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An Approximate Spectral Density for the Estimation of some Topological Indices of Alternant Systems

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A symmetric two-delta-function model spectral density is used to estimate several topological indices of alternant hydrocarbons, namely: the total π-electron energy (E_π), the modified topological index (Z), the HOMO-LUMO separation (X_{HL}) and the spectral radius of adjacency matrix (R). It is found, that the invariants defined by integration (like E_π and Z) are reproduced much better than the invariants defined as the limiting values of the spectral distribution (like X_{HL} and R). The reason for the well known linear dependence between E_π and lnZ, is discussed.

INTRODUCTION

The description of conjugated hydrocarbons through the concepts of chemical topology and graph theory is well documented to be an effective way to account for their physicochemical properties.[1] In particular, the total π-electron energy (E_π) was a subject of several theoretical approaches.

A great deal of attention has been focused recently on the spectral density formalism for the calculation of topological indices of alternant systems.[2-6] Let the eigenvalues of the adjacency matrix describing the system under study that has N carbon atoms, M carbon-carbon bonds and K Kekulé structures, be $\pm x_1$, $\pm x_2, \ldots, \pm x_{N/2}$. The spectral density function is defined as:[3]

$$\Gamma(x) = \sum_{i=1}^{N/2} [\delta(x - x_i) + \delta(x + x_i)] \tag{1}$$

The spectral density comprises all the information about eigenvalues and, therefore, the knowledge of its form is sufficient to calculate several topological invariants. The exact function is usually approximated by some model density D (x). Both discrete[5] and continuous[6] forms of D (x) were proposed in the chemical literature. Recently, some very general properties of D (x) have been deduced.[2,3,4]

During the derivation of D (x) the normalized invariants appear in a natural way. They are:[3]

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1. The McClelland quotient (MCQ):

$$e = E_{\pi} (2MN)^{-1/2}; \tag{1a}$$

where E_{π} is the sum of the moduli of eigenvalues.

2. The normalized structure count (NSC):

$$k = K^{2/N} (2M/N)^{-1/2}; \tag{1b}$$

In general case the number of Kekulé structures should be replaced by the algebraic structure count.

3. The normalized HOMO-LUMO separation (NHLS):

$$h = 1/2\, X_{HL} (2M/N)^{-1/2}; \tag{1c}$$

where X_{HL} is twice the eigenvalue with the smallest modulus.

4. The normalized spectral radius (NSR):

$$r = R (2M/N)^{-1/2}; \tag{1d}$$

where R is equal to the eigenvalue with the largest modulus.

The simplest form of D (x) is a normalized sum of two Dirac's functions:

$$D(x) = N/2\, [\delta (x - a) + \delta (x + a)]. \tag{2}$$

Such a choice leads to $e = k = h = r = 1$ and, therefore, is too crude to describe more subtle effects of the molecular topology on E_{π} and X_{HL}. In the present paper we investigate a slightly more sophisticated form of D (x) (Figure 1):

$$D(x) = N/4\, [\delta (x - a) + \delta (x + a) + \delta (x - b) + \delta (x + b)], \tag{3}$$

which is essentially a symmetrized sum of two Dirac's delta functions.

$$D(x) = [\delta (x + b) + \delta (x + a) + \delta (x - a) + \delta (x - b)] \cdot N/4$$

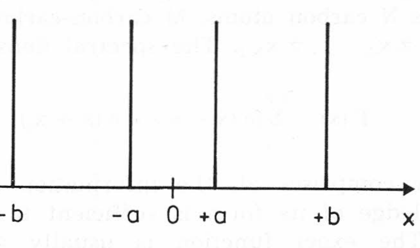

Figure 1. A symmetric two-delta function spectral density.

THEORY

The parameters a and b can be computed easily from the conditions (5) and (6),[3] while the normalization factor of N/4 guarantees equation (4) to be fulfilled:

$$\int_{-\infty}^{+\infty} D(x)\, dx = N, \tag{4}$$

$$\int_{-\infty}^{+\infty} \mathrm{D}(\mathrm{x})\, \mathrm{x}^2\, d\mathrm{x} = 2\mathrm{M}, \tag{5}$$

$$\int_{-\infty}^{+\infty} \mathrm{D}(\mathrm{x}) \ln |\, \mathrm{x} \,|\, d\mathrm{x} = 2 \ln \mathrm{K}. \tag{6}$$

From these constrains we calculate a and b as:

$$\mathrm{a} = \mathrm{d}^{1/2}\, [1 - (1 - \mathrm{k}^4)^{1/2}]^{1/2}, \tag{7}$$

$$\mathrm{b} = \mathrm{d}^{1/2}\, [1 + (1 - \mathrm{k}^4)^{1/2}]^{1/2}, \tag{8}$$

where d is the mean vertex degree of the molecular graph:

$$\mathrm{d} = 2\mathrm{M}/\mathrm{N} \tag{9}$$

The quantities a and b can be regarded as estimates for the HOMO-LUMO separation and the spectral radius. Bearing in mind definitions (1c) and (1d) we can write:

$$\mathrm{h} \approx [1 - (1 - \mathrm{k}^4)^{1/2}]^{1/2} \tag{10}$$

and

$$\mathrm{r} \approx [1 - (1 - \mathrm{k}^4)^{1/2}]^{1/2}. \tag{11}$$

The total π-electron energy depends also on D (x) in a straightforward way:

$$\int_{-\infty}^{+\infty} \mathrm{D}(\mathrm{x})\, |\, \mathrm{x} \,|\, d\mathrm{x} \approx E_{\pi}. \tag{12}$$

Within the approximation (3) this gives rise to:

$$E_{\pi} \approx (2\mathrm{MN})^{1/2}\, [(1 + \mathrm{k}^2)/2]^{1/2} \tag{13}$$

or:

$$\mathrm{e} \approx [(1 + \mathrm{k}^2)/2]^{1/2}. \tag{14}$$

The approximation (13) was first considered by Gutman *et al.*[7] Eventually, we can compute the modified topological index Z from the relation:[8]

$$\int_{-\infty}^{+\infty} \mathrm{D}(\mathrm{x}) \ln (1 + \mathrm{x}^2)\, d\mathrm{x} \approx 2 \ln \mathrm{Z}, \tag{15}$$

which results in the approximate relation:

$$\ln \mathrm{Z} \approx \mathrm{N}/4 \ln (1 + 2\mathrm{d} + \mathrm{d}^2\, \mathrm{k}^4). \tag{16}$$

DISCUSSION AND NUMERICAL CALCULATIONS

First we discuss the equations (10), (11) and (14) that express an approximate dependence of h, r and e on k. The very fact that h, r and e depend only on k is not accidental but it is a corollary of the theorem[4] which states that any approximate formulae expressing E_{π}, X_{HL} and R as the functions of N, M and K must be reducible to simple relations between the normalized topological invariants and NSC.

The modified topological index Z is a different case. Inspection of eq. (16) reveals that Z is not a simple function of k. On the first glance it is in apparent contradiction with the well known fact that E_π and $\ln Z$ are related through a approximate linear regression.[8–12] This paradox can be resolved in the following way:

Let us rewrite eq. (16) as:

$$z = (2\,MN)^{-1/2} \ln Z \approx (16\,d)^{-1/2} \ln (1 + 2\,d^2 k^4). \qquad (17)$$

If the assumption on the approximate linear relation between E_π and $\ln Z$ is valid, one expects that the ratio:

$$z/e \approx (8\,d)^{-1/2} (1 + k^2)^{-1/2} \ln (1 + 2\,d + d^2 k^4) \qquad (18)$$

varies only very slightly with both k and d. Since d takes the values between 2 and 3 and k between 0.7 and 0.9,[3] we carried out simple test computations of the ratio for these limiting values. The results, presented in Table I, show that the ratio is indeed almost constant, at least for d and k lying within the above limits.

TABLE I

The Ratio z/e for Various Values of d and k (eq. 18)

k	d		
	2.0	2.5	3.0
0.7	0.3656	0.3691	0.3704
0.8	0.3695	0.3749	0.3776
0.9	0.3774	0.3844	0.3881

We, thus, conclude that the linear relation between E_π and $\ln Z$ originates from an accidental numerical independence of the ratio on d and k rather than from more general reasons.

The accuracy of approximate formulae (7), (8), (13) and (16) has been tested against the standard set of benzenoid hydrocarbons (1030 molecules).[13,14] The results of the testing are shown in Table II.

TABLE II

Linear Regression Between Approximate and Exact Topological Invariants

Topological invariant	E_π	Z	ϵ_{HL}	R
Linear regression:				
Slope:	0.999	0.998	2.865	0.987
Intercept:	0.239	0.217	—1.793	0.571
Errors:				
RMS	0.3%	0.6%	10%	1.1%
Standard deviation:	0.5%	0.9%	16%	1.4%
Maximal:	2.5%	4.3%	131%	7.9%
Correlation coefficient:	0.9990	0.9962	0.9151	0.4300

The exact total π-electron energy is reproduced by our simple model rather accurately (Figure 2). We, therefore, conclude that this quantity is rather insensitive on the shape of spectral density, provided the approximation to density fulfills the constrains (4)—(6). The same statement is valid for the modified topological index. It should be pointed out that in all the calculations the benzene molecule was excluded, because of the degeneracy of HOMO and LUMO orbitals. The degeneracy precludes the use of a simple two-delta approximation to the density function.

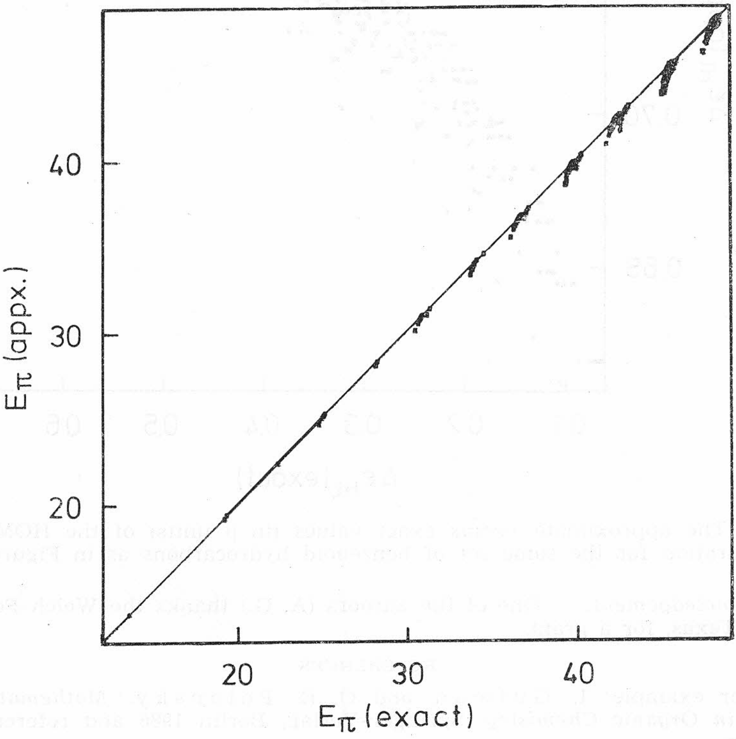

Figure 2. The approximate *versus* exact values of the total π-electron energy for the standard set of benzenoid hydrocarbons. The results are given in β units of the HMO theory.

The situation with the HOMO energy, $\epsilon_{HL} = 1/2\, X_{HL}$, and the spectral radius, R, is quite different. There is a definite correlation between the calculated and exact ϵ_{HL}, but the dependence has rather a qualitative character (Figure 3). The trend in HOMO energies is well accounted for, but the slope of regression is far from unity. Eventually, there is no meaningful correlation between the calculated and exact R.

The simple model for spectral density function presented in our paper is intented to show how some trends in topological indices can be analyzed analytically with the knowledge of very limited information about molecular graph rather than to produce very accurate formulae for these indices. It seems to be clear that the two-delta approximation is well suited for such an analysis.

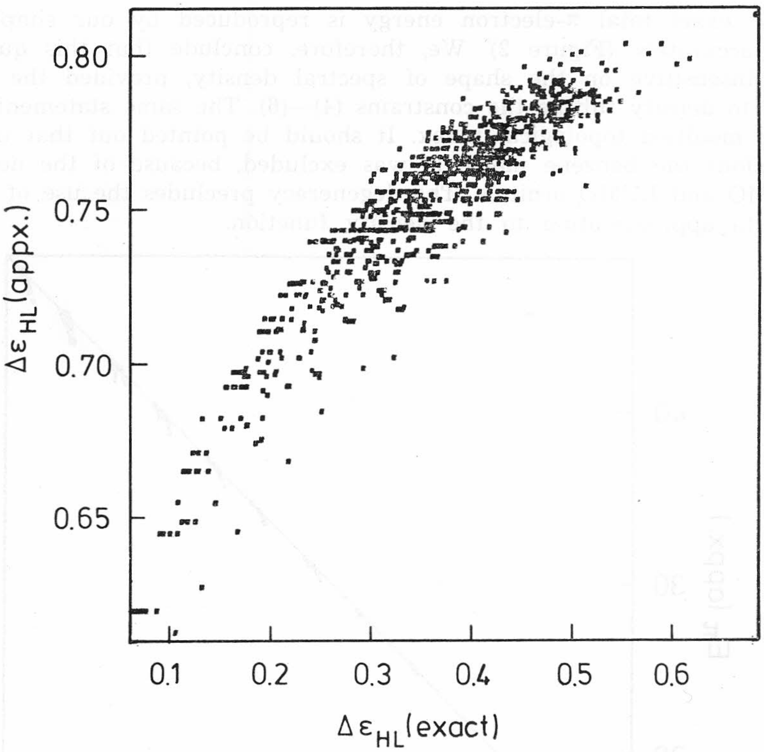

Figure 3. The approximate *versus* exact values (in β units) of the HOMO-LUMO separation for the same set of benzenoid hydrocarbons as in Figure 2.

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SAŽETAK

Procjena nekih topoloških indeksa u alernantnim sustavima pomoću jedne približne spektralne gustoće

A. Graovac i J. Cioslowski

Simetrična spektralna gustoća modelirana dvjema delta-funkcijama upotrijebljena je za procjenu slijedećih topoloških indeksa u alternantnim ugljikovodicima: ukupne π-elektronske energije (E_π), modificiranog topološkog indeksa (Z), HOMO-LUMO separacije (X_{HL}) i spektralnog polumjera (R) matrice susjedstva. Nađeno je da procjena bolje reproducira indekse vezane uz integraciju spektralne gustoće (E_π, Z) nego one (X_{HL}, R) vezane uz lokaciju delta-funkcija. Prodiskutirani su i razlozi za valjanost dobro poznate linearne ovisnosti E_π o ln Z.