# On a class of approximate formulas for total π-electron energy of benzenoid hydrocarbons

IVAN GUTMAN[#] and TANJA SOLDATOVIĆ

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

The method for obtaining approximate formulas of the ($n$, $m$)-type for the total -electron energy of benzenoid hydrocarbons (communicated in *J. Serb. Chem. Soc.* **54** (1989) 189) is simplified and extended so as to include arbitrary spectral moments. The accuracy of the formulas thus obtained is very good and these need no additional fitting by means of empirically determined parameters.

*Keywords*: total -electron energy, benzenoid hydrocarbons, spectral moments.

## INTRODUCTION

Some time ago, a method was proposed[1] for obtaining approximate formulas for the total -electron energy of benzenoid hydrocarbons, by using the expressions (known at that time) for the spectral moments $M_2$, $M_4$ and $M_6$. In the meantime analogous expressions have also been obtained[2] for the spectral moments $M_8$ and $M_{10}$, and much additional progress was achieved in the theory of total -electron energy.[3] As a consequence of this, it became possible to extend and generalize the mentioned method[1] and, at the same time, make it significantly simpler. In this paper, the results obtained along these lines are communicated.

The following (standard) notation and terminology are used.[3–5] The molecular graph, representing a benzenoid hydrocarbon, has $n$ veritces and $m$ edges. Its eigenvalues are $_1$, $_2$, ..., $_n$. Then the total -electron energy (calculated within the HMO model and expressed in -units[6]) is given by

$$E = \sum_{i\ 1}^{n} |\ _i| \tag{1}$$

whereas the $k$-th spectral moment of the same graph is

$$M_k = \sum_{i\ 1}^{n} (\ _i)^k \tag{2}$$

---

[#] Serbian Chemical Society active member.

All odd spectral moments of benzenoid systems are equal to zero. Expressions for the even spectral moments are known[2] up to $k = 10$ and read as follows:

$$M_2 = 2\,m \tag{3}$$

$$M_4 = 18\,m - 12\,n \tag{4}$$

$$M_6 = 158\,m - 144\,n + 48 + 6\,b_6 \tag{5}$$

$$M_8 = 1330\,m - 1364\,n + 704 + 8\,b_8 \tag{6}$$

$$M_{10} = 10762\,m - 11710\,n + 7380 + 10\,b_{10} \tag{7}$$

The form of the terms $b_6$, $b_8$ and $b_{10}$ has been precisely established:[2] $b_6$ is equal to the number of bay regions[5] whereas the structure-dependence of $b_8$ and $b_{10}$ is significantly more complicated. For our considerations is it important that these terms are always much smaller than the corresponding spectral moments. For instance, for bisanthrene ($C_{28}H_{14}$, $n = 28$, $m = 35$), $M_6 = 1558$, $M_8 = 9270$ and $M_{10} = 58870$, whereas $b_6 = 2$, $b_8 = 26$ and $b_{10} = 270$. Therefore, in what follows, the terms $b_6$, $b_8$, $b_{10}$ in Eqs. (5)–(7) are neglected.

## CONSTRUCTING THE APPROXIMATE FORMULAS

In a previous work,[1] the approximate three-parameter spectral density was considered, namely

$$\rho(x) = \begin{cases} 0 & \text{if } x < -q \text{ or } -p < x < +p \text{ or } x > +q \\ h & \text{if } -q \le x \le -p \text{ or } p \le x \le q \end{cases} \tag{8}$$

with $p << q$. Here, the same function $\rho(x)$ is used as our starting point. By means of it approximate, expressions $E^*$ for the total $\pi$-electron energy and $M_k^*$ for the spectral moments could be calculated (for details see[1]):

$$E^* = \frac{n}{2}\,(p + q) \tag{9}$$

$$M_k^* = \frac{n}{k+1}\,(q^k + q^{k-1}\,p + q^{k-2}\,p^2 + \dots + qp^{k-1} + p^k) \tag{10}$$

Formula (10) is applicable for even values of $k$. If $k$ is odd, then $M_k^* = M_k = 0$.

Thus, in order to find an expression for $E^*$, Eq (9), the values of the parameters $p$ and $q$ have to be known. They can be found according to the following procedure.

Select three positive even integers $r$, $s$, $t$, such that $t \le r$. Consider the equations (11) and (12):

$$q^r + q^{r-1}\,p + q^{r-2}\,p^2 + \dots + qp^{r-1} + p^r = \frac{r+1}{n}\,M_r \tag{11}$$

$$q^{r-t} + q^{r-t-1}\,p + q^{r-t-2}\,p^2 + \dots + qp^{r-t-1} + p^{r-t} = \frac{r-t+1}{n}\,M_{r-t} \tag{12}$$

$$q^s + q^{s-1} p + q^{s-2} p^2 + \ldots + qp^{s-1} + p^s = \frac{s\ 1}{n} M_s \qquad (13)$$

Neglect the terms $q^{t-1} p^{r-t-1}$, $q^{t-2} p^{r-t+2}$, ... $qp^{r-1}$ and $p^r$ on the left-hand side of Eq. (11). Then by using (12) one obtains

$$q^t \ \frac{r\ t\ 1}{n} M_{r\ t} \ \frac{r\ 1}{n} M_r$$

from which

$$q \ \left[ \frac{r\ 1}{r\ t\ 1} \ \frac{M_r}{M_{r-t}} \right]^{1/t} \qquad (14)$$

Next, in Eq. (13) neglect the terms $q^{s-3} p^3$, $q^{s-4} p^4$, ..., $qp^{s-1}$ and $p^s$. This results in

$$q^{s\ 2}(q^2 \ qp \ p^2) \ \frac{s\ 1}{n} M_s$$

which is a quadratic equation in the unknown $p$. Its solution reads:

$$p \ \frac{1}{2} \ q \ \sqrt{\frac{4(s\ 1)}{nq^{s\ 2}} M_s \ 3q^2}$$

Finally, one arrive at:

$$E_A^* \ E_A^*(r,s,t) \ \frac{n}{4} \ q \ \sqrt{\frac{4(s\ 1)}{nq^{s\ 2}} M_s \ 3q^2} \qquad (15)$$

Another approximate expression of the same kind is obtained by additionally neglecting the term $q^{s-1} p$ in (13), in this case a linear equation in the unknown $p$ is obtained. This yields:

$$E_B^* \ E_B^*(r,s,t) \ \frac{(s\ 1)M_s}{2q^{s-1}} \qquad (16)$$

In both Eqs. (15) and (16) $q$ is determined by the formula (14).

Thus, both approximations $E_A^*$ and $E_B^*$ for the total $\pi$-electron energy depend on three spectral moments: $M_r$, $M_s$ and $M_{r-t}$. When the expressions (3)–(7) are used (with $b_6 = b_8 = b_{10} = 0$), then one arrives at a class of $(n, m)$-type formulas for the total $\pi$-electron energy.

Note that Eqs. (15) and (16) are significantly simpler than the expressions reported in an earlier paper.[1] In fact, in that paper the formulas $E_A^*(4, 2, 2)$, $E_A^*(6, 2,$

2), $E_A{}^*(6, 2, 4)$, $E_A{}^*(6, 4, 2)$, $E_B{}^*(4,2,2)$, $E_B{}^*(6, 2, 2)$, $E_B{}^*(6, 2, 4)$ and $E_B{}^*(6, 4, 2)$ were considered, but were presented in a much more complicated (yet equivalent!) algebraic form.

## NUMERICAL WORK

In view of Eqs. (3)–(7), the formulas $E_A{}^*(r, s, t)$ and $E_B{}^*(r, s, t)$ for $r, s, t = 2, 4, 6, 8, 10$ with the restriction $t \ r$ were examined. However, not all such formulas are different. The following cases of coincidence between $E_A{}^*$ and $E_B{}^*$ have been noticed:

$$E_A{}^* (r, r, r) = E_B{}^* (r, r, r) \qquad \text{for } r = 2, 4, 6, ...$$

$$E_A{}^* (r, r, 2) = E_A{}^* (r, r-2, r) \qquad \text{for } r = 2, 4, 6, ...$$

$$E_B{}^* (r, r, 2) = E_B{}^* (r, r-2, r) \qquad \text{for } r = 2, 4, 6, ...$$

Note that for $r = s = t = 2$ both $E_A{}^*$ and $E_B{}^*$ reduce to the long-known McClelland formula.[3]

Bearing in mind the above coincidences, the class constructed by us embraces 136 distinct $(n, m)$-type approximate formulas fot the total -electron energy, of which only 8 have been previously[1] examined. The quality of all these formulas was tested on a standard data base consisting of 105 polycyclic Kekuléan benzenoid hydrocarbons.[7] Full details of the numerical work are available from the authors (T. S.) upon request.

Here just a limited selection of our results are presented. Some statistical data for the six best approximations of the form:

$$E = a E_A{}^* (r, s, t) \qquad (17)$$

$$E = a E_B{}^* (r, s, t) \qquad (18)$$

are given in Table I.

The multipliers $a$ were determined by least-squares fitting.

From the data given in Table I (and from the data not reported here), it can be concluded that both the approximations (17) and (18) are remarkably accurate, and that this holds for all the studied choices of $r, s, t$. The multipliers $a$ have values very close to unity, revealing that there is no need for "improving" the expressions (15) and (16) by means of empirically adjusted parameters.

TABLE I. The six best formulas of the form (17) and (18) for $r$, $s$, $t$ 10; $R$ = correlation coefficient: $ARE$ = average relative error (in %), $ME$ = maximal relative error observed (in %); notice that in all cases the multipliers $a$ have values very close to unity

| Eq. | $r$ | $s$ | $t$ | $R$ | $ARE$ | $ME$ | $a$ |
|---|---|---|---|---|---|---|---|
| (17) | 4 | 2 | 2 | 0.99981 | 0.33 | 1.2 | 1.015 |
| (17) | 4 | 2 | 4 | 0.99982 | 0.35 | 1.2 | 1.031 |
| (17) | 6 | 2 | 6 | 0.99979 | 0.37 | 1.4 | 1.031 |
| (17) | 2 | 2 | 2 | 0.99982 | 0.38 | 1.5 | 1.049 |
| (17) | 6 | 2 | 4 | 0.99976 | 0.38 | 1.4 | 1.023 |
| (17) | 6 | 6 | 4 | 0.99976 | 0.38 | 1.4 | 1.023 |
| (18) | 4 | 2 | 2 | 0.99980 | 0.33 | 1.3 | 1.010 |
| (18) | 4 | 2 | 4 | 0.99982 | 0.34 | 1.2 | 1.029 |
| (18) | 6 | 2 | 6 | 0.99978 | 0.37 | 1.4 | 1.029 |
| (18) | 2 | 2 | 2 | 0.99982 | 0.38 | 1.5 | 1.049 |
| (18) | 6 | 2 | 4 | 0.99973 | 0.40 | 1.4 | 1.020 |
| (18) | 6 | 6 | 4 | 0.99973 | 0.40 | 1.4 | 1.020 |

In spite of the quite different algebraic forms of $E_A{}^*$ and $E_B{}^*$, Eqs. (15) and (16), the accuracy of the two approximations is basically the same. From Table I, it can be seen that three among our formulas (in each of the two cases) are better than the McClelland approximation.

И З В О Д

О ЈЕДНОЈ КЛАСИ АПРОКСИМАТИВНИХ ФОРМУЛА ЗА УКУПНУ -ЕЛЕКТРОНСКУ ЕНЕРГИЈУ БЕНЗЕНОИДНИХ УГЉОВОДОНИКА

ИВАН ГУТМАН и ТАЊА СОЛДАТОВИЋ

*Природно-математички факултет , Универзитет у Крагујевцу, Крагујевац*

Једна метода за добивање апроксимативних формула $(n, m)$-типа за укупну -електронску енергију бензеноидних угљоводоника (саопштена у *J. Serb. Chem. Soc.* **54** (1989) 189) је поједностављена и проширена тако да укључује произвољне спектралне моменте. Тачност овако добивених формула је веома добра и оне не захтевају додатно подешавање помоћу емпиријски одређених параметара.

(Примљено 19. јула 2000)

REFERENCES

1. I. Gutman, A. Graovac S. Vuković, S. Marković, *J. Serb. Chem. Soc.* **54** (1989) 189
2. S. Marković, I. Gutman, *J. Mol. Struct. (Theochem)* **235** (1991) 771
3. I. Gutman, *Topics Curr. Chem.* **162** (1992) 29
4. I. Gutman, O. E. Polansky, *Mathematical Concepts in Organic Chemistry,* Springer-Verlag, Berlin, 1986

5. I. Gutman, S. J. Cyvin, *Introduction to the Theory of Benzenoid Hydrocarbons,* Springer-Verlag, Berlin, 1989
6. C. A. Coulson, B. O'Leary, R. B. Mallion, *Hückel Theory for Organic Chemists,* Academic Press, London, 1978
7. R. Zahradnik, J. Pancir, *HMO Energy Characteristics,* Plenum Press, New York, 1970.