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THE GENERALIZED Mc CLELLAND FORMULA

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Abstract: The application of the unified distribution approach leads to a generalization of the McClelland formula. It is shown that the total pi-electron energy conforms to the equation $E_{pi} = \sqrt{2MN}\, F(p)$, where F is some universal function and $p = K^{2/N}(2M/N)^{-1/2}$ is a structure parameter. It is found numerically that the function F(p) is well represented by the formula F(p) = 0.76764+0.17747p. This results in a new topological formula for E_{pi} which is more accurate then other formulae known.

INTRODUCTION

Since the formulation of an upper bound for the total pi-electron energy (E_{pi}) by McClelland[1] the formula :

$$E_{pi} \approx g\sqrt{2MN} \qquad (1)$$

(where M and N are the number of edges and vertices of the molecular graph corresponding to the conjugated system) has been investigated many times. The value of an empirical factor g has been determined numerically[2] to be 0.908 in the case of benzenoid hydrocarbons. Quite recently some theoretical work toward elucidation of the nature of this constant has been undertaken[3,4].

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In the present paper some novel approach to the problem is proposed resulting in the conclusion that g is not a constant but a function of the structure parameter $p = K^{2/N}(2M/N)^{-1/N}$ where K is the number of the Kekulé structures. The obtained formula , valid for the benzenoid hydrocarbons is tested numerically.

THEORY

Let us assume that the distribution of the positive eigenvalues of the adjacency matrix can be described by some function G(x). This distribution function must conform to the following relations :

$$2\int_0^\infty G(x)\,dx = N \qquad (2)$$

$$2\int_0^\infty G(x)\,x\,dx = E_{pi} \qquad (3)$$

$$\int_0^\infty G(x)\,x^2\,dx = M \qquad (4)$$

$$\int_0^\infty G(x)\,\ln x\,dx = \ln K \qquad (5)$$

The central point of the unified distribution approach (UDA) is to assume that G(x) has the same shape for all benzenoid hydrocarbons , that means there is some universal function g(x) related to G(x) by the equation :

$$G(x) = h\,g((x-a)/r) \qquad (6)$$

The parameters h , a and r are determined from the

constraints (2) , (4) and (5). This enables us in turn to compute E_{pi}.

Explicit calculation gives :

$$2\,h\,r\,M_0 = N \tag{7}$$

$$2\,h\,(a\,r\,M_0 + r^2\,M_1) = E_{pi} \tag{8}$$

$$h\,(a^2\,r\,M_0 + 2\,a\,r^2\,M_1 + r^3\,M_2) = M \tag{9}$$

$$h\,r\,[M_0 \ln r + A(a/r)\,] = \ln K \tag{10}$$

where $M_k = \int_0^\infty g(t)\,t^k\,dt$ and $A(z) = \int_0^\infty \ln\,(t+z)\,g(t)\,dt$.

Substituting (7) into (8) and (9) we arrive at :

$$a + r\,m_1 = E_{pi}/N \tag{11}$$

$$a^2 + 2\,a\,r\,m_1 + r^2\,m_2 = 2M/N \tag{12}$$

where $m_k = M_k/M_0$.

From eqs.(11) and (12) we evaluate r and a as :

$$r = (m_2 - m_1^2)^{-1/2}\,N^{-1}\,(2MN - E_{pi}^2)^{1/2} \tag{13}$$

$$a = N^{-1}\,[\,E_{pi} - m_1\,(m_2 - m_1^2)^{-1/2}\,(2MN - E_{pi}^2)^{1/2}\,] \tag{14}$$

Then we have :

$$M_0 \ln r + A(a/r) = 2\,M_0/N \ln K \tag{15}$$

$$\ln r + A(a/r)/M_0 = \ln K^{2/N} \tag{16}$$

Since:

$$a/r = (m_2 - m_1^2)^{1/2}\,E_{pi}\,(2MN - E_{pi}^2)^{-1/2} - m_1 \tag{17}$$

is a function of the parameter $E_{pi}(2MN)^{-1/2}$ we can rewrite eq.(16) as

$$\ln r + M_o^{-1}\,B(E_{pi}/\sqrt{2MN}) = \ln K^{2/N} \tag{18}$$

where B is some universal function. Also r can be expressed as:

$$r = E_{pi}N^{-1}(m_2-m_1^2)^{-1/2}\left(\frac{2MN}{E_{pi}^2} -1\right)^{1/2} = E_{pi}/N\ f(E_{pi}/\sqrt{2MN}) \quad (19)$$

This makes possible to rewrite (18) in the following way :

$$\ln f(E_{pi}/\sqrt{2MN}) + M_o^{-1}\ B(E_{pi}/\sqrt{2MN}) = \ln (NK^{2/N}/E_{pi}) \quad (20)$$

or :

$$C(E_{pi}/\sqrt{2MN}) = \ln (NK^{2/N}/E_{pi}) \quad (21)$$

Now , let us represent E_{pi} as :

$$E_{pi} = g\ (2MN)^{1/2} \quad (22)$$

Substituting this into (21) we get :

$$C(g) = \ln (K^{2/N}/\sqrt{2M/N}) - \ln g \quad (23)$$

The solution of equation (23) leads to the conclusion that there is some universal function F which relates E_{pi} , N , M and K by means of the formula :

$$E_{pi} = \sqrt{2MN}\,F[K^{2/N}\ (2M/N)^{-1/2}] \quad (24)$$

The equation (24) is the generalized McClelland formula. The form of the function F has to be determined numerically.

NUMERICAL RESULTS

The problem of the dependence of E_{pi} on K has been discussed several times. In particular , two contradictory results are known. The first approach states that E_{pi} is a linear function of $\ln K$[5] , whereas according to the second one , the linear relation between E_{pi} and K exists[6,7]. The corresponding equations read :

$$E_{pi}(N,M,K) \approx A\ N + B\ M + C\ \ln K \quad (25)$$

and

$$E_{pi}(N,M,K) \approx G\ N + H\ M + I\ K\ J^{M-N} \quad (26)$$

where A , B , C , G , H , I and J are numerical constants.

Considering the validity of eqs.(25) and (26) one should remember that , obviously , the following property of E_{pi} is expected :

$$E_{pi}(uN,uM,K^u) = u\ E_{pi}(N,M,K) \qquad (u \epsilon N) \qquad (27)$$

This " weak size consistency " condition[8] is fulfilled by (25) but not by (26). On the other hand eq.26 has been found to work much more accurately than eq.25[5,6]. The same conclusion has been drawn in the present paper (see below).

In order to solve the problem , what is the real interrelation between N,M,K and E_{pi} as well as what is the form of function F , a numerical testing of the formulae (24)-(26) has been performed. As a basis for calculations the standard set[9] of 1030 singlet ground state planar hydrocarbons possessing 2-8 rings has been used. All empirical parameters have been optimized by means of the least squares fitting. The results shown in Table 1 lead to the following conclusions :

1. A satisfactory representation for the function F is :

$$F(p) \approx 0.76764 + 0.17747\ p \qquad (28)$$

Thus we have a new topological formula for E_{pi} :

$$E_{pi} \approx 0.76764 \sqrt{2MN} + 0.17747\ NK^{2/N} \qquad (29)$$

2. The formula (29) , although using only 2 empirical parameters , reproduces E_{pi} with the error comparable to the one given by eqs.(24) and (25). One should note , however , that eq.(29) gives more accurate values for E_{pi} when applied to the hydrocarbons of an infinite size.

3. The formula (26) gives the most accurate values of E_{pi} for

the moderate-size hydrocarbons but fails for polymers , which can be related to its size inconsistency.

TABLE 1. THE COMPARISON OF THREE DIFFERENT TOPOLOGICAL FORMULAE FOR E_{pi}.

Formula for E_{pi}	AN + BM + ClnK	AN + BM + CKD^{M-N}	$A\sqrt{2MN} + BNK^{2/N}$
Empirical parameters	A=0.7682 B=0.4957 C=0.4290	A=0.5477 B=0.7027 C=0.2393 D=0.6658	A=0.7676 B=0.1775
Standard deviation	0.07%	0.04%	0.09%
Average error	0.10%	0.06%	0.07%
Maximal error	0.65%	0.39%	0.63%
Error for : the infinite polyacene chain	1.08%	1.65%	0.84%
the infinite zig-zag chain	0.22%	0.76%	0.17%
the graphite lattice	0.52%	1.64%	1.01%

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[8] usually , by the (strong) size consistency we would mean the condition :

$E_{pi}(N_a+N_b, M_a+M_b, K_aK_b) = E_{pi}(N_a, M_a, K_a) + E_{pi}(N_b, M_b, K_b)$

the author is indebted to the referee for mentioning this point

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