Iranian Journal of Mathematical Chemistry

General Theory of Cycle–Dependence of Total π–Electron Energy

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ARTICLE INFO	ABSTRACT
Article History: 	The theoretical treatment of cycle-effects on total π-electron energy, mainly elaborated by Nenad Trinajstić and his research group, is re-stated in a general and more formal manner. It enables to envisage several other possible ways of measuring the cycle-effects and points at further directions of research.
Keywords: 	

1. INTRODUCTION: MATHEMATICAL BACKGROUND

Let G be a graph representing the carbon–atom skeleton of a polycyclic conjugated π-Electron system [7,9,21,34]. In what follows, we refer to G as to a molecular graph. Let G possess a total of t = t(G) cycles, and let these cycles be denoted by $Z_1, Z_2, ..., Z_t$.

In order to avoid any misunderstanding, in Fig 1 are indicated all the cycles contained in the molecular graph of triphenylene G_{TP}. Thus, although G_{TP} is classified among tetracyclic graphs (i.e., G_{TP} has 4 independent cycles), it possesses a total of 11 cycles, $t(G_{TP}) = 11$.

In theoretical chemistry, it has been firmly established that the cycles in conjugated molecules have a profound influence on their physical and chemical properties, especially on those that are referred to as "aromaticity" and "local aromaticity" [27,6,30,28,13].

The considerations that follow are intimately related with the Sachs theorem and Its role in quantum chemistry. This theorem was published in its final form by Horst Sachs

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in 1964 [29], but remained fully unknown to the chemical community until the publication of the paper in 1972 [8]. Details of the Sachs theorem can be found in scores of books and review articles, for instance in [23,32,31,9,34,21,7,16]; for historical details see [11,12,35].
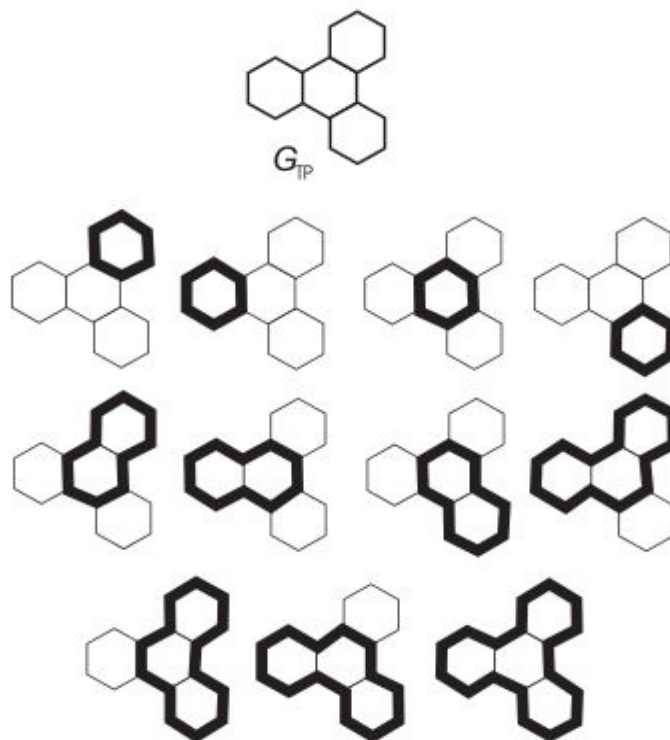

Figure 1. The molecular graph G TP of triphenylene and the cycles contained in it.

Let G be a molecular graph and $\phi(G,\lambda)$ its characteristic polynomial. Let G has n vertices, which means that $\phi(G,\lambda)$ is a monic polynomial of degree n.

A Sachs graph S is any graph whose components are cycles and/or 2-vertex Complete graphs. Denote by n(S), p(S), and c(S) the number of vertices, number of components, and number of cyclic components, respectively of the Sachs graph S. Denote by S(G) the set of all Sachs graphs that are as subgraphs contained in the graph G. Then the Sachs theorem reads,

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

Important for the present consideration is that the Sachs theorem relates the Characteristic polynomial with the structure of the underlying graph. Furthermore, it clearly and explicitly shows how the characteristic polynomial depends on the cycles Contained in the graph.

By solving the equation $\phi(G,\lambda) = 0$, one obtains the eigenvalues of the graphs G, denoted by $\lambda_1 \geq \lambda_2 \geq \cdots \geq \lambda_n$. Within the framework of the tight-binding Hüuckel molecular orbital (HMO) approximation, the total π-electron energy of the underlying conjugated molecule can then be calculated as [9, 21]

$$E(G) = \sum_{i=1}^{n} \omega_i \lambda_i \tag{2}$$

where ω_i is the occupation number of the i-th molecular orbital, $\omega_i \in \{0,1,2\}$. Thus, the Sachs theorem in an implicit manner reveals how the total π-electron energy depends on the cycles contained in the molecular graph.

In order to measure the effect of cycles, a quasi-energy E(G,ref) needs to be constructed in an analogous manner as E(G), using not the zeros of the characteristic polynomial, but the zeros of a suitably constructed "reference polynomial". Then the difference $E(G) - E(G, ref)$ provides a desired measure of the respective energy-effect, and can be directly related with the physical and chemical properties of the underlying conjugated π-electron systems.

2. MODELING THE ENERGY–EFFECTS

Let Z_1, Z_2, ..., Z_t be the cycles contained in the molecular graph G. For i = 1,2,...,t, associate a variable g_i to the cycle Z_i . Let g = (g_1 ,g_2 ,...,g_t) be a t-dimensional vector. If $g_1 = g_2 = \cdots = g_t = 0$, then we write g = 0. If $g_1 = g_2 = \cdots = g_t = 1$, then g = 1. By e_i we denote the g-vector in which all components are equal to zero, except the i-th component, which is equal to unity. Thus, $g = \sum_{i=1}^{n} g_i e_i$.

Bearing in mind Eq. (1), we define an auxiliary polynomial

$$\phi(G, g, \lambda) = \lambda^n + \sum_{S \in S(G)} (-1)^{p(S)} 2^{c(S)} Z(S) \lambda^{n-n(S)}$$

where Z(S) is the product of g_i-values of all cycles contained in the Sachs graph S. If the Sachs graph S is acyclic, then Z(S) = 1.

It is evident that $\phi(G,1,\lambda) \equiv \phi(G,\lambda)$, i.e., $\phi(G,1,\lambda)$ coincides with the ordinary characteristic polynomial. In addition, $\phi(G,0,\lambda)$ is equal to the matching polynomial, whose theory has been studied in due detail [5,15].

By solving the equation $\phi(G,g,\lambda) = 0$, one obtains the quasi-eigenvalues $\lambda_1(g)$, $\lambda_2(g)$, ..., $\lambda_n(g)$. Based on them, it is possible to compute a quasi-energy E(G,g) in the same manner as the total π-electron energy E(G) is calculated from the ordinary graph eigenvalues (as specified in the preceding section). Then, in particular, E(G,1) coincides with the ordinary total π-electron energy E(G), Eq. (2).

The quasi-energy E(G,g) has to be understood as a total-π-electron-energy-like quantity, in which the parameter g_i controls the effect of the i-th cycle contained in the

molecular graph. If $g_i = 1$, then the effect of this cycle of total π-electron energy has the usual, normal value. If $g_i = 0$ then the effect of the i-th cycle is completely neglected.

Based on this simple observation, by means of the difference $E(G,1) - E(G,g)$, and by a pertinent choice of the g-vector, it was possible to extract a variety of chemically relevant information contained in the HMO total π-electron energy. In what follows, we list a few such cases that earlier have been studied in the chemical literature. In the subsequent section, we point out other options that our general Theory makes possible.

2.1. THE TOPOLOGICAL RESONANCE ENERGY

Using the above introduced formalism, the "it topological resonance energy" is defined as
$$TRE(G) = E(G,1) - E(G,0) \tag{3}$$
It represents the effect on total π-electron energy of all cycles contained in the molecular graph G. This idea was first put forward in 1975 by Nenad Trinajstić and two of his students [18], and eventually elaborated in 1977, in the papers [33,19]. In the same time Aihara arrived at the very same idea [1]. Details and an extensive bibliography of the theory and numerous applications of the TRE model can be found in the survey [14], whereas a few interesting historical data in Trinastić's autobiography [35].

2.2. MODELS OF ENERGY−EFFECT INDIVIDUAL CYCLES

Whereas TRE represents the simultaneous effect of all cycles of total π-electron energy, an analogous reasoning lead to the expression
$$ef(G, Z_i) = E(G, 1) - E(G, 1 - e_i) \tag{4}$$
which would provide a measure of the effect of the individual cycle Z_i. This model was proposed in 1977, in the paper [4]. The idea came from Gutman, whereas Slobodan Bosanac provided the software by means of which the ef-values could be efficiently calculated. The first chemical applications of this model were communicated in [17], and were followed by many dozens of publications; mathematical details and bibliography can be found in the survey [13].

In the same year 1977, Aihara introduced an alternative model for measuring the energy-effect of individual cycles [2]. In our symbolism, this energy-effect can be expressed as
$$ef_A(G, Z_i) = E(G, e_i) - E(G, 0) \tag{5}$$
In the case of unicyclic graphs, $ef_A(G) = ef(G)$, whereas in the case of graphs with more than one cycle, the two ef-values differ. Worth mentioning is that for all graphs G and all i = 1,2,...,t, the quasi-eigenvalues $\lambda_1(e_i)$, $\lambda_2(e_i)$, ..., $\lambda_n(e_i)$, i.e., the zeros of the polynomial $\beta(G, Z_i, \lambda) = \phi(G, e_i, \lambda)$ are all real-valued. This fact was first established on a large number of examples [24,25] and eventually proved for the general case [26].

In a later article [3], Aihara himself came to the conclusion that the ef-model, Eq. (4), is superior to its ef A -version, Eq. (5).

Formula (4) can be directly extended to measure the collective energy-effect of a pair of cycles Z_i, Z_j, $ef(G, Z_i, Z_j) = E(G, 1) - E(G, 1 - e_i - e_j)$ of a triplet of cycles Z_i ,Z_j, Z_k , $ef(G, Z_i, Z_j, Z_k) = E(G, 1) - E(G, 1 - e_i - e_j - e_k)$ etc. However, to the present author's best knowledge, these multiple-energy-effects have been considered in just a single paper [22].

3. MORE POSSIBILITIES OF THE GENERAL THEORY

The choice $g = 1 - e_i$ in Eq. (4) means that we completely neglect the influence of the cycle Z_i on the value of the quasi-energy $E(G,g)$. Analogously, the choice $g = 0$ in Eq. (3) means that we completely neglect the influence of all cycles on the value of the quasi-energy $E(G,g)$.

However, we may only partially diminish the effect of cycles (by choosing $0 < g_i < 1$). In this case, a resonance energy of the form,

$$TRE_a(G, \varepsilon) = \frac{1}{\varepsilon}[E(G, 1) - E(G, (1 - \varepsilon)1)]$$

would be conceived, in which case $TRE_a (G, \varepsilon) = TRE(G)$ if $\varepsilon = 1$. For instance, by setting $\varepsilon = 1/2$, we would get a kind of "half-way" resonance energy. Anyway, ε could be viewed as a variable parameter, whose value could then be optimized (so that TRE_a best agrees with experimentally observed facts).

Another development beyond the standard TRE model would be to increase the effect of cycles above their usual value. The resonance energy obtained in this way would be,

$$TRE_b(G, \varepsilon) = \frac{1}{\varepsilon}[E(G, (1 + \varepsilon)1) - E(G, 1)] \tag{7}$$

in which case $TRE_b (G, \varepsilon) = TRE(G)$ if $\varepsilon = -1$. It can be shown that

$$\lim_{\varepsilon \to 0} TRE_a (G, \varepsilon) = \lim_{\varepsilon \to 0} TRE_b(G, \varepsilon) = \frac{\partial E(G, x1)}{\partial x}\Big|x = 1 \tag{8}$$

The partial derivative on the right–hand side of (8) was earlier studied in [10,20], where it was shown to be equal to the sum of contributions of individual cycles contained in the molecular graph G.

Analogous extensions could be done also with the individual energy-effect ef(G), Eq. (4). Thus, one might consider

$$ef_a(G, Z_i, \varepsilon) = \frac{1}{\varepsilon}[E(G, 1) - E(G, 1 - \varepsilon e_i)] \tag{9}$$

or

$$ef_b(G, Z_i, \varepsilon) = \frac{1}{\varepsilon}[E(G, 1 + \varepsilon e_i) - E(G, 1)] \tag{10}$$

which evidently become equal to ef(G,Z_i) for ε = +1 and ε = −1, respectively. In connection with this, it can be shown that,

$$\lim_{\varepsilon \to 0} ef_a(G, Z_i, \varepsilon) = \lim_{\varepsilon \to 0} ef_b(G, Z_i, \varepsilon) = \frac{\partial E(G,g)}{\partial g_i}\Big|g = 1.$$

4. CONCLUDING REMARKS

The fact is that the variable-parameter energy-effects defined via Eqs. (6) , (7), (9) , (10), and similar have never been studied in theoretical chemistry. Their "ordinary" versions, Eqs. (3)–(5), were put forward in the 1970s, when the interest for HMO-based aromaticity criteria might have been at a maximum. In the meantime, the usage of HMO-based theories gradually lost their attractiveness, and nowadays it is unlikely that the models mentioned in the preceding section will be further elaborated and attempted to find chemical applications. Therefore, the present paper should be considered as a summary of what the research group of Nenad Trinajstić achieved in the study of cycle-effects in polycyclic conjugated molecules, and what could have had achieved, but did not. Sincere congratulations and best wishes to N.T.'s 80th birthday.

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