

## NEW APPROACH TO THE McCLELLAND APPROXIMATION

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Abstract

A novel derivation of McClelland's estimate (1) is proposed, based on the finding of the maximum of the functional  $E$ , eq. (2), with constraints (6) and (7). McClelland's approximation (5) for total pi-electron energy is demonstrated to be closely related with the assumption that the MO energy levels are distributed in a uniform manner, eq. (13). A theoretical derivation of the empirical constant 0.92 in McClelland's formula (5) is offered.

In a paper<sup>1</sup> published in 1971, McClelland reported the first upper and lower bounds for the HMO total pi-electron energy of conjugated molecules. In particular, he showed that for a conjugated hydrocarbon of the formula  $C_nH_{2n-2m}$ ,

$$E \leq (2 m n)^{1/2}$$

Here  $n$  is the number of carbon atoms and  $m$  the number of carbon-carbon bonds.  $E$  denotes the HMO total pi-electron energy<sup>2</sup> of the pertinent conjugated system (expressed, as usual, in beta units).

If  $x_1, x_2, \dots, x_n$  are the eigenvalues of the molecular graph<sup>3</sup>, then  $E$  is defined as

$$E = \sum_{i=1}^n g_i x_i \quad (2)$$

with  $g_i$  being the occupation number of the  $i$ -th molecular orbital. Here and later we will assume that the eigenvalues  $x_i$  are labelled in non-increasing order. Then in the case which will be considered in the present paper, namely a neutral closed-shell conjugated hydrocarbon in ground electronic state, the occupation numbers conform to the following relations:

$$\begin{aligned} g_i &= 2 & \text{for } i &= 1, 2, \dots, n/2 \\ \text{and} & & & \\ g_i &= 0 & \text{for } i &= n/2+1, n/2+2, \dots, n \end{aligned} \quad (3)$$

and

$$\sum_{i=1}^n g_i = n \quad (4)$$

In Ref. 1 the approximate formula

$$E = 0.92 (2 m n)^{1/2} \quad (5)$$

was also proposed, the multiplier 0.92 being determined by least-squares fitting.

The discovery of the estimate (1) was followed by a number of papers<sup>4</sup>, examining various more sophisticated upper and lower bounds for E and also for other HMC reactivity indices<sup>5</sup>.

The approximate topological formula (5) predicts equal total pi-electron energy for all isomers having the formula  $C_nH_{2n-2m}$ , what is in contradiction with observed experimental facts<sup>6</sup>. Therefore improvements of McClelland's formula (5) were necessary. Some attempts along these lines were proposed elsewhere<sup>7</sup>. On the other hand, the right-hand side of the expression (5) correctly reproduces the gross part of E (some 95% or more). This also means that the main topological invariants which determine E are n (= the number of vertices of the molecular graph<sup>3</sup>) and m (= the number of edges of the molecular graph<sup>3</sup>).

The results of the present work are based on the following two relations, which hold for the eigenvalues of all schlicht graphs.

$$\sum_{i=1}^n x_i = 0 \quad (6)$$

and

$$\sum_{i=1}^n x_i^2 = 2m \quad (7)$$

Both identities (6) and (7) are well-known in graph spectral theory<sup>3</sup> and can be easily deduced either by matrix-theoretical<sup>4</sup> or by graph-theoretical reasoning<sup>8</sup>.

Eqs. (6) and (7) can be understood as certain information about the distribution of the graph eigenvalues. On the other hand, according to eq. (2),  $E$  is a function of the graph eigenvalues and must obviously be sensitive to their distribution. This stimulated us to pose the following

P r o b l e m. Which is (A) the maximum and (B) the minimum possible value of  $E$  if the graph eigenvalues are constrained to fulfil the conditions (6) and (7) and only these conditions?

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<sup>4</sup> Note that

$$\sum_{i=1}^n (x_i)^k = \text{Tr} (A)^k \quad , \quad k = 1, 2, \dots$$

where  $A$  is the adjacency matrix of the molecular graph<sup>3,8</sup> and  $\text{Tr}$  stands for the trace of a matrix.

The answer to the problem (A) is obtained using variation calculus. From (2) follows

$$\delta E = \sum_{i=1}^n \varepsilon_i \delta x_i = 0 \quad (8)$$

because  $E$  is required to be maximal. In addition, from (6) and (7),

$$\sum_{i=1}^n \delta x_i = 0 \quad (9)$$

and

$$\sum_{i=1}^n x_i \delta x_i = 0 \quad (10)$$

Multiplying eq. (8) by  $-L$  and eq. (9) by  $M$  and adding them to eq. (10), we obtain

$$\sum_{i=1}^n (x_i - L \varepsilon_i + M) \delta x_i = 0$$

i.e.

$$x_i - L \varepsilon_i + M = 0 \quad \text{for all } i = 1, 2, \dots, n$$

The multipliers  $L$  and  $M$  are now readily determined. From (4) and (6),

$$L = M$$

i.e.

$$x_i = L(g_i - 1)$$

Because of (3), the above equality implies

$$x_i = L \quad \text{for } i = 1, 2, \dots, n/2$$

and

(11)

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

Finally, from (11) and (7),

$$n L^2 = 2 m$$

i.e.

$$L = (2m/n)^{1/2}$$

Thus we reached the following result.

Theorem 1. The eigenvalue distribution which gives a maximum value for  $E$  and which simultaneously fulfils the relations (6) and (7) is

$$x_1 = x_2 = \dots = x_{n/2} = (2m/n)^{1/2}$$

$$x_{n/2+1} = x_{n/2+2} = \dots = x_n = -(2m/n)^{1/2}$$

The maximum value for  $E$  is then

$$E_{\max} = (2 m n)^{1/2} \quad (12)$$

Eq. (12) implies, of course, McClelland's inequality (1). In fact, Theorem 1 can be understood as an explanation of the origin of the estimate (1). It is an interesting and by no means obvious finding that formula (1) becomes an equality only under the assumption that all bonding MO's have equal energies (and also that all antibonding MO's have equal energies). Whenever not all bonding energy levels are mutually equal, the total pi-electron energy will be necessarily less than  $(2 m n)^{1/2}$ .

The solution of the (B) part of the above problem is more or less evident. We present it in a form which is complementary to Theorem 1.

Theorem 2. The eigenvalue distribution which gives a minimum value for  $E$  and which simultaneously fulfils the relations (6) and (7) is

$$x_1 = (m)^{1/2}$$

$$x_2 = x_3 = \dots = x_{n-1} = 0$$

$$x_n = -(m)^{1/2}$$

The minimum value for  $E$  is then

$$E_{\min} = 2(m)^{1/2}$$

Note that the eigenvalue distribution described in Theorem 2 really occurs in the case of stars (i.e. graphs having a vertex of degree  $n-1$  and  $n-1$  vertices of degree one).

In order to design further topological formulas for total  $\pi$ -electron energy, one may try to assume other, more realistic, distributions of the graph eigenvalues. A particularly attractive trial of this kind is the hypothesis that the eigenvalues are uniformly distributed, i.e.

$$x_i - x_{i+1} = D \quad (13)$$

with  $D$  being a constant, independent of  $i$ ,  $i=1,2,\dots,n-1$ . From (13) follows straightforwardly that

$$x_i = x_1 - (i - 1)D \quad (14)$$

for  $i = 1,2,\dots,n$ . Substituting (14) back into (6), one comes to the conclusion that

$$D = 2 x_1 / (n - 1) \quad (15)$$

Combining (14), (15) and (7), the relation

$$x_1 = (6 m(n - 1) / (n^2 + n))^{1/2}$$

is obtained after appropriate algebraic transformations.



The above results can be summarized in the following manner.

Theorem 3. The uniform eigenvalue distribution (13) which simultaneously fulfils the relations (6) and (7) is

$$x_i = (n + 1 - 2i) \sqrt{\frac{6m}{n(n^2 - 1)}} \quad \text{for } i = 1, 2, \dots, n$$

The corresponding expression for E is then

$$E = F(n) \cdot (2mn)^{1/2}$$

with

$$F(n) = \frac{n}{2} \sqrt{3/(n^2 - 1)}$$

The function F(n) for some chemically relevant values of n is given as follows.

n	F(n)
4	0.894
6	0.878
8	0.873
10	0.870
14	0.868
18	0.867
22	0.867

The limit of F(n) is, of course,  $(3/4)^{1/2} = 0.8660$ . We

see that  $F(n)$  varies within quite narrow ranges and that its value is rather close to 0.92 - the empirical constant in the formula (5). Hence we may conclude that McClelland's semiempirical topological formula (5) is in a certain sense related to, and a consequence of the assumption of a uniform distribution of the molecular orbital energy levels.

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