

Relating Total π -Electron Energy of Benzenoid Hydrocarbons with HOMO and LOMO Energies

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Abstract

Within the Hückel molecular orbital model, the total π -electron energy, E_π , the highest occupied molecular orbital (HOMO) energy, E_{HOMO} , and the lowest occupied molecular orbital (LOMO) energy, E_{LOMO} , can be expressed in terms of eigenvalues of the adjacency matrix of the underlying molecular graph. In this paper, relations between E_π , E_{HOMO} , and E_{LOMO} are examined. Approximate expressions are established, relating E_π with E_{HOMO} and E_{LOMO} in the case of benzenoid hydrocarbons.

1 Introduction

In this paper we apply spectral graph theory to the Hückel molecular orbital (HMO) model. Let G be a molecular graph [4, 5, 11, 22], possessing n vertices and m edges. Let the eigenvalues of the adjacency matrix of G be $\lambda_1, \lambda_2, \dots, \lambda_n$, forming the spectrum of G [3]. We label the eigenvalues so that

$$\lambda_1 \geq \lambda_2 \geq \dots \geq \lambda_n.$$

Then, assuming that n is even, the main energy-based quantities of the HMO theory can be expressed as follows [5, 11, 22]:

- The energy of the lowest occupied molecular orbital (LOMO) is $E_{LOMO} = \lambda_1$.

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- The energy of the highest occupied molecular orbital (HOMO) is $E_{HOMO} = \lambda_{n/2}$.
- The energy of the lowest unoccupied molecular orbital (LUMO) is $E_{LUMO} = \lambda_{n/2+1}$.
- The HOMO–LUMO gap is $\Delta_{HL} = \lambda_{n/2} - \lambda_{n/2+1}$.
- The total π -electron energy is

$$E_{\pi} = 2 \sum_{i=1}^{n/2} \lambda_i . \quad (1)$$

In the above formulas, the energies are expressed in the standard β -units. For details of the HMO theory see [2, 17, 23]. Recall that the HMO model yields its best results (i.e., results that are in the best agreement with experimental findings) in the case of benzenoid hydrocarbons, see for instance in [7, 18, 21].

For the molecular graphs of benzenoid systems with an even number of vertices [6, 9],

$$\lambda_i = -\lambda_{n-i+1} \quad \text{for } i = 1, 2, \dots, n/2$$

$$\sum_{i=1}^{n/2} \lambda_i^2 = m \quad (2)$$

and

$$\prod_{i=1}^{n/2} \lambda_i = K$$

where K is the number of Kekulé structures. Therefore, for Kekuléan benzenoid hydrocarbons (i.e., when n =even and $K > 0$),

$$E_{HOMO} > 0 \quad , \quad E_{LUMO} = -E_{HOMO} \quad , \quad \Delta_{HL} = 2 E_{HOMO} > 0$$

and

$$E_{\pi} = \sum_{i=1}^n |\lambda_i| .$$

The dependence of HMO total π -electron energy on molecular structure was much investigated. The first result along these lines is the McClelland formula [19]

$$E_{\pi} \approx a \sqrt{2mn} \quad (3)$$

where $a \approx 0.9$ is a fitting parameter. By later detailed studies [7, 15] it was established that this seems to be the best n, m -type approximation for E_{π} . However, already in the

1970s, it was objected [10] that the McClelland formula is insensitive of the (small, but significant) energy differences between isomers.

Evidently, in order to go beyond the (n, m) -approximations, one needs to include into consideration some additional topological parameters. In the recent mathematical literature, several bounds for graph energy have been discovered, which make it possible to relate E_π with the HOMO and LOMO energies. Expressed in HMO terms, these bounds are as follows:

$$E_\pi < \sqrt{2mn - n[E_{LOMO} - E_{HOMO}]^2} \quad (4)$$

$$E_\pi < \sqrt{(n-2)[2m - (E_{HOMO})^2 - (E_{LOMO})^2]} + E_{HOMO} + E_{LOMO} \quad (5)$$

$$E_\pi < \sqrt{(n-4)[2m - 2(E_{HOMO})^2 - 2(E_{LOMO})^2]} + 2E_{HOMO} + 2E_{LOMO} \quad (6)$$

$$E_\pi > \frac{E_{HOMO} E_{LOMO} n + 2m}{E_{HOMO} + E_{LOMO}} \quad (7)$$

$$E_\pi > \frac{2\sqrt{E_{HOMO} E_{LOMO}}}{E_{HOMO} + E_{LOMO}} \sqrt{2mn} \quad (8)$$

$$E_\pi > \sqrt{\frac{2E_{HOMO} E_{LOMO}}{(E_{HOMO})^2 + (E_{LOMO})^2}} \sqrt{2mn} \quad (9)$$

$$E_\pi > \sqrt{\frac{2E_{HOMO} E_{LOMO}}{(E_{HOMO})^2 + (E_{LOMO})^2}} \sqrt{(n-2)[2m - (E_{HOMO})^2 - (E_{LOMO})^2]} + E_{HOMO} + E_{LOMO} \quad (10)$$

$$E_\pi > \sqrt{\frac{2E_{HOMO} E_{LOMO}}{(E_{HOMO})^2 + (E_{LOMO})^2}} \sqrt{(n-4)[2m - 2(E_{HOMO})^2 - 2(E_{LOMO})^2]} + 2E_{HOMO} + 2E_{LOMO} \quad (11)$$

The bound (4) was deduced in [12]. The bounds (5) and (6) are reported here for the first time, but they straightforwardly follows from the considerations in the paper [13]. Relations (7) and (8) were established by Oboudi [20], whereas (9)–(11) by one of the present authors [8]. In the case of Kekuléan benzenoid hydrocarbons (consisting of two or more hexagons), all the above inequalities are strict.

In the next section we prove an additional results of the same type, namely inequality

(12).

Theorem 1. *If $E_{HOMO} \geq (3 - \sqrt{8}) E_{LOMO}$, then there is a counterpart of Oboudi's bound (7):*

$$E_\pi < \frac{E_{HOMO} E_{LOMO} n + 4m}{E_{HOMO} + E_{LOMO}}. \quad (12)$$

2 Proving Theorem 1

For the sake of simplicity, denote $E_{LOMO} = \lambda_1$ and $E_{HOMO} = \lambda_{n/2}$ by a and b , respectively.

Noting that

$$\frac{a}{2} - \lambda_i \leq \frac{a}{2} \quad \text{and} \quad \frac{b}{2} - \lambda_i \leq -\frac{b}{2}$$

holds for all $i = 1, 2, \dots, n/2$, we may be tempted to write

$$\left(\frac{a}{2} - \lambda_i\right) \left(\frac{b}{2} - \lambda_i\right) \leq -\frac{ab}{4}$$

which, however, in the general case is incorrect. Examine, therefore, the inequality

$$\left(\frac{a}{2} - x\right) \left(\frac{b}{2} - x\right) \geq -\frac{ab}{4}$$

which can be rewritten as

$$2x^2 - (a + b)x + ab \geq 0.$$

It will hold for all values of the variable x provided the discriminant

$$D = (a + b)^2 - 8ab = b^2 - 6ab + a^2$$

is negative-valued or zero. The relation $D \leq 0$ happens to hold when b belongs to the interval (b_1, b_2) where $b_1 = (3 - \sqrt{8})a$ and $b_2 = (3 + \sqrt{8})a$ are the solutions (in the variable b) of the equation $b^2 - 6ab + a^2 = 0$. Note that $3 - \sqrt{8} \approx 0.17157$.

The condition $b \leq b_2$ is satisfied in a trivial manner. What remains is the condition $b_1 \leq b$. Assume thus that $b \geq (3 - \sqrt{8})a$. Then the inequality

$$\left(\frac{a}{2} - \lambda_i\right) \left(\frac{b}{2} - \lambda_i\right) \geq -\frac{ab}{4}$$

i.e.,

$$2\lambda_i^2 - (a + b)\lambda_i + ab \geq 0 \quad (13)$$

holds for all values of $i = 1, 2, \dots, n/2$. For at least one value of i the above inequalities are strict.

Summing (13) over $i = 1, 2, \dots, n/2$, and taking into Eqs. (1) and (2), we arrive at

$$2m - (a+b)\frac{E_\pi}{2} + ab\frac{n}{2} > 0$$

which directly implies

$$E_\pi > \frac{abn + 4m}{a + b}$$

i. e., the upper bound (12).

3 Approximate formulas for total π -electron energy

McClelland obtained his formula (3) by using the upper bound $E_\pi \leq \sqrt{2mn}$ [19]. Also other upper and lower bounds for HMO total π -electron energy were found to be reasonably well linearly correlated with E_π , see [7, 12–15] for details. In line with this, in this paper we examine approximate formulas for total π -electron energy of the form

$$E_\pi \approx AE^* + B \tag{14}$$

where E^* is one of the expressions occurring on the right-hand side of Eqs. (4)–(11) as well as (12), whereas A and B are determined by least-squares fitting.

In all our earlier works [7, 12–15], the quality of the correlation of the type (14) was tested on a sample consisting of 105 non-isomeric polycyclic Kekuléan benzenoids from the book [24]. Thus, in this sample the parameters n and m vary significantly, and their effect overshadows those of other topological features.

In order to eliminate the effect of the parameters n and m , in the present work we employ sets of benzenoid isomers. In particular, our samples consist of all possible catacondensed benzenoids with a fixed number h of hexagons, $h = 6, 7, 8, 9, 10$. These samples were created by means of the computer program CaGe. Their sizes are 36, 118, 411, 1489, and 5572, respectively. Recall that $n = 4h + 2$ and $m = 5h + 1$.

In Kekuléan benzenoid hydrocarbons, E_{HOMO} is significantly smaller than E_{LOMO} . For instance, in the case of heptacenes ($h = 7$), $0.13 \leq E_{HOMO} \leq 0.59$, whereas the minimum value of E_{LOMO} is 2.52; in the case of octacenes ($h = 8$), $0.11 \leq E_{HOMO} \leq 0.53$, whereas $E_{LOMO} \geq 2.53$. Taking this into account, the right-hand side of (8) can be

transformed as

$$\frac{2\sqrt{E_{HOMO}E_{LOMO}}}{E_{HOMO} + E_{LOMO}}\sqrt{2mn} \approx \frac{2\sqrt{E_{HOMO}E_{LOMO}}}{E_{LOMO}}\sqrt{2mn} = 2\sqrt{\frac{E_{HOMO}}{E_{LOMO}}}\sqrt{2mn}$$

implying a further test-formula

$$E^* = \sqrt{\frac{E_{HOMO}}{E_{LOMO}}}\sqrt{2mn}. \tag{15}$$

The same test-formula would be obtained also from (9).

The results of our numerical testings are shown in the following table; R = the correlation coefficient, ARE = average relative error (in %), MRE = maximal relative error (in %).

	Eq.	R	ARE	MRE		Eq.	R	ARE	MRE
$h = 6$	(4)	0.8552	0.14	0.43		(9)	0.9356	0.09	0.27
	(5)	0.8638	0.13	0.44		(10)	0.9359	0.09	0.27
	(6)	0.8559	0.14	0.45		(11)	0.9362	0.09	0.27
	(7)	0.9075	0.11	0.32		(12)	0.4416	0.24	0.87
	(8)	0.9358	0.09	0.28		(15)	0.9351	0.09	0.27
$h = 7$	(4)	0.7593	0.15	0.58		(9)	0.8925	0.11	0.47
	(5)	0.7847	0.15	0.57		(10)	0.8930	0.11	0.47
	(6)	0.7755	0.15	0.57		(11)	0.8934	0.11	0.47
	(7)	0.8482	0.13	0.51		(12)	0.3109	0.23	1.15
	(8)	0.8929	0.11	0.48		(15)	0.8919	0.11	0.47
$h = 8$	(4)	0.7269	0.16	0.69		(9)	0.8836	0.11	0.45
	(5)	0.7473	0.15	0.60		(10)	0.8843	0.11	0.45
	(6)	0.7373	0.15	0.61		(11)	0.8849	0.11	0.45
	(7)	0.8292	0.13	0.51		(12)	0.2363	0.21	1.34
	(8)	0.8831	0.11	0.46		(15)	0.8835	0.11	0.45
$h = 9$	(4)	0.6827	0.15	0.86		(9)	0.8607	0.11	0.59
	(5)	0.7069	0.15	0.76		(10)	0.8614	0.11	0.59
	(6)	0.6973	0.15	0.77		(11)	0.8303	0.11	2.47
	(7)	0.7978	0.13	0.68		(12)	0.2089	0.20	1.45
	(8)	0.8598	0.11	0.58		(15)	0.8607	0.11	0.59
$h = 10$	(4)	0.6624	0.15	0.98		(9)	0.8495	0.10	0.60
	(5)	0.6887	0.14	0.88		(10)	0.8502	0.10	0.60
	(6)	0.6800	0.14	0.89		(11)	0.8509	0.10	0.59
	(7)	0.7828	0.12	0.76		(12)	0.2114	0.19	1.53
	(8)	0.8485	0.10	0.61		(15)	0.8496	0.10	0.60

From the above table we see that there are five approximate expressions for E_π , namely those based on Eqs. (8), (9), (10), (11), and (15), that have nearly the same accuracy, and that are better than the other examined approximations. Their correlation coefficients are not impressive, but they all reproduce about 99.9% of the HMO total π -electron energy of benzenoid hydrocarbons.

On the other hand, since these formulas have quite different algebraic forms, we must conclude that our study did not succeed to reveal the true (*LOMO*, *HOMO*)-dependence of E_π . Additional research along these lines would be required. George Hall's famous pessimistic opinion [16] that "*the variation in Δ_{HL} from molecule to molecule follows too complicated a pattern to be summarized in general rules*" seems to have not been overcome.

Within classes of isomeric benzenoids, the *LOMO*-energy varies within very narrow limits. In the case of catacondensed species with $h = 6, 7, 8, 9, 10$, these limits are (2.51, 2.62), (2.52, 2.64), (2.53, 2.67), (2.54, 2.68), and (2.54, 2.70), respectively. Bearing this in mind, we may treat the parameter E_{LOMO} as a constant. If so, then the formula (15) is additionally simplified as

$$E^* = \sqrt{E_{HOMO}} \sqrt{2mn} \quad \text{or, equivalently,} \quad E^* = \sqrt{\Delta_{HL}} \sqrt{2mn}. \quad (16)$$

The approximation based on Eq. (16) was recently considered in [14], but was tested only for the Zahradník–Pancíř sample of non-isomeric benzenoids. When testing it for the present samples of isomeric catacondensed benzenoids, we arrive at the following results:

	<i>R</i>	<i>ARE</i>	<i>MRE</i>
$h = 6$	0.9428	0.09	0.25
$h = 7$	0.9038	0.10	0.45
$h = 8$	0.8981	0.10	0.42
$h = 9$	0.8773	0.10	0.57
$h = 10$	0.8668	0.10	0.57

Surprisingly, the approximation (16), in spite of its simple form, is (slightly) better than any of the (*LOMO*, *HOMO*)-type formulas examined above. Therefore, until a numerically better or theoretically more justified dependence of total π -electron energy of benzenoid hydrocarbons on E_{LOMO} and E_{HOMO} is discovered, the approximation based on Eq. (16) may be viewed as the best what we have at the present moment. As shown

in Ref. [14],

$$E_{\pi} \approx \left(A + B \sqrt{E_{HOMO}} \right) \sqrt{2mn} \quad ; \quad A = 0.889, B = 0.035$$

or

$$E_{\pi} \approx \left(A + B \sqrt{\Delta_{HL}} \right) \sqrt{2mn} \quad ; \quad A = 0.889, B = 0.025.$$

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