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# THE GENERALIZED CIOSLOWSKI FORMULA

Ivan Gutman

Faculty of Science, University of Kragujevac, P.O.Box 60, YU-34000 Kragujevac, Yugoslavia

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Abstract

A result of Cioslowski [Match 20, 95 (1986)], concerning the total pi-electron energy of benzenoid hydrocarbons is generalized. Further possible applications of Cioslowski s unified distribution approach are pointed out.

## INTRODUCTION: THE UNIFIED DISTRIBUTION APPROACH

In two recent papers[1,2] Cioslowski developed the so-called unified distribution approach (UDA), by which a remarkable result about the dependence of the total pi-electron energy ($E_{pi}$) of benzenoid hydrocarbons on the topological invariants N, M and K was deduced, namely

$$E_{pi} = (2\ M\ N)^{1/2}\ F[K^{2/N}\ (2M/N)^{-1/2}]\ . \qquad (1)$$

Here and later we use the same notation as in Ref. 1. Whence, N is the number of vertices and M the number of edges of the molecular graph corresponding to the benzenoid molecule, whereas K is the respective number of Kekulé structures. F(x) is a universal function of the variable x, which within UDA remains unspecified. (Under universal function we understand a function which is same for all memberes of the class of molecules considered. In other words, a universal function does not depend on parameters which are structural invariants of the molecules under examination.)

Within UDA the distribution of the positive eigenvalues $x_1, x_2, \ldots, x_{N/2}$ of the adjacency matrix of the molecular graph is described by a distribution function G(x). Thus

$$\int G(x)\, dx = N/2 \tag{2}$$

$$\int x\, G(x)\, dx = E_{pi} \tag{3}$$

$$\int x^2\, G(x)\, dx = M \tag{4}$$

$$\int \ln x\, G(x)\, dx = \ln K\ . \tag{5}$$

The mathematical basis of UDA is the assumption that G(x) has the same shape for all benzenoid hydrocarbons, that is

$$G(x) = h\, g(\ (x-a)/r\ ) \tag{6}$$

where g(x) is a universal function while h, a and r are parameters depending on the structure of the particular benzenoid system considered.

By substituting (6) back into (2),(3) and (4) it has been shown[1] that

$$h\ r = N/(2M_0) \tag{7}$$

$$r = (m_2 - m_1^2)^{-1/2}\ N^{-1}\ (2\ M\ N - E_{pi}^2)^{1/2} \tag{8}$$

$$a = N^{-1}\ [E_{pi} - m_1(m_2 - m_1^2)^{-1/2}\ (2\ M\ N - E_{pi}^2)^{1/2}]\ . \tag{9}$$

The definition of the auxiliary quantities $M_0$, $m_1$ and $m_2$ can be found in Ref. 1. For the purpose of the present study it is sufficient to note that $M_0$, $m_1$ and $m_2$ depend only on $g(x)$ and are therefore independent of the structure of any particualr benzenoid molecule.

By means of elementary algebraic transformations, eqs. (8) and (9) can be put into the form

$$r = (2M/N)^{1/2}\ P(e) \tag{10}$$

$$a = (2M/N)^{1/2}\ Q(e) \tag{11}$$

where

$$P(x) = (m_2 - m_1^2)^{-1/2}\ (1 - x^2)^{1/2} \tag{12}$$

$$Q(x) = x - m_1 (m_2 - m_1^2)^{-1/2} (1 - x^2)^{1/2} \qquad (13)$$

and

$$\varepsilon = (2 M N)^{-1/2} E_{pi} \quad . \qquad (14)$$

It is easily seen that P(x) and Q(x) are universal functions.

Combining the above findings with eq. (5) the formula (1) was deduced. We now demonstrate that instead of (5) a more general condition, eq. (15), can be employed, leading to a generalization of the Cioslowski formula (1).

## THE GENERALIZATION

Suppose that the positive eigenvalues of the adjacency matrix of the molecular graph obey the condition

$$\sum_{i=1}^{N/2} f(x_i) = J \qquad (15\ a)$$

where f(x) is some function and J is a certain invariant of the molecular graph. Then within the UDA formalism,

$$\int f(x)\ G(x)\ dx = J \qquad (15\ b)$$

which, because of (6) and (7) yields

$$(M_0)^{-1} \int f(\ r(z+a/r)\ )\ g(z)\ dz = 2J/N \quad . \tag{16}$$

Bearing in mind (10) and (11) we see that the left-hand side of (16) is <u>not</u> a universal function of the variable e, given by eq. (14).

There are, however, two important special cases when (16) can be further simplified.

<u>Case 1</u>: the function f(x) has the property $f(uv) = f(u) + f(v)$. This condition is obeyed if (and only if) f(x) is proportional to ln x, and is basically covered by eq. (5). Therefore we need not elaborate this case any further.

<u>Case 2</u>: the function f(x) has the property $f(uv) = f(u)f(v)$. This means that J is just one of the moments of the graph eigenvalues.

Combining eq. (16) with (10) and (11) we obtain

$$f((2M/N)^{1/2})\ (M_0)^{-1}\ f(P(e)) \int f(z + Q(e)/P(e))\ g(z)\ dz = \\ = 2J/N \ . \tag{17}$$

Introducing the universal function R(x)

$$R(x) = (M_0)^{-1}\ f(P(e)) \int f(z + Q(e)/P(e))\ g(z)\ dz \tag{18}$$

we get

$$R(e) = p \tag{19}$$

with

$$p = 2J/[N\ f((2M/N)^{1/2})] \tag{20}$$

and where e is defined via eq. (14). Assuming further that the inverse S(x) of the function R(x) exists, one arrives at

$$E_{pi} = (2\ M\ N)^{1/2}\ S(p) \tag{21}$$

where p is given by (20). The universal functions in eqs. (1) and (21) are, of course, not identical.

DISCUSSION

Eq. (21) enables one to deduce a number of approximate topological formulas for $E_{pi}$, based on the knowledge of explicit combinatorial expressions for the lower moments of the graph eigenvalues of benzenoid systems[3].

If, in particular, we choose $f(x) = x^2$, then J = M and by eq. (20), p = 1. Consequently,

$$E_{pi} = C\ (2\ M\ N)^{1/2} \tag{22}$$

where C is a constant, equal to S(1). This, of course, is just the McClelland formula[4].

As another example, choose $f(x) = x^4$, which corresponds[5] to J = 9M - 6N . Then $p = (9\ M\ N - 6\ N^2)/(2\ M^2)$ and

$$E_{pi} = (2\ M\ N)^{1/2}\ S[(9\ M\ N - 6\ N^2)/(2\ M^2)] \quad . \qquad (23)$$

This provides a certain improvement of the McClelland approximation (22) and a novel isomer-undistinguishing topological formula for total pi-electron energy[6].

The results of numerical testing of eq. (23) and other special cases of eq. (21) will be reported elsewhere.

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