The Use of the Gauss-Chebyshev Quadrature in Estimation of the Total π-Electron Energy of Benzenoid Hydrocarbons

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The application of the Gauss-Chebyshev quadrature to the integral type formula for the total π-electron energy (E_π) leads to the well-known relation between the Hosoya modified topological index $\tilde{Z}$ and E_π. Possible alternative formulae are discussed and tested on some benzenoid hydrocarbons.

Introduction

Hosoya and Gutman have introduced [1] the modified topological index $\tilde{Z}_G$ as

$$\tilde{Z}_G = i^{-N}\,\Phi(G, i), \tag{1}$$

where $\Phi(G, x)$ is the characteristic polynomial [2] of the molecular graph G having N vertices and M edges; and $i = \sqrt{-1}$. In the case of the benzenoid hydrocarbons, the index $\tilde{Z}_G$ has been found to be related to the total π-electron energy corresponding to G by means of the formula [1, 3, 4]

$$E_\pi = 2.640 \ln \tilde{Z}_G + 0.141. \tag{2}$$

The approximately linear dependence of E_π on $\ln \tilde{Z}_G$ has been attributed to the almost linear relation between the functions $\ln(1 + x^2)$ and $|x|$ for $-3 \leqq x \leqq 3$ [3].

It has been shown [5] that the total π-electron energy conforms to the integral formula

$$E_\pi = \frac{1}{\pi} \int_{-\infty}^{+\infty} x^{-2} F(x)\,\mathrm{d}x, \tag{3}$$

where

$$F(x) = \ln[(-i\,x)^N \Phi(G, i/x)]. \tag{4}$$

The Gauss-Chebyshev Quadrature

The direct integration in (3) cannot be carried out because of the non-elementary character of the integral. However, there are some other possibilities to deal with (3) in order to obtain approximate formulae for E_π. The first one is to use a suitable function $F^*(x)$ that reproduces the asymptotic behaviour of $F(x)$ and then to evaluate the integral. This procedure has been worked out extensively by Gutman and co-workers [4, 6, 7]. The second possibility, which seems to be unnoticed in chemical literature, is to evaluate (3) by means of approximate numerical quadratures. In the present paper we discuss the use of one of such approaches; namely the Gauss-Chebyshev quadrature [8].

This kind of the numerical integration is applicable to functions with the weighting factor $(1 - x^2)^{-1/2}$. The formula for the L-point quadrature is

$$\int_{-1}^{+1} (1 - x^2)^{-1/2} h(x)\,\mathrm{d}x \approx \frac{\pi}{L} \sum_{j=1}^{L} h\left[\cos\frac{(2j-1)\,\pi}{2L}\right]. \tag{5}$$

Let us substitute $x = t(1 - t^2)^{-1/2}$ in the integral (3). Then we obtain

$$E_\pi = \frac{1}{\pi} \int_{-1}^{+1} \frac{\mathrm{d}t}{\sqrt{1 - t^2}}\, t^{-2} F\left(\frac{t}{\sqrt{1 - t^2}}\right). \tag{6}$$

Thus, the application of (5) provides

$$E_\pi \approx \frac{1}{L} \sum_{j=1}^{L} (\cos a_j)^{-2} F(\operatorname{ctg} a_j), \tag{7}$$

where

$$a_j = \frac{(2j-1)\,\pi}{2L}. \tag{8}$$

Although, the accurate result in (7) is achieved for $L \to \infty$, and the computation of E_π with an error of 0.01 requires L of the order 100, some discussion is needed for the two simple cases $L = 2$ and $L = 3$.

For $L = 2$ we have $a_1 = \frac{1}{4}\pi$ and $a_2 = \frac{3}{4}\pi$. This gives

$$E_\pi^{(2)} = 2F(1) = 2 \ln \tilde{Z}_G, \tag{9}$$

where $E_\pi^{(2)}$ is the approximation for E_π. The formula (9) greatly underestimates E_π, but when we assume that $E_\pi^{(2)}$ and E_π are linearly related by

$$E_\pi = a\,E_\pi^{(2)} + b, \tag{10}$$

where a and b are some empirical parameters, we arrive immediately at the Hosoya-Gutman-Aihara relation (2).

Table 1. Comparison of the various approximations for E_π.

Compound	$E_\pi^{(2)}$	$E_\pi^{(3)}$	E_π Eq. (10)	E_π Eq. (13)	E_π exact
Benzene	5.991	6.744	8.015	8.054	8.000
Naphthalene	10.272	11.636	13.677	13.691	13.682
Anthracene	14.545	16.499	19.327	19.295	19.314
Phenanthrene	14.612	16.607	19.416	19.420	19.448
Tetracene	18.821	21.368	24.984	24.906	24.931
Chrysene	18.947	21.564	25.150	25.132	25.192
Triphenylene	19.000	21.638	25.219	25.217	25.274
Pyrene	16.957	19.308	22.518	22.532	22.505
Perylene	21.324	24.284	28.294	28.266	28.245
Coronene	26.067	29.824	34.567	34.651	34.572

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The same treatment for $L = 3$ leads to

$$E_\pi^{(3)} = \tfrac{1}{3}[M + \tfrac{8}{3} F(\sqrt{3})], \quad (11)$$

Since

$$F(\sqrt{3}) = \ln [(-\sqrt{3}\, i)^N \Phi(G, i/\sqrt{3})] = \ln Y_G, \quad (12)$$

the evaluation of $E_\pi^{(3)}$ requires just the same computational effort as the evaluation of $E_\pi^{(2)}$. Y_G can be treated as some new topological index corresponding to the graph G.

The numerical testing, carried out on a set of 10 selected benzenoid hydrocarbons, shows that the formula

$$E_\pi = a\, E_\pi^{(3)} + b \quad (13)$$

with the optimized parameters $a = 1.152$ and $b = 0.282$ gives almost the same error in E_π as the formula (10) with $a = 1.323$ and $b = 0.090$ (Table 1). Thus we have an alternative approach for an estimation of the total π-electron energy of benzenoid systems. Finally, it should be pointed out that the application of the Gauss-Chebyshev quadrature with $L > 3$ points leads to a family of various other approximations for E_π.

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