

Remark on the moment expansion of total π -electron energy

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Received August 25, 1991/Accepted October 24, 1991

Summary. The truncated expansion of the function $|x|$ was frequently used to express the total Hückel π -electron energy (E) in terms of moments. We now present an identity which connects E with an infinite series of moments. This series is convergent. Lower and upper bounds for E are obtained, based on the same infinite moment expansion.

Key words: Hückel theory – Total π -electron energy – Moments

1. Introduction

The fact that the quantity E in Eq. (1) for the total Hückel π -electron energy:

$$E_{\text{tot}} = n\alpha + E\beta \quad (1)$$

satisfies the relation:

$$E = \sum_{j=1}^n |x_j| \quad (2)$$

was known already to the earliest researchers in this area [1–3]. In Eq. (2) x_j stands for the eigenvalue of the respective adjacency matrix [4, 5] and n is the total number of π -centers in the respective conjugated molecule. The function $|x|$ means the absolute value of the variable x . Usually, the quantity E is considered instead of E_{tot} and is also named “total π -electron energy”; this is formally achieved by expressing the energy levels in so-called β -units ($\alpha = 0, \beta = 1$). When β -units are employed, then x_j coincides with the energy of the j -th MO. Equation (2) holds provided all the bonding MOs are doubly occupied and all the antibonding MOs are empty and provided the trace of the underlying adjacency matrix is zero [4]. As well known [5], this latter condition is obeyed only in the zeroth order “same α , same β ” version of the Hückel model and even then only by aromatic and unsaturated hydrocarbons. In spite of all these limitations, the quantity E continues to attract the attention of theoretical chemists and is extensively studied in the chemical literature over almost half a century; for a recent review of the work on Hückel total π -electron energy and a critical evaluation of the range of its chemical applicability see [6].

The approximation of the function $|x|$ in Eq. (2) by means of a truncated power series:

$$|x| \approx \sum_{k=0}^L a_{2k} x^{2k} \quad (3)$$

has been proposed and/or utilized by a large number of researchers [7–16]. Equation (3) immediately leads to a moment-expansion of E , namely:

$$E \approx \sum_{k=0}^L a_{2k} M_{2k}. \quad (4)$$

Here and later M_r denotes the r -th spectral moment defined as

$$M_r = \sum_{k=1}^n (x_j)^r.$$

The importance of Eq. (4) lies in the fact that we know how the first few moments depend on molecular structure (see [17–20] and the references cited therein). Therefore by means of Eq. (4) we gain a considerable insight into the structural factors which influence the value of the quantity E in Eq. (1) and thus may somewhat better understand the structure-dependence of total π -electron energy of conjugated π -electron systems. The disadvantage of Eq. (4) is that the coefficients a_{2k} on its right-hand side strongly depend on the truncation parameter L . In particular, for $L \rightarrow \infty$:

$$\lim a_0 = 0 \quad (5a)$$

$$\lim[(-1)^{k-1} a_{2k}] = \infty, \quad k > 0. \quad (5b)$$

The expansion (3) is certainly divergent in the point-wise sense, but it always can be chosen to be convergent in the L^2 sense (for respective details see e.g. [21]). Consequently, the truncation of the right-hand side of Eq. (4) need not result in serious numerical errors in E . The real problem, however, lies in the fact that in structure-dependence studies E has to be partitioned into contributions which are interpreted as the effects of particular structural features of the molecule examined. When Eq. (4) is used for this purpose, then the calculated energy-effects are functions of the coefficients a_{2k} and are thus significantly influenced by the actual value of the truncation parameter L . In a recently studied example the results of such an energy-partitioning were shown to be chemically unreliable [12, 15]. The limits (5) are, of course, equivalent to the well-known nonexistence (i.e. divergence) of an infinite power-series expansion of the function $|x|$. Some authors tried to overcome this difficulty by expanding $|x|$ in powers of $x - x_0$, $x_0 \neq 0$ [3, 18, 22], but then E is not at all expressed in terms of spectral moments. Only if the latter expansion is truncated, the resulting approximate formula for E can be transformed into the form of Eq. (4). Then, however, the above mentioned problems with the L -dependence of the coefficients a_{2k} and the infiniteness of their limit values cannot be avoided.

In this paper we approach the moment expansion of total π -electron energy from a different direction and obtain a mathematically exact and point-wise convergent power-series formula.

2. An auxiliary result

As already mentioned, x_1, x_2, \dots, x_n denote the eigenvalues of the adjacency matrix (and are, consequently, closely related to the HMO energy levels). Then

the polynomial $P(x)$, determined via Eq. (6):

$$P(x) = \prod_{j=1}^n (x - x_j) \quad (6)$$

is the secular (or characteristic) polynomial of the respective π -electron system [4].

In what follows we demonstrate a property of any polynomial $P(x)$ whose zeros are x_1, x_2, \dots, x_n .

Let $P'(x) = (d/dx)P(x)$. Then from Eq. (6):

$$\begin{aligned} P'(x) &= (x - x_2)(x - x_3)(x - x_4) \cdots (x - x_n) \\ &\quad + (x - x_1)(x - x_3)(x - x_4) \cdots (x - x_n) \\ &\quad + (x - x_1)(x - x_2)(x - x_4) \cdots (x - x_n) \\ &\quad + \cdots + (x - x_1)(x - x_2)(x - x_3) \cdots (x - x_{n-1}) \\ &= \sum_{j=1}^n P(x)/(x - x_j) \end{aligned}$$

i.e.:

$$P'(x)/P(x) = \sum_{j=1}^n (x - x_j)^{-1}. \quad (7)$$

The identity (7) readily yields:

$$\frac{1}{t} P' \left(\frac{1}{t} \right) / P \left(\frac{1}{t} \right) = \sum_{j=1}^n (1 - tx_j)^{-1}. \quad (8)$$

The term $(1 - tx_j)^{-1}$ on the right-hand side of Eq. (8) is just the sum of a geometric progression, i.e.:

$$(1 - tx_j)^{-1} = \sum_{r=0}^{\infty} (tx_j)^r$$

provided:

$$|tx_j| < 1. \quad (9)$$

Consequently, if the condition (9) holds for all $j = 1, 2, \dots, n$, then:

$$\sum_{j=1}^n (1 - tx_j)^{-1} = \sum_{j=1}^n \sum_{r=0}^{\infty} (tx_j)^r = \sum_{r=0}^{\infty} M_r t^r$$

and, bearing in mind Eq. (8):

$$\frac{1}{t} P' \left(\frac{1}{t} \right) / P \left(\frac{1}{t} \right) = \sum_{r=0}^{\infty} M_r t^r. \quad (10)$$

3. The main result

In 1940 Coulson [1] showed that the total Hückel π -electron energy, satisfying Eq. (2), conforms to the remarkable integral formula:

$$E = \frac{1}{\pi} \int_{-\infty}^{+\infty} F(x) dx \quad (11)$$

where

$$F(x) = n - ixP'(ix)/P(ix). \quad (12)$$

In Eq. (12) $P(x)$ is the secular polynomial and $i = \sqrt{-1}$. (For details on Coulson integral formulas for E see [23], pp. 139–143.)

Substituting $ix = 1/t$ and using the identity (10) we transform the integrand (12) into:

$$F(x) = n - \sum_{r=0}^{\infty} M_r (-i/x)^r. \quad (13)$$

Taking into account that $M_0 = n$, Eq. (13) is further simplified as:

$$F(x) = - \sum_{r=1}^{\infty} M_r (-i/x)^r = \sum_{k=1}^{\infty} (-1)^{k-1} M_{2k} x^{-2k} + i \sum_{k=1}^{\infty} (-1)^{k-1} M_{2k-1} x^{-(2k-1)}. \quad (14)$$

This latter formula holds for all values of the variable x , such that $|x| > |x_j|$, $j = 1, 2, \dots, n$.

Let A be a positive number, such that $A > |x_j|$, $j = 1, 2, \dots, n$. Let $\mathbb{D} = (-\infty, -A] \cup [A, +\infty)$. Then Eq. (14) is applicable for all $x \in \mathbb{D}$. Combining Eqs. (11), (12) and (14) we attain at:

$$E = \frac{1}{\pi} \int_{\mathbb{D}} \sum_{k=1}^{\infty} (-1)^{k-1} M_{2k} x^{-2k} dx + \frac{1}{\pi} \int_{\mathbb{D}} \sum_{k=1}^{\infty} (-1)^{k-1} M_{2k-1} x^{-(2k-1)} dx + \frac{1}{\pi} \int_{-A}^{+A} F(x) dx. \quad (15)$$

The second integral on the right-hand side of Eq. (15) is equal to zero because the respective integrand is an odd function of x . Recalling further that:

$$\int_{\mathbb{D}} x^{-2k} dx = 2(2k-1)^{-1} A^{-(2k-1)}$$

we readily arrive at our final result.

Theorem 1

Let A be any positive real number which exceeds all the eigenvalues x_1, x_2, \dots, x_n . Then the total Hückel π -electron energy E satisfies the identity:

$$E = \frac{2}{\pi} \sum_{k=1}^{\infty} (-1)^{k-1} (2k-1)^{-1} A^{-(2k-1)} M_{2k} + E_0 \quad (16)$$

where

$$E_0 = \frac{2}{\pi} \int_0^A [n - ixP'(ix)/P(ix)] dx. \quad (17)$$

This identity holds if and only if the condition (2) is obeyed.

4. Moment-expansion-based bounds for total π -electron energy

The integrand in Eq. (17) is a positive-valued bell-shaped function with maximum at $x = 0$ [24]. Because $F(0) = n$, for all real values of x the function $F(x)$ is bounded as follows:

$$0 < F(x) \leq n.$$

Applying these relations to Eq. (17) one immediately concludes that:

$$0 < E_0 < (2/\pi)An = (2/\pi)AM_0. \quad (18)$$

The inequalities (18) together with Eq. (16) result in the following lower and upper bounds for total π -electron energy.

Theorem 2

Let A be any positive real number which exceeds all eigenvalues x_1, x_2, \dots, x_n . Then the total Hückel π -electron energy E is bounded from both below and above by the same infinite series of moments:

$$\begin{aligned} \frac{2}{\pi} \sum_{k=1}^{\infty} (-1)^{k-1} (2k-1)^{-1} A^{-(2k-1)} M_{2k} < E \\ < \frac{2}{\pi} \sum_{k=0}^{\infty} (-1)^{k-1} (2k-1)^{-1} A^{-(2k-1)} M_{2k}. \end{aligned} \quad (19)$$

The estimates (19) are not very narrow and much better lower and upper bounds for E are known (see, for instance, [25]). We pointed out the relations (19) because of their appealing form and because they may contribute towards a better understanding of the moment-expansion techniques.

5. Concluding remarks

Equation (16) represents a kind of moment expansion of the total π -electron energy. It, however, reveals that only one part of E , namely $E - E_0$, can be expanded into a point-wise convergent infinite series of moments. This part of E depends solely on even moments. Furthermore, the moments $M_2, M_6, M_{10}, \dots, M_{4m+2}, \dots$ have positive (stabilizing) contributions to E whereas the moments $M_4, M_8, M_{12}, \dots, M_{4m}, \dots$ have negative (destabilizing) effects. This latter regularity precisely parallels the previously formulated “loop rule” [9].

The other, “irreducible” part of total π -electron energy, which cannot be expanded in terms of moments, is given by Eq. (17). Because the parameter A in Eq. (17) is necessarily greater than the maximal MO energy level, the quantity E_0 is numerically quite significant and is by no means negligible, as compared to $E - E_0$. The existence of such an “irreducible” component was systematically overlooked in the previous moment-expansion studies of the total π -electron energy. This should be considered as a major pitfall in the efforts to express E (solely) in terms of spectral moments.

The quantity E_0 evidently deserves a particular attention. The bounds (18) for E_0 are very weak indeed and certainly need to be improved. Using a previously elaborated method [24] we can approximate the integrand $F(x)$, Eq. (12), by means of a simple algebraic function:

$$F(x) \approx M_0 M_2 (M_2 + M_0 x^2)^{-1}$$

which by applying Eq. (17) yields:

$$E_0 \approx \frac{2}{\pi} (M_0 M_2)^{1/2} \operatorname{arctg}[A(M_0/M_2)^{1/2}].$$

We note in passing that in the case of uncharged conjugated hydrocarbon molecules, M_0 and $\frac{1}{2}M_2$ are equal to the numbers of carbon atoms and carbon-carbon bonds, respectively [4].

Theorem 1, being a mathematically exact result, in an implicit manner indicates that the strategy of approximating the total π -electron energy only by means of linear combinations of certain spectral moments is not a good one. A nonnegligible part of E behaves in a way which cannot be adequately described by moment-based expressions. Therefore the method of moment expansion (although used over a very long period of time and by numerous researchers [3, 4, 7–16, 18, 22]) should be critically revisited and augmented by an appropriate analysis of the “irreducible” term E_0 .

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