

Iterative estimation of total π -electron energy

LEMI TÜRKER¹ and IVAN GUTMAN^{2, *#}

¹Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey and ²Faculty of Science, University of Kragujevac, P. O. Box 60, 34000 Kragujevac, Serbia and Montenegro

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Abstract: In this work, the lower and upper bounds for total π -electron energy (E) was studied. A method is presented, by means of which, starting with a lower bound E_L and an upper bound E_U for E , a sequence of auxiliary quantities E_0, E_1, E_2, \dots is computed, such that $E_0 = E_L, E_0 < E_1 < E_2 < \dots$, and $E_\infty = E_U$. Therefore, an integer k exists, such that $E_k \leq E < E_{k+1}$. If the estimates E_L and E_U are of the McClelland type, then k is called the *McClelland number*. For almost all benzenoid hydrocarbons, $k = 3$.

Keywords: total π -electron energy, bound for total π -electron energy, McClelland number.

INTRODUCTION

In this paper the total π -electron energy ($E = E(G)$) of conjugated hydrocarbons, as computed within the framework of the Hückel molecular-orbital approximation, where G stands for the underlying molecular graph is considered. Details of the theory of this important quantum-theory-based π -electron characteristic of conjugated molecules were outlined in a recent review,¹ as well as in several earlier publications.^{2–4} The estimation of E (that is, the construction of lower and upper bounds for E) is one of the most extensively elaborated topic in this theory; in the review¹ an exhaustive bibliography on this matter can be found.

The first estimates for $E(G)$ were reported by McClelland.⁵ Of these, the upper bound

$$E_{MC} = \sqrt{2nm} \quad (1)$$

played a significant role in the subsequent development of the theory of E ; for details and further references see the review.¹ In formula (1) n and m stand, respectively, for the number of vertices and edges of the molecular graph G , *i.e.*, for the

* Author for correspondence.

Serbian Chemical Society active member.

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number of carbon atoms and carbon–carbon bonds of the respective conjugated molecules.³

The importance of (1) is based on the fact that the total π -electron energy of conjugated hydrocarbons can be reasonably well approximated by means of the simple formula⁵

$$E \approx a E_{MC} \quad (2)$$

with $a \approx 0.9$. The quality of the approximation (2) was confirmed by several extensive comparative numerical studies.^{4,6,7}

Eventually several lower bounds for E were discovered,^{8–13} all having the form gE_{MC} , where g is some constant. These are referred to as lower bounds of McClelland type. The simplest among them is⁸ $1/2 E_{MC}$, which will be employed in the present work.

IMPROVING ESTIMATES FOR E

Suppose that a lower bound E_L and an upper bound E_U for the total π -electron energy E are known. In other words, assume that for all members G of a considered class of molecular graphs the inequalities

$$E_L < E(G) < E_U \quad (3)$$

are satisfied.

Construct a sequence E_0, E_1, E_2, \dots in the following manner. Let $E_0 = E_L$ and let for $i = 1, 2, \dots$, the quantity E_i be recursively defined as

$$E_i = \sqrt{E_{i-1}E_U}$$

It is easy to show that

$$E_0 < E_1 < E_2 < \dots$$

and that

$$\lim_{i \rightarrow \infty} E_i = E_U$$

Then, in view of (3), for a certain k it must be

$$E_k \leq E(G) < E_{k+1} \quad (4)$$

where k depends on the choice of E_L, E_U , as well as on the actual molecular graph G . Evidently, the estimates (4) are better than (3), and their quality increases with increasing value of k . Furthermore,

$$E(G) \approx \sqrt{E_k E_{k+1}}$$

should be a reasonably good approximation for the total π -electron energy, especially if k is large enough.

If both E_L and E_U are of the McClelland type, say $E_L = g_L E_{MC}$ and $E_U = g_U E_{MC}$, then each member of the series E_0, E_1, E_2, \dots will be of the McClelland type. In particular,

$$\begin{aligned} E_1 &= (g_L)^{1/2} (g_U)^{1/2} E_{MC} \\ E_2 &= (g_L)^{1/4} (g_U)^{3/4} E_{MC} \\ E_3 &= (g_L)^{1/8} (g_U)^{7/8} E_{MC} \\ &\dots \quad \dots \\ E_i &= (g_L)^{1/2^i} (g_U)^{1-1/2^i} E_{MC} \\ &\dots \quad \dots \end{aligned}$$

In what follows, the case when⁸ $g_L = 1/2$ and when⁵ $g_U = 1$ is examined. Then for $i = 0, 1, 2, \dots$,

$$E_i = 2^{-1/2^i} E_{MC}$$

If for a conjugated system whose molecular graph is G , in accordance with Eq. (4),

$$2^{-1/2^k} E_{MC} \leq E(G) < 2^{-1/2^{k+1}} E_{MC} \quad (5)$$

then we say that k is the *McClelland number* of that conjugated system. Then

$$E(G) \approx 8^{-1/2^{k+2}} E_{MC}. \quad (6)$$

Numerical values of the multipliers $2^{-1/2^k}$ and $8^{-1/2^{k+2}}$ for the first few values of k are given in Table I. The maximal possible relative error of the approximate McClelland-type formula (6) is also indicated in Table I.

TABLE I. The multipliers occurring in the lower bound (5) and in the approximate formula (6), pertaining to the McClelland number k . Note that the multiplier occurring in the upper bound (5) is equal to the lower-bound-multiplier for $k + 1$. When employing the approximate formula (6), the maximal relative error (in %) cannot exceed the value of MRE

k	$2^{-1/2^k}$	$8^{-1/2^{k+2}}$	MRE
1	0.7071	0.7711	9.05 %
2	0.8409	0.8781	4.43 %
3	0.9170	0.9371	2.19 %
4	0.9576	0.9680	1.09 %
5	0.9786	0.9839	0.54 %
6	0.9892	0.9919	0.27 %
7	0.9946	0.9956	0.14 %

NUMERICAL WORK AND CONCLUDING REMARKS

In the general case, the McClelland number k depends on the structure of the particular conjugated molecule to which it corresponds. In view of this, for the practical applicability of Eqs. (5) and (6), it is essential that all (or, at least, the majority) of the conjugated molecules have equal McClelland numbers. In order to test this requirement the k -values for benzenoid hydrocarbons from the book¹⁴ were computed. (Recall that this set became the standard for testing bounds and approximate formulas in the theory of benzenoid hydrocarbons; for details see the papers.^{4,6,7})

Of the 105 benzenoid hydrocarbons examined, only naphthalene, phenanthrene and triphenylene had $k = 4$, whereas for all others it was found that the McClelland number was equal to 3. We are inclined to expect that the three mentioned benzenoid systems are the only exceptions of the general rule, namely that *the McClelland number of all (Kekuléan) benzenoid hydrocarbons is equal to 3*.

The above claim is corroborated by the fact that for $k = 3$ the multiplier in Eq. (6) is remarkably close to the value of the parameter a in Eq. (2), determined by least-squares fitting.^{1,4-7} In the future, it is intended to test the above stated ($k = 3$)-rule on a significantly larger class of conjugated molecules, aiming at its extension to non-benzenoid, in particular non-alternant, polycyclic π -electron systems.

ИЗВОД

ИТЕРАТИВНА ПРОЦЕНА ВРЕДНОСТИ УКУПНЕ π -ЕЛЕКТРОНСКЕ ЕНЕРГИЈЕLEMI TIRKER¹ и ИВАН ГУТМАН²

¹Технички универзитет Средњег Истаока, Анкара, Турска и ²Природно-математички факултет у Крагујевцу

У раду се разматрају доње и горње границе за укупну π -електронску енергију (E). Изложена је метода помоћу које се, полазећи од једне доње границе E_L и једне горње границе E_U за E , одређује низ E_0, E_1, E_2, \dots , такав да је $E_0 = E_L, E_0 < E_1 < E_2 < \dots$, и $E_\infty = E_U$. Због тога, постоји цео број k , такав да је $E_k \leq E < E_{k+1}$. Ако су границе E_L и E_U Меклеландовог типа, онда k називамо *Меклеландов број*. За скоро све бензеноидне угљоводонике, $k = 3$.

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