Dependence of the total π-electron energy on a large number of non-bonding molecular orbitals

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Abstract: Using a recently developed method for computing the effect of non-bonding molecular orbitals (NBMOs) on the total π-electron energy (E), it was found that the dependence of E on the number n_0 of NBMOs is almost perfectly linear. We now show that this regularity remains valid for very large values of n_0, in particular, to hold up to $n_0 = 20$.

Keywords: total π-electron energy, non-bonding molecular orbitals, chemical graph theory.

INTRODUCTION

This paper is concerned with the total π-electron energy of conjugated molecules, as computed within the simple, tight-binding Hückel molecular-orbital model.[1,2] This quantity, expressed – as usual – in the units of the resonance integral β will be denoted by E. The dependence of E on molecular structure has been examined in numerous studies, over a period longer than half a century; for details and additional references see the books,[1,3,4] the reviews,[5,6] and elsewhere.[7–10] Already in the 1970s the question of how E is influenced by the presence of non-bonding molecular orbitals (NBMOs) was posed. On the basis of numerical examples,[11] one could immediately conclude that NBMOs diminish the value of E. The analytical expression proposed for this dependence[1,12]

$$E \approx a\sqrt{2m(n - n_0)} \tag{1}$$

where m and n are the number of vertices and edges of the molecular graph,[1,3] and $a \approx 0.92$ is an empirical fitting parameter, was eventually found[7,8] to be incorrect. The reason why such a long time was needed to discover the inadequacy of formula (1) lies in the fact that it was not known how to separate the effect on NMBOs on E from the effects of other structural features of the underlying conjugated π-electron system (such as cycles, Kekulé

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structures, branching of the carbon-atom skeleton, *etc.*). Only quite recently,[8] a method was put forward by means of which the effect of NBMOs could be directly evaluated. In Ref. 8 the effect of two NBMOs ($n_0 = 2$) was studied. In a further study[9] the method was extended so as to be applicable to greater values of n_0. However, the size of the molecular graphs needed for these studies rapidly increases with increasing n_0: in order to be able to go up to $n_0 = 7$ one had to perform calculations on graphs with 181 vertices.[9] The results obtained in these studies[9] were surprising and by no means anticipated by theory: an almost perfect linear correlation exists between E and n_0.

The aim of the present work is to check if such a linear relation is valid for conjugated π-electron species possessing much more than a few NBMOs. The main conclusion is that the E/n_0-correlation shows no deviation from linearity even in the case of very large values of n_0. In particular, this linearity was checked until $n_0 = 20$.

THE METHOD

In order to quantitatively determine the effect of NBMOs on E we have recently developed a pertinent method.[8,9] The method employs molecular graphs denoted by $P_N(j_1, j_2, \ldots, j_k)$, depicted in Fig. 1. This graph is obtained from the N-vertex path P_N, by attaching to it k pendent vertices (denoted by $x_1, x_2, \ldots x_k$) at positions $j_1, j_2, \ldots, j_k$. By a_i is denoted the number of vertices of $P_N(j_1, j_2, \ldots, j_k)$, lying between the vertices j_i and j_{i+1}, $i = 1, 2, \ldots$, $k-1$. In addition a_0 and a_k are the number of vertices lying left from j_1 and right from j_k, respectively; see Fig. 1.
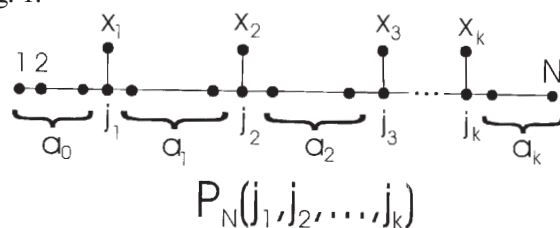

Fig. 1. The molecular graph $P_N(j_1, j_2, \ldots, j_k)$ studied in this work. According to the notation indicated, $P_N(j_1, j_2, \ldots, j_k)$ has $N + k$ vertices, where $N = a_0 + a_1 + a_2 + \ldots + a_k + k$. For additional details see text.

Among the numbers $a_0, a_1, a_2, \ldots, a_k$ some are even (*i.e.*, $a_i = 0, 2, 4, 6, \ldots$) and some are odd (*i.e.*, $a_i = 1, 3, 5, 7, \ldots$) Let $\omega(a_0, a_1, a_2, \ldots, a_k)$ among them be odd. It was shown,[9] that

$$n_0(P_N(j_1, j_2, \ldots, j_k)) = \omega(a_0, a_1, a_2, \ldots a_k)$$

If the vertex x_i in $P_N(j_1, j_2, \ldots, j_k)$ is shifted by one (either to the left or to the right), then the parity of the numbers a_{i-1} and a_i is changed and, consequently, the value of n_0 either increases by two or decreases by two or remains the same. By pertinently shifting several of the vertices $x_1, x_2, \ldots, x_k$, the number of NBMOs can vary from 0 to $k + 1$ (if both N and k are odd) or from 1 to k (if N is even and k is odd) or from 1 to $k + 1$ (if N is odd and k is even) or from 0 to k (if both N and k are even). If, in addition, the branching points $j_1, j_2, \ldots,$ j_k are positioned sufficiently far from each other, and sufficiently far from the terminal vertices of the path P_N, then the respective energy-differences result almost completely from

the variations of n_0. By detailed numerical testing,[8,9] it was found that the total π-electron energies of two different systems represented by graphs of the form $P_N(j_1, j_2, \ldots, j_k)$ and having an equal number of NBMOs differ by less than $0.005\,\beta$ provided $a_i > 20$ for all $i = 0, 1, \ldots, k$. Thus, the branching points $j_1, j_2, \ldots, j_k$ can be viewed as being sufficiently far from each other if the condition $a_i > 20$ is obeyed for all i. In our calculations, in order to be on the safe side, slightly greater values for a_i, namely $a_i = 22, 23, 24$ or $a_i = 25$ were chosen, see Tables I and II.

With this choice, different molecular graphs of the type $P_N(j_1, j_2, \ldots, j_k)$ have a fixed number of vertices ($= N + k$) and edges ($= N + k - 1$), possess no cycles, have the same branching pattern with the branching points being sufficiently distant from each other and from the terminal vertices of the N-vertex chain. Consequently, in the differences of the E-values of such molecular graphs, all (known) effects influencing the total π-electron energy, except the effect of NBMOs, will cancel out.

NUMERICAL WORK

From the results outlined in the preceding section, it follows that if one wants to compute the energy-effects of a larger number of NBMOs, one must deal with graphs of the type $P_N(j_1, j_2, \ldots, j_k)$ with large values of the parameter k and, therefore, with enormously large number of vertices. In order to be able to reach $n_0 = 20$, one must choose $k = 19$, which requires $N = 499$ and $N = 500$. In other words, it is necessary to compute the eigenvalues and energies of molecular graphs with $n = 518$ and $n = 519$ vertices. (Recall that the usually studied molecular graphs hardly ever possess more than 50 vertices. The molecular graphs of the largest conjugated systems ever synthesized have around 200 vertices.[13])
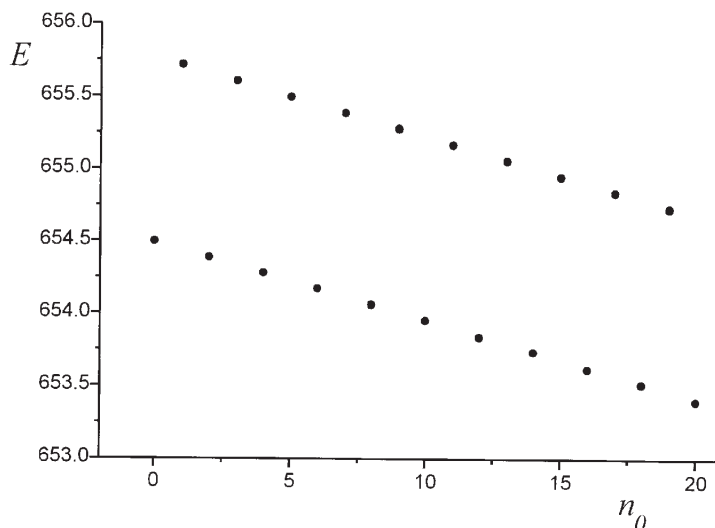

Fig. 2. Correlation between the total π-electron energy (E) and the number of non-bonding molecular orbitals (n_0) for the systems $P_N(j_1, j_2, \ldots, j_k)$ specified in Tables I and II. The respective regression lines are given by Eqs. (2) and (3).

The species considered in this work, together with their n_0- and E-values, are given in Tables I and II. The plot of E *vs.* n_0 is shown in Fig. 2.

TABLE I. The species $P_N(j_1, j_2, \ldots, j_k)$ considered, with $k = 19$ and $N = 499$ (*cf.* Fig. 1); n_0 is the number of NBMOs and E the total π-elektron energy. Note that the E-values of systems having equal numbers of NBMOs differ insignificantly

$(j_1, j_2, \ldots, j_{19})$	n_0	E
$(25, 50, 75, 100, 125, 150, 175, 200, 225, 250, 275, 300, 325, 350, 375, 400, 425, 450, 475)$	0	654.4989
$(25, 51, 75, 100, 125, 150, 175, 200, 225, 250, 275, 300, 325, 350, 375, 400, 425, 450, 475)$	2	654.3897
$(25, 50, 75, 100, 125, 150, 175, 200, 224, 250, 275, 300, 325, 350, 375, 400, 425, 450, 475)$	2	654.3897
$(25, 50, 75, 99, 125, 150, 176, 200, 225, 250, 275, 300, 325, 350, 375, 400, 425, 450, 475)$	4	654.2805
$(25, 50, 75, 100, 125, 150, 175, 200, 226, 250, 275, 301, 325, 350, 375, 400, 425, 450, 475)$	4	654.2805
$(25, 50, 74, 100, 125, 150, 174, 200, 226, 250, 275, 300, 325, 350, 375, 400, 425, 450, 475)$	6	654.1711
$(25, 50, 76, 100, 125, 150, 175, 200, 225, 251, 275, 300, 325, 350, 375, 401, 425, 450, 475)$	6	654.1713
$(24, 50, 76, 100, 125, 150, 175, 199, 225, 250, 274, 300, 325, 350, 375, 400, 425, 450, 475)$	8	654.0578
$(25, 50, 75, 100, 124, 150, 175, 200, 224, 250, 275, 300, 326, 350, 375, 400, 426, 450, 475)$	8	654.0620
$(25, 50, 75, 100, 124, 150, 176, 200, 224, 250, 275, 300, 325, 351, 375, 401, 425, 450, 475)$	10	653.9523
$(25, 50, 75, 100, 125, 150, 175, 201, 225, 251, 275, 301, 325, 351, 375, 401, 425, 450, 475)$	10	653.9521
$(26, 50, 74, 100, 126, 150, 174, 200, 226, 250, 274, 300, 325, 350, 375, 400, 425, 450, 475)$	12	653.8390
$(26, 50, 76, 100, 125, 150, 175, 200, 225, 250, 274, 300, 324, 350, 375, 400, 426, 450, 476)$	12	653.8352
$(25, 50, 74, 100, 125, 151, 175, 201, 225, 250, 274, 300, 326, 350, 374, 400, 425, 451, 475)$	14	653.7339
$(25, 51, 75, 100, 124, 150, 175, 199, 225, 250, 276, 300, 324, 350, 376, 400, 426, 450, 475)$	14	653.7339
$(26, 50, 76, 100, 125, 150, 174, 200, 224, 250, 275, 300, 326, 350, 376, 400, 426, 450, 476)$	16	653.6165
$(26, 50, 76, 100, 125, 150, 174, 200, 224, 250, 275, 300, 324, 350, 374, 400, 424, 450, 474)$	16	653.6168
$(26, 50, 76, 100, 126, 150, 176, 200, 226, 250, 276, 300, 326, 350, 376, 400, 426, 450, 475)$	18	653.5108
$(25, 51, 75, 101, 125, 151, 175, 201, 225, 249, 275, 299, 325, 349, 375, 399, 425, 449, 475)$	18	653.5146
$(24, 50, 74, 100, 126, 150, 176, 200, 224, 250, 276, 300, 324, 350, 376, 400, 424, 450, 476)$	20	653.3970
$(26, 50, 76, 100, 126, 150, 176, 200, 226, 250, 274, 300, 324, 350, 374, 400, 424, 450, 474)$	20	653.3977

TABLE II. Same as for Table I, for $N = 500$

$(j_1, j_2, \ldots, j_{19})$	n_0	E
$(25, 50, 75, 100, 125, 150, 175, 200, 225, 250, 275, 300, 325, 350, 375, 400, 425, 450, 475)$	1	655.7151
$(25, 50, 75, 100, 125, 150, 175, 200, 225, 251, 276, 301, 326, 351, 376, 401, 426, 451, 476)$	1	655.7189
$(25, 50, 75, 100, 125, 150, 175, 200, 225, 250, 275, 300, 325, 350, 375, 400, 425, 451, 475)$	3	655.6057
$(25, 50, 75, 100, 125, 150, 175, 201, 225, 250, 275, 300, 325, 350, 375, 400, 425, 450, 475)$	3	655.6059
$(25, 50, 75, 100, 125, 150, 176, 200, 225, 250, 275, 300, 324, 350, 375, 400, 425, 450, 475)$	5	655.4967
$(26, 50, 75, 100, 125, 150, 175, 200, 225, 250, 275, 300, 325, 350, 375, 400, 426, 450, 476)$	5	655.4965
$(25, 50, 75, 101, 125, 150, 175, 199, 225, 250, 275, 300, 325, 351, 375, 400, 425, 450, 475)$	7	655.3875
$(25, 50, 75, 100, 124, 150, 175, 200, 225, 250, 275, 301, 325, 350, 375, 399, 425, 449, 476)$	7	655.3873
$(26, 50, 75, 101, 125, 150, 175, 201, 225, 250, 275, 301, 325, 350, 375, 400, 425, 450, 475)$	9	655.2746
$(25, 50, 75, 100, 125, 149, 175, 201, 225, 249, 275, 301, 325, 351, 376, 401, 426, 451, 476)$	9	655.2813
$(26, 50, 76, 100, 126, 150, 176, 200, 226, 250, 275, 300, 325, 350, 375, 400, 425, 450, 475)$	11	655.1646
$(25, 50, 75, 99, 125, 150, 175, 201, 225, 250, 274, 300, 325, 350, 375, 399, 425, 449, 475)$	11	655.1687
$(26, 50, 75, 101, 125, 150, 176, 200, 225, 249, 275, 300, 324, 350, 375, 401, 425, 450, 475)$	13	655.0561
$(25, 49, 75, 100, 125, 149, 175, 200, 224, 250, 275, 301, 325, 350, 376, 400, 425, 451, 475)$	13	655.0597
$(25, 51, 75, 100, 124, 150, 176, 200, 224, 250, 275, 300, 324, 350, 376, 400, 425, 451, 475)$	15	654.9500
$(24, 50, 75, 101, 125, 150, 174, 200, 225, 251, 275, 301, 325, 350, 374, 400, 426, 450, 475)$	15	654.9462
$(25, 49, 75, 101, 125, 151, 175, 200, 226, 250, 274, 300, 326, 350, 376, 400, 425, 451, 475)$	17	654.8404
$(24, 50, 76, 100, 125, 149, 175, 201, 225, 250, 276, 300, 326, 350, 375, 401, 425, 449, 475)$	17	654.8365
$(24, 50, 74, 100, 124, 150, 176, 200, 225, 251, 275, 301, 325, 349, 375, 401, 425, 451, 475)$	19	654.7267
$(25, 51, 75, 99, 125, 149, 175, 199, 225, 251, 275, 301, 325, 349, 375, 401, 425, 449, 475)$	19	654.7306

From the data given in Tables I and II, it can be seen that the E-values pertaining to the molecular graphs $P_N(j_1, j_2, \ldots, j_k)$ with equal n_0 are practically equal, differing – as required – by less than 0.005β. This detail confirms that n_0 is the chief parameter responsible for the differences in the E-values.

Figure 2 shows that the correlation between E and n_0 is linear, of very good quality. By least-squares fitting, for the 21 data points with $N = 499$:

$$E = -(0.0550 \pm 0.0001)n_0 + (654.500 \pm 0.001); \quad n_0 = 0, 2, 4, \ldots, 20 \qquad (2)$$

and for the 20 data points with $N = 500$

$$E = -(0.0549 \pm 0.0001)n_0 + (655.771 \pm 0.001); \quad n_0 = 1, 3, 5, \ldots, 19 \qquad (3)$$

The respective correlation coefficients are $R = -0.99997$ and $R = -0.99998$.

As seen, the slopes of the two regression lines are (within the limits of statistical uncertainty) identical. No curvilinearity in the examined regressions could be detected.
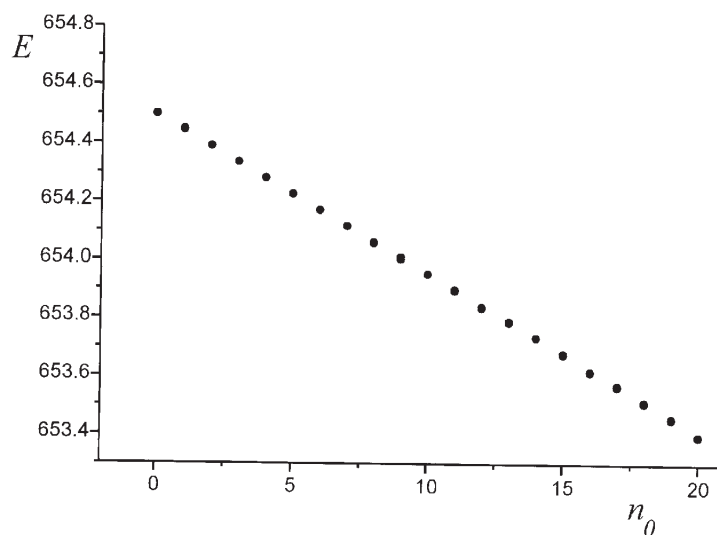

Fig. 3. Same data as in Fig. 2, after diminishing the E-values for odd n_0 by 1.271β. The regression line thus obtained is $-(0.05497 \pm 0.00007)n_0 + (654.5005 \pm 0.0008)$, with the correlation coefficient $R = -0.99997$.

The regression line (3) lies by 1.271β-units above the line (2). This is the (expected) consequence of the fact that the molecular graphs pertaining to $N = 500$ have one vertex more than those pertaining to $N = 499$. Thanks to the identity of the slopes of (2) and (3), the two data sets could be combined by subtracting 1.271 from the E-values with odd n_0. This results in the line shown in Fig. 3.

CONCLUDING REMERKS

A previously elaborated model[9] was extended here to very large values of n_0, making it possible to formulate the following rule: *Provided other effects are kept constant, the effect of non-bonding molecular orbitals on the total π-electron energy is linearly propor-*

tional to the number of NBMOs. This surprisingly simple regularity was by no means anticipated in previous theoretical considerations. We established it by means of computer experiments, and – at the present moment – cannot offer any theoretical rationalization for it. This latter task remains a challenge for the future.

ИЗВОД

ЗАВИСНОСТ УКУПНЕ π-ЕЛЕКТРОНСКЕ ЕНЕРГИЈЕ ОД ВЕЛИКОГ БРОЈА НЕВЕЗНИХ МОЛЕКУЛСКИХ ОРБИТАЛА

ИВАН ГУТМАН, ДРАГАН СТЕВАНОВИЋ, СЛАВКО РАДЕНКОВИЋ, СВЕТЛАНА МИЛОСАВЉЕВИЋ и НАТАША ЦМИЉАНОВИЋ

Природно-математички факултет у Крагујевцу и Природно-математички факултет у Нишу

Применом једне недавно развијене методе за одређивање утицаја невезних молекулских орбитала на укупну π-електронску енергију (E), нађено је да је зависност E од броја n_0 невезних молекулских орбитала скоро потпуно линеарна. У овом раду показујемо да се ова правилност одржава и код веома великих вредности n_0, конкретно да важи до $n_0 = 20$.

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