

The McClelland approximation and the distribution of π -electron molecular orbital energy levels

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Abstract: The total π -electron energy E of a conjugated hydrocarbon with n carbon atoms and m carbon–carbon bonds can be approximately calculated by means of the McClelland formula $E \approx g\sqrt{2mn}$, where g is an empirical fitting constant, $g \approx 0.9$. It was claimed that the good quality of the McClelland approximation is a consequence of the fact that the π -electron molecular orbital energy levels are distributed in a nearly uniform manner. It will now be shown that the McClelland approximation does not depend on the nature of the distribution of energy levels, *i.e.*, that it is compatible with a large variety of such distributions.

Keywords: total π -electron energy, McClelland formula, Hückel molecular orbital theory.

The total π -electron energy E is one of the most thoroughly studied theoretical characteristics of conjugated molecules that can be calculated within the Hückel molecular orbital (HMO) approximation.^{1,2} Research on E is currently very active.^{3–8} Long time ago McClelland proposed the simple approximate formula:⁹

$$E \approx g\sqrt{2mn} \quad (1)$$

where n is the number of carbon atoms and m the number of carbon–carbon bonds, and where g is an empirically determined fitting parameter, $g \approx 0.9$. In the meantime a large number of other (n,m) -type approximate expressions for E have been proposed, but, as demonstrated by detailed comparative studies,^{10–13} none of these could exceed the accuracy of Eq. (1).

In 1983 the present author discovered¹⁴ that a result closely similar to Eq. (1) can be obtained by assuming that the HMO energy levels are uniformly distributed. Eventually such a distribution-based approach to E was elaborated in more detail.^{15,16} The conclusion of the works^{14–16} was that the McClelland approximation (Eq. (1)) is connected with the assumption that the HMO π -electron energy levels of conjugated hydrocarbons are distributed in a (nearly) uniform manner.

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The reasoning by means of which this conclusion was obtained will be briefly repeated.

If $\lambda_1, \lambda_2, \dots, \lambda_n$ are the Eigen values of the molecular graph representing the respective conjugated molecule, then:¹⁻³

$$E = \sum_{i=1}^n |\lambda_i| \quad (2)$$

As is well known,^{1,2} the graph Eigen values satisfy the relation:

$$E = \sum_{i=1}^n (\lambda_i)^2 = 2m \quad (3)$$

Without loss of generality, Eqs. (2) and (3) may be rewritten as:

$$E = n \int_{-\infty}^{+\infty} |x| \Gamma(x) dx$$

and

$$E = n \int_{-\infty}^{+\infty} x^2 \Gamma(x) dx = 2m$$

where $\Gamma(x)$ is the probability density of the distribution of the graph Eigen values. It should be mentioned in passing that the exact expression for $\Gamma(x)$ is:

$$\Gamma(x) = \frac{1}{n} \sum_{i=1}^n \delta(x - \lambda_i)$$

with δ denoting the Dirac delta-function.

In situations when the actual form of the probability density $\Gamma(x)$ is not known (*i.e.*, when the spectrum of the molecular graph is not known), one tries to guess an approximate expression for it, denoted by $\Gamma^*(x)$, which must satisfy the conditions:

$$\int_{-\infty}^{+\infty} \Gamma^*(x) dx = 1 \quad (4)$$

$$\int_{-\infty}^{+\infty} x^2 \Gamma^*(x) dx = \frac{2m}{n} \quad (5)$$

and, of course, $\Gamma^*(x) \geq 0$ for all values of x . Then the quantity E^* ,

$$E^* = n \int_{-\infty}^{+\infty} |x| \Gamma^*(x) dx \quad (6)$$

is expected to provide a reasonably good approximation for the total π -electron energy E . In the works,^{14,16} the simplest possible choice for $\Gamma^*(x)$ was tested, namely,

$$\Gamma^*(x) = b \quad \text{for } -a \leq x \leq +a \quad \text{and otherwise } \Gamma^*(x) = 0 \quad (7)$$

The form of the function (7) is shown in Fig. 1.

The parameters a and b can easily be determined from the conditions Eq. (4) and (5), resulting in

$$a = \sqrt{\frac{6m}{n}} \quad \text{and} \quad b = \sqrt{\frac{n}{24m}} \quad (8)$$

By inserting the conditions given by Eq. (7) back into Eq. (6), one obtains:

$$E^* = a^2bn$$

which combined with Eq. (8) yields:

$$E^* = g^* \sqrt{2mn} \quad (9)$$

with g^* being a constant equal to $\sqrt{3}/2$. Not only is the algebraic form of the expression (9) identical to the McClelland approximation (Eq. (1)), but also the value of the multiplier $g^* = 0.8660$ is remarkably close to the (earlier) empirically determined value for g .

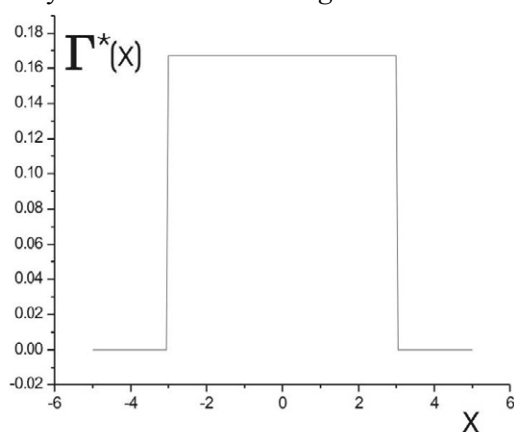


Fig. 1. The form of the probability density (Eq. 7) for $a = 3$ and $b = 1/6$. The Eigen values of the molecular graph are assumed to be uniformly distributed within the interval $(-a, +a)$, i.e., within the interval $(a, -a)$, the probability density is assumed to be constant (equal to b). Outside this interval, the probability density is set to be equal to zero.

Thus, it can be seen that by assuming a uniform distribution of the Eigen values of a molecular graph, the McClelland formula (Eq. (1)) can be reproduced. What has hitherto been overlooked is that formula (1) can also be deduced by using many other probability densities.

OBTAINING FORMULA (1) FROM A VARIETY OF MODEL FUNCTIONS $\Gamma^*(x)$

Suppose that the model based on Eq. (7) is required to be upgraded by including the information that the MO energies around the non-bonding level (corresponding to $x = 0$) are more numerous than those far from the non-bonding level, see diagram 1 in Fig. 2. This can be achieved by means of the function:

$$\Gamma^*(x) = b \left[1 - \left(\frac{x}{a} \right)^2 \right] \quad \text{for} \quad -a \leq x \leq +a \quad \text{and otherwise} \quad \Gamma^*(x) = 0 \quad (10)$$

Then, by direct calculation in a fully analogous manner as described in the preceding section, formula (9) is obtained with $g^* = \sqrt{5}/4$.

If, however, the opposite is assumed, namely that the MO energies around the non-bonding level are less numerous than those far from the non-bonding level (see diagram 2 in Fig. 2), and therefore set

$$\Gamma^*(x) = b \left(\frac{x}{a} \right)^2 \quad \text{for } -a \leq x \leq +a \quad \text{and otherwise } \Gamma^*(x) = 0 \quad (11)$$

then Eq. (9) is again obtained, this time for $g^* = \sqrt{15}/4$.

The model function Γ^* may be made still more complicated, with two minima or two maxima (diagrams 3 and 4 in Fig. 2), *i.e.*,

$$\Gamma^*(x) = b \left(\frac{x}{a} \right)^2 \left[1 - \left(\frac{x}{a} \right)^2 \right] \quad \text{for } -a \leq x \leq +a \quad \text{and otherwise } \Gamma^*(x) = 0 \quad (12)$$

or

$$\Gamma^*(x) = b \left[\left(\frac{x}{a} \right)^2 - \frac{1}{2} \right]^2 \quad \text{for } -a \leq x \leq +a \quad \text{and otherwise } \Gamma^*(x) = 0 \quad (13)$$

but Eq. (9) is still obtained with $g^* = 5\sqrt{21}/(12\sqrt{2})$ and $g^* = 5\sqrt{7}/(2\sqrt{187})$, respectively.

Hitherto, it was required that the model function be symmetric with regard to $x = 0$, *i.e.*, that $\Gamma^*(-x) = \Gamma^*(x)$, *i.e.*, that the pairing theorem be obeyed.^{1,2} However, even this plausible restriction is not necessary, as shown by the examples:

$$\Gamma^*(x) = b \left[\left(\frac{x}{a} \right)^2 - 1 \right]^2 \quad \text{for } -a \leq x \leq +a \quad \text{and otherwise } \Gamma^*(x) = 0 \quad (14)$$

and

$$\Gamma^*(x) = b \left[\left(\frac{x}{a} \right)^2 + 1 \right]^2 \quad \text{for } -a \leq x \leq +a \quad \text{and otherwise } \Gamma^*(x) = 0 \quad (15)$$

Also the functions (14) and (15) imply the validity of Eq. (9), with $g^* = 3\sqrt{3}/16$ and $g^* = 9\sqrt{5}/(16\sqrt{2})$, respectively. The forms of the functions (14) and (15) are shown in diagrams 5 and 6 in Fig. 2.

In order to further demonstrate the arbitrariness of the form of the model function that leads to the McClelland approximation, an example with a singularity at $x = 0$ was constructed (see diagram 7 in Fig. 2):

$$\Gamma^*(x) = b \left(\frac{|x|}{a} \right)^{-1/2} \quad \text{for } -a \leq x \leq +a \quad \text{and otherwise } \Gamma^*(x) = 0 \quad (16)$$

In spite of the (physically impossible) property of the model function (16) that $\Gamma(x) \rightarrow \infty$ for $x \rightarrow 0$, Eq. (9) is also obtained with $g^* = \sqrt{5}/3$.

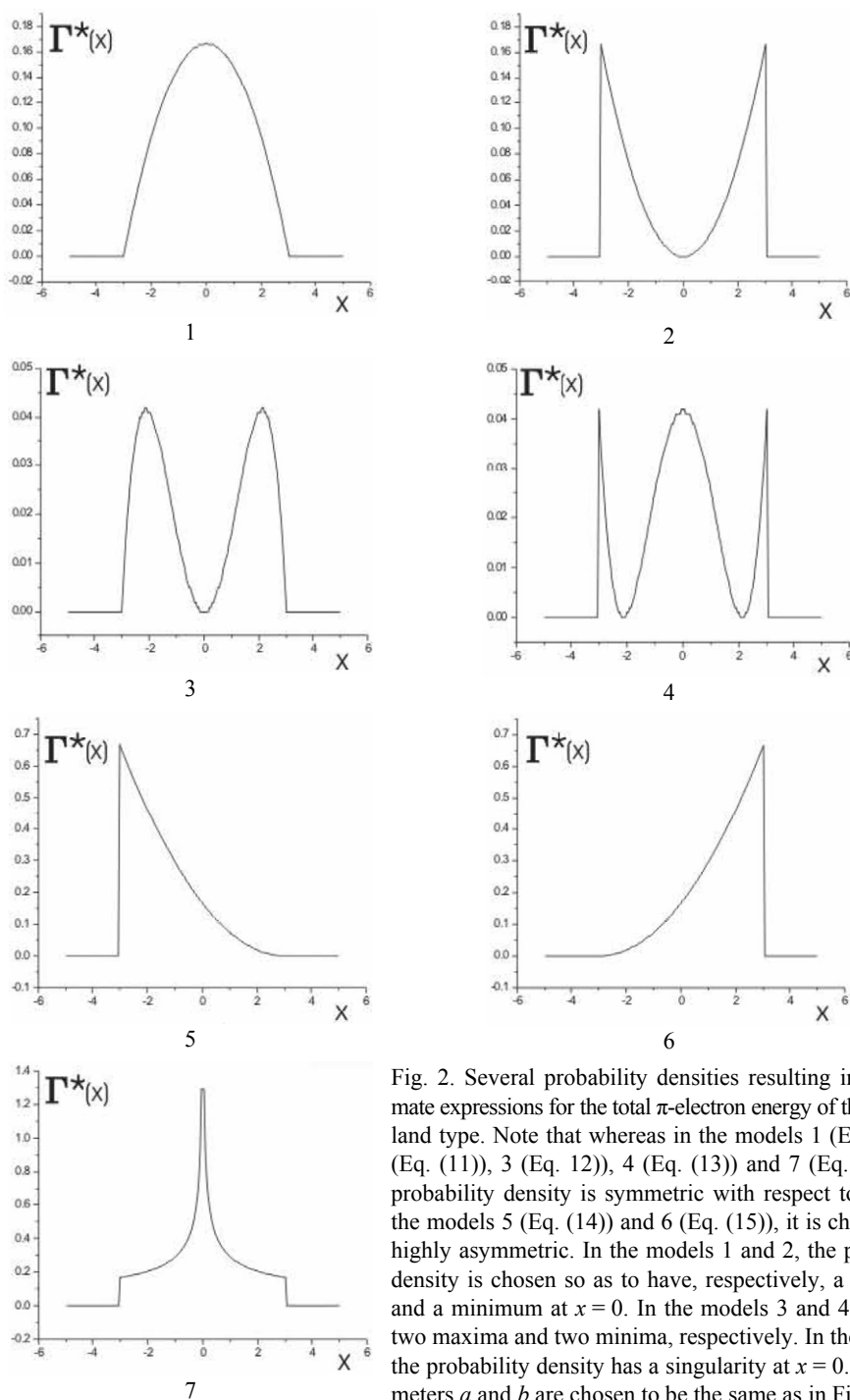


Fig. 2. Several probability densities resulting in approximate expressions for the total π -electron energy of the McClelland type. Note that whereas in the models 1 (Eq. (10)), 2 (Eq. (11)), 3 (Eq. (12)), 4 (Eq. (13)) and 7 (Eq. (16)), the probability density is symmetric with respect to $x = 0$. In the models 5 (Eq. (14)) and 6 (Eq. (15)), it is chosen to be highly asymmetric. In the models 1 and 2, the probability density is chosen so as to have, respectively, a maximum and a minimum at $x = 0$. In the models 3 and 4, there are two maxima and two minima, respectively. In the model 7, the probability density has a singularity at $x = 0$. The parameters a and b are chosen to be the same as in Fig. 1.

CONCLUDING REMARKS

In the seven examples for $\Gamma^*(x)$ given in the preceding section, Eq. (9) is always arrived at, but the multiplier g^* assumes different numerical values. In our opinion this detail is of lesser importance. Namely, it is possible to construct model functions $\Gamma^*(x)$, such that g^* in Eq. (9) has any desired value.

For instance, if for some $t \geq -1$,

$$\Gamma^*(x) = b \left[1 + t \left(\frac{x}{a} \right)^2 \right] \quad \text{for } -a \leq x \leq +a \quad \text{and otherwise } \Gamma^*(x) = 0 \quad (17)$$

then

$$g^* = \frac{3\sqrt{5}}{4} \frac{t+2}{\sqrt{(t+3)(3t+5)}}$$

By varying the parameter t , the multiplier in Eq. (9) assumes values between $3\sqrt{5}/8 = 0.8385$ and $\sqrt{15}/4 = 0.9682$, see Fig. 3. Therefore, the model function (17) can always be chosen so as to exactly "reproduce" the empirically determined value of g in the McClelland formula (Eq. (1)). This, of course, would be fully artificial and without any scientific justification.

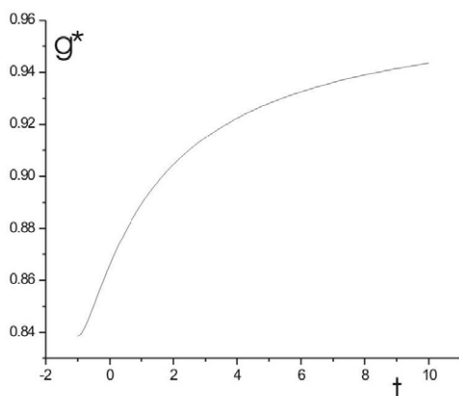


Fig. 3. Dependence of the multiplier g^* in Eq. (9) on the parameter t of the probability density (17). In order that $\Gamma^*(x)$ be positive valued, it must be $t > -1$.

The main conclusion of the present work is that the McClelland approximation (Eq.(1)) has nothing to do with the distribution of the HMO π -electron energy levels and that no inference on this distribution can be made based on the fact that Eq. (1) in a surprisingly accurate manner reproduces the actual E -values.

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ИЗВОД

МЕКЛЕЛАНДОВА АПРОКСИМАЦИЈА И РАСПОДЕЛА π -ЕЛЕКТРОНСКИХ
МОЛЕКУЛСКО ОРБИТАЛНИХ ЕНЕРГЕТСКИХ НИВОА

ИВАНГУТМАН

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Укупна π -електронска енергија E конјугованих угљководоника са n угљеникових атома и m угљеник–угљеник веза може се приближно израчунати помоћу формуле $E \approx g\sqrt{2mn}$, где је g емпиријска константа, $g \approx 0,9$. Раније је изнета тврдња да је добар квалитет Мекле-ландове апроксимације заснован на чињеници да су π -електронски молекулско орбитални енергетски нивои расподељени приближно униформно. Сада показујемо да Меклеландова апроксимација не зависи од природе расподеле енергетских нивоа, то јест да је она компати-билна са бројним, веома различитим расподелама.

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