Monte Carlo Approach to Total π -Electron Energy of Conjugated Hydrocarbons

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Approximating the π -electron molecular orbital energy levels by uniformly distributed random variables, a McClelland-type formula for the total π -electron energy is obtained. Conditions are determined under which a given distribution function will result in a formula of McClelland type.

The total π -electron energy (E), as calculated within the Hückel molecular orbital model, has for a long time been attracting the attention of theoretical chemists [1, 2]. Especially important seems to be the recent finding [2] that a precise linear relationship exists between E and the kinetic energy of the π -electrons.

In the following the conjugated molecule under consideration will be represented by its molecular graph [3]. This graph has n vertices and m edges. For the sake of simplicity we shall assume that the molecule considered is an alternant hydrocarbon and that n (=the number of carbon atoms) is an even number. If $x_1, x_2, \dots, x_n$ are the eigenvalues [3] of the molecular graph, labeled in a non-increasing order, then

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

A relation which will be needed in the forthcoming discussion is [3]

$$\sum_{j=1}^{n/2} x_j^2 = m. \quad (2)$$

Now, if $x_1, x_2, \dots, x_{n/2}$ are viewed as random numbers, that is $n/2$ independent realizations of a random variable X , then their sample mean $e(X)$ and sample dispersion $d(X)$ are given by

$$e(X) = \frac{1}{n/2} \sum_{j=1}^{n/2} x_j = E/n, \quad (3)$$

$$d(X) = \frac{1}{n/2} \sum_{j=1}^{n/2} [x_j - e(X)]^2 = 2m/n - (E/n)^2. \quad (4)$$

Since obviously $d(X) \geq 0$, we get from (4)

$$E \leq \sqrt{2mn}, \quad (5)$$

which is just the McClelland upper bound for the total π -electron energy [4].

In the same paper [4] in which the upper bound (5) has been deduced, it has been established that E can be fairly well reproduced by the expression

$$E = a \sqrt{2mn}, \quad (6)$$

where a is an empirical parameter, whose value is about 0.9. The accuracy of (6) was verified in [5], where a comparative study of a great number of approximate topological formulas has been performed.

It has been shown [6] that the upper bound (5) is related to the assumption that all the (positive) graph eigenvalues are degenerate. Namely, the following result was deduced in [6]:

Lemma 1. Under the constraint (2), the greatest possible value of E is $(2mn)^{1/2}$, and this maximum is reached if and only if $x_1 = x_2 = \dots = x_{n/2}$.

On the basis of Lemma 1 one may be inclined to expect that the validity of the approximation (6) is also stipulated by a relatively small deviation of graph eigenvalues from their mean value. Surprisingly, however, if the opposite is true, namely if all eigenvalues are mutually distinct, an expression for E , closely similar to (6) exists [6]:

Lemma 2. If the numbers x_j are equidistant, that is $x_{j+1} - x_j = \text{const}$ for all $j = 1, 2, \dots, n/2 - 1$, then under the constraint (2),

$$E = a(n) \sqrt{2mn}, \quad (7)$$

where the function $a(n) = [3n^2/(4n^2 - 4)]^{1/2}$ rapidly converges to $(3/4)^{1/2} = 0.87$ when n tends to infinity.

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Comparing Lemmas 1 and 2 we see that quite different distributions of the graph eigenvalues may lead to McClelland-type formulas for the total π -electron energy. In the present paper further arguments in favour of this conclusion will be given. For the beginning we formulate the following result.

Lemma 3. If $x_1, x_2, \dots, x_{n/2}$ are random numbers, uniformly distributed in the interval $(0, p)$, then for an arbitrary positive value of p ,

$$\langle E \rangle = b \sqrt{2 \langle m \rangle n}, \quad (8)$$

where $b = (3/4)^{1/2} = 0.87$ equals the limit value of the function $a(n)$ in (7). In (8), $\langle E \rangle$ and $\langle m \rangle$ denote the expectation values of E and m , as defined via (1) and (2).

Numerical work

In order to test Lemma 3 we have chosen the interval $(0, p)$ by generating a random number $r \in (0, 1)$ and setting $p = 1/r$. Then by generating the random numbers $r_j \in (0, 1)$, $j = 0, 1, 2, \dots$ we defined $n/2 = [50 r_0]$ and $x_j = p r_j$, $j = 1, 2, \dots, n/2$ and calculated E and m by means of (1) and (2). After repeating this procedure 20 times (for a fixed value of p), we determined the parameter b in (8) by least squares fitting.

In Table 1 are presented ten typical results obtained in this manner.

Proof of Lemma 3

Suppose that X is a continuous random variable, uniformly distributed in the interval $(0, p)$. Then its distribution function $q(x)$ is equal to $1/p$. Bearing in mind (1) and (2), we have

$$\langle E \rangle = (n/2) \int_0^p 2x q(x) dx = np/2, \quad (9)$$

$$\langle m \rangle = (n/2) \int_0^p x^2 q(x) dx = np^2/6. \quad (10)$$

Elimination of the parameter p from (9) and (10) results immediately in (8). Note the very good agreement between the parameter b in (8) and the empirically determined value for a in McClelland's formula (6).

A more careful examination of the above proof shows that the assumption of the uniform distribu-

tion of the variable X is not at all necessary for the derivation of a McClelland-type formula for E .

Indeed, let X be a continuous random variable whose values lie in the interval $(0, p)$ and whose distribution function is $q(x)$. Suppose that the first and the second moment of X are proportional to p and p^2 , respectively:

$$\int_0^p x q(x) dx = c_1 p, \quad (11)$$

$$\int_0^p x^2 q(x) dx = c_2 p^2, \quad (12)$$

where c_1 and c_2 are constants, independent of p . Then, according to (9) and (10),

$$\langle E \rangle = n c_1 p \quad (13)$$

and

$$\langle m \rangle = n c_2 p^2 / 2, \quad (14)$$

and therefore

$$\langle E \rangle = c \sqrt{2 \langle m \rangle n}, \quad (15)$$

where

$$c = c_1 c_2^{-1/2}. \quad (16)$$

Clearly, the distribution function $q(x)$ must depend in a pertinent way on the parameter p .

We show now that for an arbitrary function $f(x)$ which is non-negative in the interval $(0, 1)$ and whose integral

$$I = \int_0^1 f(x) dx \quad (17)$$

Table 1. Monte Carlo estimation of the parameter b in (8). Each result is obtained by a least squares fitting of data for 20 "random molecules".

No.	b	Correlation coefficient
1	0.888	0.9995
2	0.879	0.99990
3	0.863	0.99990
4	0.854	0.998
5	0.862	0.9997
6	0.904	0.998
7	0.828	0.9998
8	0.855	0.9990
9	0.835	0.9997
10	0.882	0.998

exists, we can choose the distribution function $q(x)$ as

$$q(x) = (Ip)^{-1} f(x/p), \quad (18)$$

and $q(x)$ has the properties (11) and (12). As a matter of fact, for a distribution function of the form (18), the k -th moment of X is proportional to p^k . This can be easily seen by direct calculation of the k -th moment:

$$\int_0^p x^k q(x) dx = (p^k/I) \int_0^1 y^k f(y) dy, \quad (19)$$

where $y = x/p$. Hence

$$c_1 = \int_0^1 x f(x) dx \bigg/ \int_0^1 f(x) dx, \quad (20)$$

$$c_2 = \int_0^1 x^2 f(x) dx \bigg/ \int_0^1 f(x) dx,$$

and we have arrived at the following result:

Theorem 1. Let $f(x)$ be a function having non-negative values in the interval $(0, 1)$, whose integral (17) exists. If $x_1, x_2, \dots, x_{n/2}$ are random numbers, distributed in the interval $(0, p)$ according to (18), then for an arbitrary positive value of p , a McClelland-type relation (15) exists between $\langle E \rangle$, $\langle m \rangle$ and n , where the multiplier c is determined via (16), (20) and (21).

Choosing $f(x) = 1$, the above theorem reduces to Lemma 3.

Theorem 1 shows that the existence of a McClelland-type dependency between the total π -electron energy and the topological parameters n and m is almost independent of the assumed distribution of graph eigenvalues. This also explains the success of the approximate topological formula (6) [5]. The distribution of graph eigenvalues influences, however, the value of the empirical constant a . The fact that the parameters a in (6) and b in (8) have very close numerical values indicates that the assumptions made in Lemma 3 are not very far from the reality.

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