match no. 26 pp. 123-135 1991

McCLELLAND-TYPE APPROXIMATIONS FOR TOTAL π-ELECTRON ENERGY OF BENZENOID HYDROCARBONS*

Ivan GUTMAN

Faculty of Science, University of Kragujevac, Kragujevac, Yugoslavia

(received: June 1991)

Abstract. McClelland-type approximate formulas for total π-electron energy have the form $C\, m^p\, n^{1-p}$ where n and m are the numbers of carbon atoms and carbon-carbon bonds, respectively, of the conjugated hydrocarbon examined, p is a fixed parameter and C is an empirically adjusted constant. The original McClelland approximation corresponds to $p = 1/2$. We show how McClelland-type formulas are obtained by combining the information contained in various spectral moments.

Introduction

One of the general goals of theoretical chemistry is to reveal the dependence of various physico-chemical properties of substances on molecular structure. A long examined special problem of this kind is the question how the HMO total π-electron energy (E) of a conjugated molecule depends on the topology of the π-electron network. Bearing in mind the direct relation between E and the standard gas-phase enthalpies of the respective compounds [1,2] the answer to this question

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* Part LXXII of the series *"Topological Properties of Benzenoid Systems"*

would help us to better understand the structural factors influencing the thermodynamic stability (and, consequently, the aromaticity) of polycyclic conjugated molecules. The relatively simple mathematical form of E gives hope that the elucidation of its topology-dependence is a feasible task. The first work along these lines appeared in the early fourties [3] and the problem is continuously examined ever since.

For a bibliography of the early works on E see [4]. A detailed survey of the theory of total π-electron energy can be found in [2].

An important step forward in the study of E was the discovery made by McClelland [5] that in the case of conjugated hydrocarbons, E is bounded from above by a simple function of the numbers of carbon atoms (n) and carbon-carbon bonds (m):

$$E \leq \sqrt{2\ m\ n}\ . \tag{1a}$$

The finding of the estimate (1a) stimulated a number of further investigations [6-10] which resulted in a variety of lower and upper bounds for E. In particular, the following lower bound for E

$$E \geq (16/27)^{1/2}\ \sqrt{2\ m\ n} \tag{1b}$$

was recently shown to hold for benzenoid hydrocarbons [10].

In the same paper [5] McClelland showed that a fairly good linear correlation exists between E and its upper bound, namely that E can be approximated by means of

$$E \approx C\ m^{1/2}\ n^{1/2} \tag{2}$$

where C is a constant obtained by least-squares fitting. Taking into account eqs. (1a) and (1b) it is reasonable to expect that formula (2) may correctly reproduce the size-dependency of E. Indeed, numerical

testing revealed [11-14] that in the case of benzenoid hydrocarbons the McClelland expression (2) gives excellent results and is able to reproduce some 99.6% of E. Furthermore, (2) was found [11-14] to be the most accurate approximation among all known (n,m)-type formulas for E.

In this paper we develop a method for approximating E by using the spectral moments. We then show that the McClelland formula (2) is a necessary consequence of taking into account only the structural information contained in the second spectral moment. By employing higher spectral moments we arrive at a class of generalized forms of the McClelland approximation, namely

$$E \approx C\, m^{p}\, n^{1-p} \quad . \tag{3}$$

Numerical testing shows that the best results with formula (3) are obtained by choosing p = 1/2 and p = 1/3.

Eigenvalues and Spectral Moments of Conjugated Molecules

Let the conjugated hydrocarbon considered be represented by a molecular graph in the usual manner [2]. Let $x_1, x_2, \ldots, x_n$ be the eigenvalues of the adjacency matrix of this graph. In other words x_1, $x_2, \ldots x_n$ constitute the spectrum of the respective molecular graph [15].

If the graph eigenvalues are arranged in a non-decreasing order, then the HMO total π-electron energy (in β units) conforms to the relation

$$E = 2 \sum_{i=1}^{[n/2]} x_i \tag{4}$$

where [n/2] denotes the integer part of n/2. If $x_{[n/2]} \geq 0 \geq x_{[n/2]+1}$

then eq. (4) is readily transformed into

$$E = \sum_{i=1}^{n} |x_i| \quad . \tag{5}$$

Eq. (5) is true for the great majority of conjugated systems of chemical interest; it holds for all benzenoid hydrocarbons.

The quantity

$$M_k = \sum_{i=1}^{n} (x_i)^k \tag{6}$$

is called the k-th spectral moment (of the respective graph of the respective conjugated molecule). Although spectral moments have been empolyed in the topological theory of conjugated molecules already in the early seventies [16,17] only quite recently they found remarkable applications in both molecular [18-20] and solid-state physical chemistry [20-23].

According to the definition (6) the zeroth spectral moment is, in a trivial manner, given by

$$M_0 = n \quad . \tag{7}$$

Because of the pairing theorem [2], the odd spectral moments of alternant hydrocarbons (and therefore of all benzenoids) are equal to zero:

$$M_{2k+1} = 0 \qquad k = 1,2,3,\ldots \quad .$$

It is well known that the secon spectral moment conforms to a simple relation:

$$M_2 = 2\ m \quad . \tag{8}$$

The fourth spectral moment of benzenoid systems was first reported in [17] and was eventually rediscovered several times [7,8,24,25]. It has a remarkably simple form:

$$M_4 = 18\ m - 12\ n \quad .$$

Dias [26] and later independently Hall [25] arrived at results which are equivalent to the formula

$$M_6 = M_6^o + 6\ r_6$$

where

$$M_6^o = 158\ m - 144\ n + 48$$

and where r_6 denotes the number of bay regions. Since r_6 is much smaller (usually two or more orders of magnitude) than the term M_6^o, it can be neglected in many practical applications (see e.g. [9,13]).

Combinatorial expressions for the eight and the tenth spectral moments of benzenoid hydrocarbons are also known [27]. They are of the form

$$M_k = M_k^o + k\ r_k \quad , \quad k = 8,\ 10$$

where

$$M_8^o = 1330\ m - 1364\ n + 704$$

$$M_{10}^o = 10762\ m - 11710\ n + 7380$$

and where r_8 and r_{10} are small correction terms which in a complicated (but precisely determined way [27]) depend on the structure of the benzenoid molecule considered.

In this work we approximate M_k , $k = 6,8,10$ by means of M_k^o .

Spectral Density of Conjugated Molecules

The spectral density (called also [20,22] density of states, DOS) is a function $\Gamma(G, x)$ associated to a graph G with the property that $\int_a^b \Gamma(G, x)\, dx$ is equal to the number of eigenvalues of G lying in the interval (a, b). Within the spectral-density-formalism eqs. (4)-(6) are rewritten as

$$E = 2 \int_0^{\infty} x\, \Gamma(G, x)\, dx = \int_{-\infty}^{+\infty} |x|\, \Gamma(G, x)\, dx \tag{9}$$

$$M_k = \int_{-\infty}^{+\infty} x^k\, \Gamma(G, x)\, dx \quad . \tag{10}$$

The spectral-density formalism seems to be first introduced into the topological theory of conjugated molecules by Burdett and Lee [21-23] and independently by Cioslowski [28-31]. Bearing in mind that a finite graph has a discrete spectrum, the respective spectral density is of the form

$$\Gamma(G, x) = \sum_{i=1}^{n} \delta(x - x_i) \tag{11}$$

where $\delta(x)$ stands for the Dirac delta function. Obviously, the knowledge of $\Gamma(G, x)$ is equivalent to the knowledge of all the eigenvalues of G. However, in many applications it is meaningful to approximate the right-hand side of (11) by a reasonably chosen analytical function [13,28-31].

On the Origin of the McClelland Approximation

Suppose that the entire information which we possess about the graph spectrum of a conjugated system it its k-th spectral moment (plus the trivial zeroth moment). What can we say about E ?

We may try to represent the spectral density by means of an analytical function. Since this function must depend on the structure of the molecular graph and since we possess a limited information about this dependence, at most what we can do is to employ the Ansatz

$$\Gamma(G, x) = A\, \gamma(B\, x) \tag{12}$$

where A and B are scaling parameters depending on G whereas $\gamma(x)$ is a universal function equal for all members of a class of conjugated systems (e.g. for all Kekulèan benzenoid hydrocarbons). The Ansatz is essentially the same as Cioslowski's "universal distribution approximation" [31].

Substituting (12) back into (9) and (10) we immediately obtain

$$M_k = A\, B^{-(k+1)}\, L_k \qquad k = 0,2,4,6,\ldots$$

$$E = A\, B^{-2}\, L$$

where the auxiliary quantity L_k depends solely on k :

$$L_k = \int_{-\infty}^{+\infty} x^k\, \gamma(x)\, dx$$

while L is a constant:

$$L = \int_{-\infty}^{+\infty} |x|\, \gamma(x)\, dx \quad .$$

Direct calculation yields

$$E^{(k)} = Q_k \left[M_k \, (M_0)^{k-1} \right]^{1/k} \tag{13}$$

where the multiplier Q_k depends solely on k :

$$Q_k = L \left[L_k \, (L_0)^{k-1} \right]^{-1/k} .$$

Here $E^{(k)}$ stands for the approximation of E obtained by using the k-th spectral moment and k = 2,4,6,... .

Now, if k = 2 then because of (7) and (8) formula (13) reduces to the original McClelland approximation (2). Thus we proved the following result.

If the only available information about the spectrum of the molecular graph are the zeroth and the second moments, and if the spectral density conforms to (12), then irrespective of the actual form of the function $\gamma(x)$ the total π-electron energy is approximated by means of the McClelland formula (2)..

Beyond the McClelland Approximation

For k = 4,6,8 and 10 substituting M_4, M_6^o, M_8^o and M_{10}^o, respectively, back into (13) we obtain novel (n,m)-type topological formulas for E, namely,

$$E^{(4)} = (18)^{1/4} \, Q_4 \left[(m - \frac{2}{3} n) \, n^3 \right]^{1/4} \tag{14}$$

$$E^{(6)} = (158)^{1/6} \, Q_6 \left[(m - \frac{72}{79} n + \frac{24}{79}) \, n^5 \right]^{1/6} \tag{15}$$

$$E^{(8)} = (1330)^{1/8} \, Q_8 \left[(m - \frac{682}{665} n + \frac{352}{665}) \, n^7 \right]^{1/8} \tag{16}$$

$$E^{(10)} = (10762)^{1/10}\, Q_{10} \left[(m - \frac{5855}{5381}\, n + \frac{3690}{5381})\, n^{9} \right]^{1/10} \quad . \qquad (17)$$

In benzenoid systems the structural parameters n and m obey the identities [32]

$$n = 4\, h + 2 - n_{i} \qquad (18)$$

$$m = 5\, h + 1 - n_{i} \qquad (19)$$

where h and n_{i} are the numbers of hexagons and internal vertices, respectively. Note that n_{i} is usually much smaller than n, m and h. Bearing in mind (18) and (19) we conclude that for sufficiently large benzenoid systems (i.e. for large values of h) the parameters n and m are roughly related as $n/m \approx 4/5$.

Now, for large benzenoid systems the expressions in brackets on the right-hand sides of eqs. (14)-(17) are several orders of magnitude smaller than n^{k-1}. Since $E^{(k)}$ is already an approximation, we will not lose much if we substitute n in these expressions by 0.8 m and neglect the small constant terms. This results in

$$E^{(k)} = C_{k}\, m^{1/k}\, n^{(k-1)/k} \quad , \quad k = 4,6,8,10 \qquad (20)$$

where $C_{4} = (42/5)^{1/4}\, Q_{4}$, $C_{6} = (16906/395)^{1/6}\, Q_{6}$, $C_{8} = (158802/665)^{1/8}\, Q_{8}$ and $C_{10} = (7501114/5381)^{1/10}\, Q_{10}$. Obviously, these are special cases of McClelland-type approximate formulas (3), p = 1/k. As a matter of fact, eqs. (20) provide a straightforward motivation for the study of the class of topological formulas given by (3).

Numerical Work

For testing the McCleiland-type approximation (3) we employed the same data base as in our previous works [11-14], namely a sample consisting of 106 Kekulèan benzenoid hydrocarbons from the book [33]. The exponent p was systematically varied between -10 and $+10$ and the correlation coefficients and the average relative errors were determined. The correlation coefficient has a maximum (= 0.99984) at $p = 0.49 \pm 0.02$ whereas the average relative error has a minimum (= 0.34%) at $p = 0.35 \pm 0.03$. Details of these calculations have been reported elsewhere [34].

Thus the correlation coefficient as an optimization criterion clearly indicates that the original McClelland approximation (namely eq. (3) with $p = 1/2$) is the best in the entire class of topological formulas examined. If, however, we optimize the exponent p with respect to the average relative error, then a value apparently close to $p = 1/3$ is obtained. Using $p = 1/3$ in the expression (3), the expected error of a calculated E-value is reduced by almost 20% relative to the analogous error of the original McClelland formula (2).

The tantalizing fact in connection with this finding is that $p = 1/3$ does not correspond to any of the approximations of the type (13). Because $p = 1/k$, the optimal value of k found by us is close to 3. This is in disharmony with eq. (13) in which k must be an even number.

Formally, this difficulty could be resolved by averaging $E^{(k)}$ over two or more values of k ; a geometric mean would suit here the best. Taking into account formula (20), it is not difficult to see that the combination $E^{(2,4,4)} = [E^{(2)}\ E^{(4)}\ E^{(4)}]^{1/3}$ has the required behaviour, namely

$$E^{(2,4,4)} = C\ m^{1/3}\ n^{2/3} \quad . \tag{21}$$

It is, however, not at all clear why such an artificial construction would have to be applied. Since our empirical testing [34] shows that the formula (21) is superior to the approximation (20), it remains a task for the future to find a convincing theoretical explanation for its success.

Acknowledgement. This paper contains results which the author obtained at the Vanderbilt University, Nashville, Tennessee in 1989 and 1990. In February 1990 the paper was accepted for publication by the *Zeitschrift für physikalische Chemie (Leipzig)*, but did not appear there because in the meantime the journal ceased to exist. The financial support of this research by the Fulbright Program and the hospitality of the staff of the Chemistry Department of the Vanderbilt University are gratefully acknowledged.

References

[1] L. J. Schaad and B. A. Hess, J. Amer. Chem. Soc. **94**, 3068 (1972).

[2] I. Gutman and O. E. Polansky, *Mathematical Concepts in Organic Chemistry*, Springer-Verlag, Berlin 1986.

[3] C. A. Coulson, Proc. Cambridge Phil. Soc. **36**, 201 (1940).

[4] I. Gutman, Match **4**, 195 (1978).

[5] B. J. McClelland, J. Chem. Phys. **54**, 640 (1971).

[6] I. Gutman, Chem. Phys. Letters **24**, 283 (1974).

[7] L. Türker, Match **16**, 83 (1984).

[8] J. Cioslowski, Z. Naturforsch. **40a**, 1167 (1985).

[9] I. Gutman, L. Türker and J. R. Dias, Match **19**, 147 (1986).

[10] I. Gutman, J. Chem. Soc. Faraday Trans. **86**, 3373 (1990).

[11] I. Gutman, L. Nedeljković and A. V. Teodorović, Bull. Soc. Chim. Beograd **48**, 495 (1983).

[12] I. Gutman, S. Marković, A. V. Teodorović and Ž. Bugarčić, J. Serb. Chem. Soc. **51**, 145 (1986).

[13] I. Gutman, A. Graovac, S. Vuković and S. Marković, J. Serb. Chem. Soc. **54**, 189 (1989).

[14] I. Gutman, Topics. Curr. Chem., in press.

[15] D. Cvetković, M. Doob and H. Sachs, *Spectra of Graphs - Theory and Application*, Academic Press, New York 1980.

[16] I. Gutman and N. Trinajstić, Chem. Phys. Letters **17**, 535 (1972); **20**, 257 (1973).

[17] I. Gutman, Croat. Chem. Acta **46**, 209 (1974).

[18] Y. Jiang, A. Tang and R. Hoffmann, Theor. Chim. Acta **66**, 183 (1984).

[19] Y. S. Kiang and A. C. Tang, Internat. J. Quantum Chem. **29**, 229 (1986).

[20] Š. Pick, Coll. Czech. Chem. Commun. **53**, 1607 (1988).

[21] J. K. Burdett, S. Lee and W. C. Sha, Croat. Chem. Acta **57**, 1193 (1984).

[22] J. K. Burdett and S. Lee, J. Amer. Chem. Soc. **107**, 3050, 3063 (1985).

[23] J. K. Burdett, S. Lee and T. J. McLarnan, J. Amer. Chem. Soc. **107**, 3083 (1985).

[24] J. R. Dias, Nouv. J. Chim. **9**, 125 (1985).

[25] G. G. Hall, Theor. Chim. Acta **70**, 323 (1986).

[26] J. R. Dias, Theor. Chim. Acta **68**, 107 (1985).

[27] S. Marković and I. Gutman, J. Mol. Struct. (THEOCHEM), in press.

[28] J. Cioslowski, Match **20**, 95 (1986).

[29] J. Cioslowski and O. E. Polansky, Theor. Chim. Acta **74**, 55 (1988).

[30] A. Graovac and J. Cioslowski, Croat. Chem. Acta **61**, 797 (1988).

[31] J. Cioslowski, Topics Curr. Chem. **153**, 85 (1990).

[32] I. Gutman and S. J. Cyvin, *Introduction to the Theory of Benzenoid Hydrocarbons*, Springer-Verlag, Berlin 1989.

[33] R. Zahradnik and J. Pancir, *HMO Energy Characteristics*, Plenum Press, New York 1970.

[34] I. Gutman, D. Utvić and A. K. Mukherjee, J. Serb. Chem. Soc. **56**, 59 (1991).