-singular AM $\underline{A}$. By adding a vertex, arbitrarily bound to the vertices of the same sort, an odd bipartite graph AM $\underline{U}$ is received:

$$\underline{U} = \begin{Vmatrix} \underline{A} & \underline{u} \\ \underline{u}^+ & 0 \end{Vmatrix}$$

where $\underline{u}$ is the adjacency vector of a new vertex. This graph is known to have a zero eigenvalue:

$$\left| U \right| = \underline{u}^+ \cdot \underline{A}^{-1} \cdot \underline{u} = 0$$

A vector $[\underline{A}^{-1} \cdot \underline{u}, -1]$ can be proved to be the eigenvector of the matrix $\underline{U}$ that corresponds to zero eigenvalue. It will be called a zero eigenvector further. Thus, IAM $\underline{A}^{-1}$ is the

generator of zero eigenvectors of all the possible odd bipartite graphs derived from a given one, as it is shown above. Zero eigenvalues being interpreted as non-bonding levels of chemical compounds, their computation represents a great interest in chemical aspect [1]. The computational procedure is not a tedious one, moreover, it can be regarded as an absorbing exercise due to simple technique proposed by Longuet-Higgins [3]. Our approach to the finding of zero eigenvector is intended for mass computer calculations.

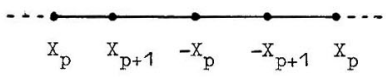
Zero eigenvectors can be normalized by factor

$$N = (\underline{u}^{+} \cdot \underline{A}^{-2} \cdot \underline{u} + 1)^{-1/2}$$

If the additional vertex is connected with the single p-th vertex of the initial graph, the normalized zero vector is proportional to the p-th column $(\underline{A}^{-1})_p$ of the symmetrical IAM $\underline{A}^{-1}$ and can be represented as

$$[(\underline{A}^{-1})_p, -1] \left\{ (\underline{A}^{-1})_p^{+} \cdot (\underline{A}^{-1})_p + 1 \right\}^{-1/2}$$

IAM can find an interesting application in studying the graphs with an infinite simple chain. These have asymptotic zero eigenvalues. Zero eigenvectors are not fully determined within the chain, but they are always quasiperiodic with a four-vertex period:



$$Z^2 = X_p^2 + X_{p+1}^2 = \text{const}$$

(X_p and X_{p+1} are the zero eigenvector elements on the adjacent

chain vertices; Z is the chain constant). However zero eigenvectors on the chain ends are completely determined by the topology of the end-subgraphs. We assume the latter to be characterized by the arbitrary AMs $\underline{B}$ and $\underline{D}$ (the loops and the multiple edges are possible, so the matrix elements of $\underline{B}$ and $\underline{D}$ are not integer in general case); these two end-subgraphs are bound to the chain by the p-th and q-th vertices respectively. To satisfy the secular equations, asymptotic zero eigenvectors are to be chosen as $[(\underline{B}^{-1})_p, -1, -(B^{-1})_{pp}, 1, \ldots]$ for $\underline{B}$ and similarly for $\underline{D}$. Further we shall deal with the matrices $\underline{B}$ and $\underline{B}^{-1}$ only, because the properties considered are of general character and they hold true for any end-subgraph.

It is reasonable to normalize the chain constant Z to 1 by means of factor

$$N_B = (X_p^2 + X_{p+1}^2)^{-1/2} = \left\{(B^{-1})_{pp}^2 + 1\right\}^{-1/2} = 1/Z$$

Then the whole zero eigenvector $\underline{X}$ for the graph with the infinite chain takes the form:

$$\underline{X} = [N_B(B^{-1})_p, -N_B, -N_B(B^{-1})_{pp}, N_B, \ldots, \pm N_D, \mp N_D(D^{-1})_{qq}, \mp N_D, \pm N_D(D^{-1})_q] \qquad (1)$$

Its elements for the end-subgraph can be simply calculated according to Longuet-Higgins [3].

The topology of an end-subgraph with AM $\underline{B}$ is characterized by two remarkable parameters:

$$\text{phase } \Phi_B = -\text{arc tg } (B^{-1})_{pp}^{-1} \qquad (2)$$

$$\text{effective length } L_B = 2N_B^2(B^{-1})_p^+ \cdot (B^{-1})_p + \sin^2\Phi_B \qquad (3)$$

Φ_B determines the zero eigenvector phase at the beginning of the chain (in the neighbourhood of the end-subgraph with AM $\underline{B}$). This phase remains unchanged if a couple of the chain vertices is added to the end-subgraph, but it gains $\pi/2$ if the only one vertex is added. L_B determines the length of the subgraph concerned as the length of the equivalent chain portion. Thus, L_B, although non-integer, is measured in the same units as the chain length, i.e. by the number of vertices, and it increases by 1 with adding one chain vertex more to the end-subgraph. Both of these characteristics are effective in polymethine dye theory [4]. The parameter Φ_B can be interpreted as an electron donation ability of the polymethine dye end-group. It can be calculated according to (2) and coincides numerically with the relative parameter Φ_0 described in [5]. In some previous papers [4, 6] Φ_0 was limited to positive values only. Here we consider it possible for Φ_B to take any values within the interval $[-\pi/2, +\pi/2]$. L_B can be treated as an end-group contribution into the first absorption maximum of the dye with a rather long polymethine chain. Formula (3) corresponds to the generally accepted definition of L_B [4], while the later paper [5] deals with its half value. Additive atomic contributions into the end-group effective length are represented by squared elements of the normalized zero eigenvector as $N_B^2(B_{pr}^{-1})(B_{rp}^{-1})$.

Effective length L is useful for the normalization of the zero vector. If the chain consists of n vertices and $n \rightarrow \infty$, then normalization factor N_L can be expressed as follows:

$$N_L = \sqrt{2}(n - 1 + L_B + L_D)^{-1/2}$$

This factor normalizes vector $\underline{X}$ with an accuracy to the terms

of n^{-1} order inclusively.

The eigenvalues λ_k neighbouring zero also can be represented through N_L, with an accuracy to the terms of n^{-2} order inclusively:

$$\lambda_k = N_L^2(\Phi_B + \Phi_D + k\pi); \; k = \pm 0, \pm 1, \ldots \tag{4}$$

The interval between these equidistant eigenvalues is equal to

$$\lambda_{k+1} - \lambda_k = \pi N_L^2$$

The inverse value

$$(\lambda_{k+1} - \lambda_k)^{-1} = (n - 1 + L_B + L_D)/(2\pi)$$

shows that the effective length of an end-subgraph is equal to the additional density of the infinite chain eigenvalues in zero neighbourhood caused by the presence of the very these end-subgraphs bound to the infinite chain. As (3) states, the effective length is always not negative - that is the property of any "length".

Parameters Φ and L can be found with the help of the well known Sachs' theorem in terms of the strict graph theory [7]. In hand treatment another technique is quite convenient, which is based on the recurrent computation of the secular polynomial minor coefficients [8]. Computer calculation of Φ and L usually involves direct computation of both determinant and minors of a dye end-group AM [9]. The method proposed in this paper proves to be effective for calculation and algorithmization as well, since it includes only standard procedures. The number of operations to be fulfilled does not exceed that for the previous methods.

As a rule, the analytical treatment is not applied in the graph theory. However the technique under consideration makes it possible to introduce such an approach, due to intermediate calculation of the zero eigenvectors. As the perturbation theory states [10], the derivatives of the matrix eigenvalues by its elements can be expressed in explicit form through coefficients C_{kr} of the normalized eigenvectors. If AM symmetry is taken into account we obtain:

$$\partial \lambda_k / \partial B_{rs} = (2 - \delta_{rs}) C_{kr} C_{ks},$$

where δ_{rs} is Kronecker symbol.

Since Φ_B in (2) depends only upon $\underline{B}$ elements, the differentiation of (4) by B_{rs} with considering the formula just represented above and proceeding to the limit $n \to \infty$ and $C_{kr} \to X_r$ give the following:

$$\partial \Phi_B / \partial B_{rs} = (2 - \delta_{rs}) N_B^2 (B^{-1})_{rp} (B^{-1})_{ps}$$

So, the Φ_B derivative on the infinitesimal changing of the rs-edge is expressed directly through the IAM $\underline{B}^{-1}$ elements.

The analogous L_B derivative can be obtained by the calculation of the next degree of the vector $(\underline{B}^{-1})_p$:

$$\partial L_B / \partial B_{rs} = 2(\delta_{rs} - 2) N_B^2 \left\{ (B^{-2})_{rp} (B^{-1})_{ps} + (B^{-2})_{sp} (B^{-1})_{pr} \right\} - \\ - 2 L_B (B^{-1})_{pp} \partial \Phi_B / \partial B_{rs}$$

Perturbational treatment enables us to estimate Φ and L dependence upon the end-subgraph topology, and thereby it gives us a chance to describe the change of polymethine dye redox properties and the shift of dye absorption maximum by small changing

the structure of dye end-groups.

It is possible to make some strict conclusions in regard to phase, like theorems proposed in [1] concerning the number of zeroes in the graph spectra.

Theorem 1°. If any simple four-vertex chain within the end-subgraph is substituted by an edge, then the phase does not change (fig. 1a). It comes from periodicity of zero eigenvector mentioned above. Therefore, cycloheptatrienyl and cyclopropenyl end-groups of polymethine dyes have the same electron donation ability (fig. 1b).

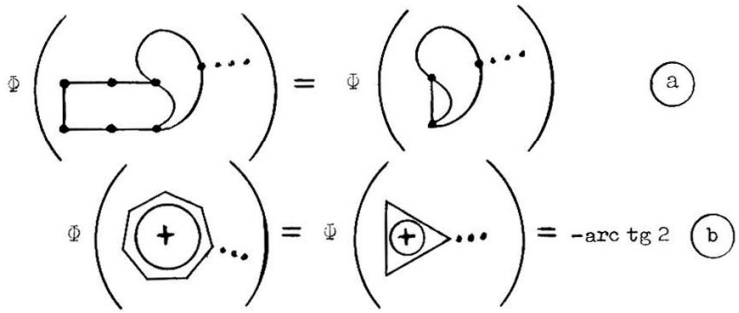


FIG. 1. ••• means an infinite chain.

Theorem 2°. Any subgraph with $\Phi = \pm \pi/2$ bound by a single vertex to another subgraph does not change the phase of the latter, i.e. even alternant substituents like vinyl, phenyl etc, do not influence the electron donation ability of any end-group (fig. 2).

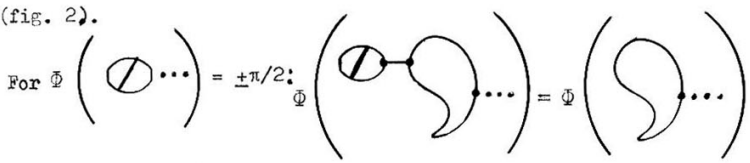


FIG. 2.

Proof. A subgraph with AM $\underline{T}$ and $\Phi_T = \pm \pi/2$ is bound to an arbitrary subgraph with AM $\underline{S}$ through the t-th vertex. Zero eigenvector turns to zero on this vertex, as it follows from (2). An infinite chain is connected to the s-th vertex of the subgraph with the AM $\underline{S}$. Let us represent the AM $\underline{B}$ of the obtained complex subgraph as a block one: $\begin{Vmatrix} \underline{S} & \underline{F} \\ \underline{F}^+ & \underline{T} \end{Vmatrix}$ where $\underline{F}$ is a rectangular matrix of rank 1, a single non-zero element reflecting a bond between two subgraphs considered. IAM $\underline{B}^{-1}$ can be represented analogously:

$$\underline{B}^{-1} = \begin{Vmatrix} \underline{V}_S & \underline{V}_F \\ \underline{V}_F^+ & \underline{V}_T \end{Vmatrix}$$

Then $\underline{V}_S \cdot S + \underline{V}_F \cdot F^+ = \underline{I}_S$ and $\underline{V}_S \cdot \underline{F} + \underline{V}_F \cdot \underline{T} = \underline{0}$ and, consequently, $\underline{V}_S - \underline{S}^{-1} = \underline{V}_S \cdot \underline{F} \cdot \underline{T}^{-1} \cdot \underline{F}^+ \cdot \underline{S}^{-1}$, where $\underline{I}_S$ is the identity matrix of the same order as matrix $\underline{S}$.

It can be shown that $\underline{F} \cdot \underline{T}^{-1} \cdot \underline{F}^+$ is a matrix of a rank not greater than 1; its single possible non-zero element being equal to $(T^{-1})_{tt}$. It turns to null-matrix on the condition: $\Phi_T = \pm \pi/2$, as $(T^{-1})_{tt} = 0$ in this case. Then $(V_S)_{SS} = (S^{-1})_{SS}$, which proves the proposed theorem. Moreover, $\underline{V}_S = \underline{S}^{-1}$, i.e. the connection of a subgraph with its $\Phi_T = \pm \pi/2$ does not change the zero eigenvector of the graph with the infinite chain within the initial subgraph.

If a subgraph AM has its exact zero eigenvalues, it is a singular one, that is why IAM does not exist and formula (2) fails in this case. To escape the uncertainty let us consider the nearest chain vertex belonging to the end-subgraph under consideration. If after that Φ takes the value $\pm \pi/2$, as it is shown in fig. 3a, then Φ of the initial subgraph is to be

assigned zero value.

If AH of the obtained subgraph is also a singular one (fig. 3b), it proves the degenerated zero eigenvectors for the graph with the infinite chain, thereby Φ is indefinite. The set of the degenerated zero eigenvectors always includes local ones that take zero values within the whole infinite chain (fig. 3c).

The case when $\Phi = \pm \pi/2$ or 0 suggests existence of the exact non-degenerated zero eigenvalue and the corresponding vector of the whole graph, regardless of the odd chain length. The zero eigenvector turns to zero on the end-subgraph vertex adjacent to the chain if $\Phi = \pm \pi/2$ and on the first chain vertex if $\Phi = 0$ (fig. 3d).

It is possible to determine the phase change of an aritrary subgraph on adding a subgraph with $\Phi = 0$ to it through the single vertex (that is the case of some substituents like methylene). Taking into account theorem 2° and phase changing by $\pi/2$ on adding one chain vertex, we come to conclusion that Φ of the subgraph obtained is equal to Φ of the initial one without the vertex - to which the added subgraph was bound (fig. 3e).

Returning to the finite graphs it is possible to use the parameter Φ for designing the graphs with the exact zeroes in their spectra.

Theorem 3°. If a graph consists of two subgraphs with a single common vertex, then its spectrum contains a zero eigenvalue i f and only i f that the sum of subgraph phases is equal to zero (fig. 4a). It can be illustrated by the compound obtained by conjugation of cyclopentadienyl and cyclo-

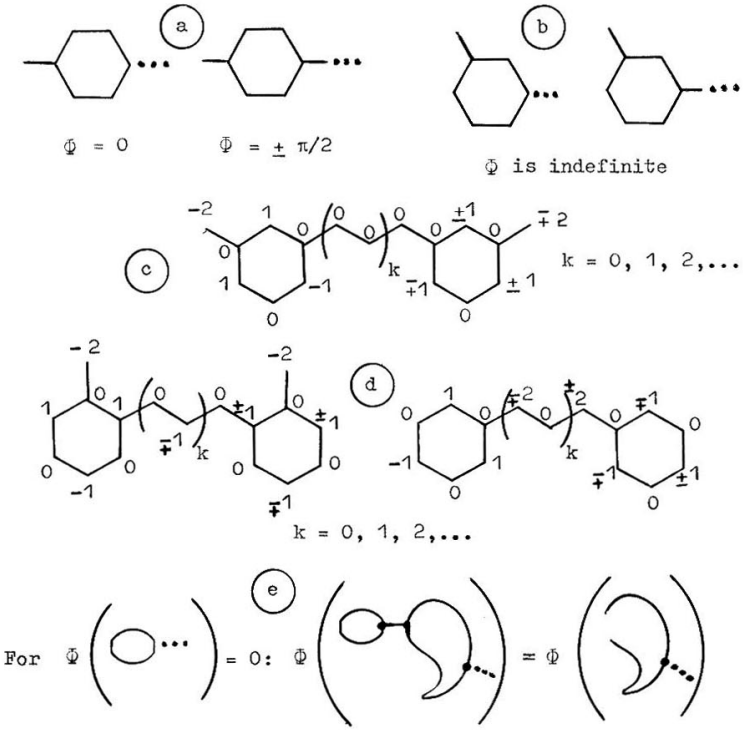

a
Φ = 0
Φ = ± π/2
b
Φ is indefinite
c
k = 0, 1, 2,...
d
k = 0, 1, 2,...
e
For Φ = 0: Φ = Φ

FIG. 3

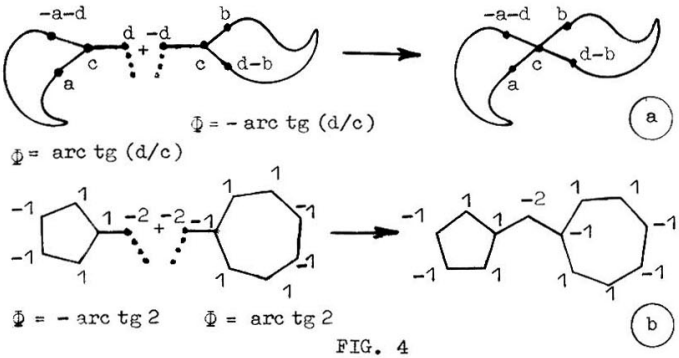

-a-d
d -d
b
c
c
d-b
a
Φ = - arc tg (d/c)
Φ = arc tg (d/c)
a
Φ = - arc tg 2
Φ = arc tg 2
b

FIG. 4

heptatrienyl residues through methine group (fig. 4b).

The proof is evident: on condition that $\Phi_1 + \Phi_2 = 0$, zero eigenvectors on two subgraphs are "sewn together" without any perturbation.

Thus, the phase represented through the IAM elements proves to be the powerful instrument for investigation of some spectral properties of the chemical graphs.

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