

Generalizing the McClelland Bounds for Total π -Electron Energy

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In 1971 McClelland obtained lower and upper bounds for the total π -electron energy. We now formulate the generalized version of these bounds, applicable to the energy-like expression $E_X = \sum_{i=1}^n |x_i - \bar{x}|$, where x_1, x_2, \dots, x_n are any real numbers, and \bar{x} is their arithmetic mean. In particular, if x_1, x_2, \dots, x_n are the eigenvalues of the adjacency, Laplacian, or distance matrix of some graph G , then E_X is the graph energy, Laplacian energy, or distance energy, respectively, of G .

Key words: Total π -Electron Energy; Energy of Graph; Laplacian Energy of Graph; Bounds for Energy.

1. Introduction

The total π -electron energy, E_π , and the closely related resonance energies are quantities much studied in the theoretical chemistry of conjugated molecules. Their details are outlined in the books [1, 2], the recent reviews [3–5], and elsewhere [6–9]. For the majority of conjugated hydrocarbons, E_π satisfies the relation [1]

$$E_\pi = \sum_{i=1}^n |\lambda_i|, \quad (1)$$

where $\lambda_1, \lambda_2, \dots, \lambda_n$ are the eigenvalues of the molecular graph, i. e., the eigenvalues of the respective adjacency matrix \mathbf{A} .

For those conjugated systems for which (1) holds, McClelland obtained the bounds [10]

$$\sqrt{2m + n(n-1) |\det \mathbf{A}|^{2/n}} \leq E_\pi \leq \sqrt{2mn}, \quad (2)$$

where n is the number of carbon atoms and m the number of carbon-carbon bonds.

The right-hand side of (1) is applicable to any graph, both molecular and non-molecular. In view of this, the concept of *graph energy* was introduced, defined as [1]

$$E_A = E_A(G) = \sum_{i=1}^n |\lambda_i|, \quad (3)$$

where G now stands for any graph. This extension of (1) proved to be of great value for the theory of total

π -electron energy, resulting in numerous new discoveries (for details see [1, 5–8] and some of the most recent publications in this area [11–16]). The inequalities (2) remain valid if E_π is replaced by E_A . Then, of course, n is the number of vertices and m the number of edges of the graph G .

The graph energy concept was recently modified and applied to the Laplacian eigenvalues. This *Laplacian energy* was defined as [17, 18]

$$E_L = E_L(G) = \sum_{i=1}^n \left| \mu_i - \frac{2m}{n} \right|$$

for $\mu_1, \mu_2, \dots, \mu_n$ being the eigenvalues of the Laplacian matrix \mathbf{L} of the graph G . It should be noted that

$$\sum_{i=1}^n \mu_i = 2m, \quad (4)$$

and therefore $2m/n$ is just the average value of the Laplacian eigenvalues.

A further variant of (3) was considered in the paper [19], namely the *distance energy*, defined as

$$E_D = E_D(G) = \sum_{i=1}^n |\rho_i|,$$

where $\rho_1, \rho_2, \dots, \rho_n$ are the eigenvalues of the distance matrix \mathbf{D} of the graph G .

Because of (4) as well as

$$\sum_{i=1}^n \lambda_i = 0 \text{ and } \sum_{i=1}^n \rho_i = 0,$$

we see that E_A , E_L , and E_D are special cases of an energy-like quantity E_X ,

$$E_X = \sum_{i=1}^n |x_i - \bar{x}|, \quad (5)$$

where x_1, x_2, \dots, x_n are some real numbers, and \bar{x} is their arithmetic mean. It seems that the general expression (5) was first considered by Viviana Consonni and one of the present authors [20]. They employed E_X , based on the eigenvalues of several graph matrices, for designing quantitative structure-property relations (QSPR) for a variety of physico-chemical properties of a number of classes of organic compounds.

In what follows we show how the McClelland bounds (2) can be generalized so as to hold for E_X . For this we need to recall some elementary facts from statistics.

Let x_1, x_2, \dots, x_n be arbitrary real numbers. Then their arithmetic mean and variance are

$$\bar{x} = \frac{1}{n} \sum_{i=1}^n x_i \quad (6)$$

and

$$\text{Var}(x) = \frac{1}{n} \sum_{i=1}^n (x_i - \bar{x})^2. \quad (7)$$

2. The Generalized Lower Bound

Let x_1, x_2, \dots, x_n be real numbers. Define a polynomial

$$P(x) = \prod_{i=1}^n (x - x_i).$$

Note that if x_1, x_2, \dots, x_n are the eigenvalues of some matrix \mathbf{M} , then $P(x)$ is just the characteristic polynomial of that matrix. In particular, if $x_i = \lambda_i$, then $P(x)$ is the characteristic polynomial of the underlying graph. If $x_i = \mu_i$, then $P(x)$ is the Laplacian characteristic polynomial.

Theorem 1. Let E_X be defined via (5). Then

$$E_X \geq \sqrt{n \text{Var}(x) + n(n-1)|P(\bar{x})|^{2/n}}. \quad (8)$$

Equality in (8) is attained if and only if n is even and if half of the x_i 's are equal to some constant C_1 and the other half equal to some other constant C_2 ; the constants C_1 and C_2 may be equal.

Proof. Consider $(E_X)^2$ and apply (5):

$$\begin{aligned} (E_X)^2 &= \sum_{i=1}^n \sum_{j=1}^n |x_i - \bar{x}| |x_j - \bar{x}| \\ &= \sum_{i=1}^n (x_i - \bar{x})^2 + \sum_{i \neq j} |x_i - \bar{x}| |x_j - \bar{x}|. \end{aligned} \quad (9)$$

Now, by (7),

$$\sum_{i=1}^n (x_i - \bar{x})^2 = n \text{Var}(x). \quad (10)$$

In the other summation (that goes over $i \neq j$) there are $n(n-1)$ summands. Then, in view of the inequality between the arithmetic and geometric mean,

$$\begin{aligned} &\frac{1}{n(n-1)} \sum_{i \neq j} |x_i - \bar{x}| |x_j - \bar{x}| \\ &\geq \left(\prod_{i \neq j} |x_i - \bar{x}| |x_j - \bar{x}| \right)^{1/[n(n-1)]} \\ &= \left(\prod_{i=1}^n |x_i - \bar{x}|^{2(n-1)} \right)^{1/[n(n-1)]} \\ &= \left(\prod_{i=1}^n |x_i - \bar{x}| \right)^{2/n} = \left| \prod_{i=1}^n (\bar{x} - x_i) \right|^{2/n} = |P(\bar{x})|^{2/n}. \end{aligned}$$

Therefore

$$\sum_{i \neq j} |x_i - \bar{x}| |x_j - \bar{x}| \geq n(n-1) |P(\bar{x})|^{2/n}. \quad (11)$$

Substituting (10) and (11) back into (9) one obtains

$$(E_X)^2 \geq n \text{Var}(x) + n(n-1) |P(\bar{x})|^{2/n}$$

and inequality (8) follows.

Equality in (8) will be attained if all summands $|x_i - \bar{x}| |x_j - \bar{x}|$ are mutually equal, which will happen if all $|x_i - \bar{x}|$, $i = 1, 2, \dots, n$, are mutually equal. This means that x_i may assume only two different values, $\bar{x} + C$ and $\bar{x} - C$, for some C .

Suppose that $x_i = \bar{x} + C$ holds for $i = 1, 2, \dots, n_1$ and $x_i = \bar{x} - C$ for $i = n_1 + 1, n_1 + 2, \dots, n_1 + n_2$, where $n_1 + n_2 = n$. Then by (6), the arithmetic mean of the x_i 's will be $\bar{x} + (n_1 - n_2)C/n$. Because the arithmetic mean of the x_i 's is \bar{x} , it must be $n_1 = n_2$.

This completes the proof of Theorem 1. \square

If $\bar{x} = 0$, which happens in the case of the eigenvalues of the adjacency and distance matrices, then the term $|P(\bar{x})|$ in (8) becomes equal to the absolute value of the determinant of the respective matrix.

3. The Generalized Upper Bound

Theorem 2. Let E_X be defined via (5). Then

$$E_X \leq n \sqrt{\text{Var}(x)}. \quad (12)$$

Equality in (12) is attained under the precisely same conditions as in the case of the lower bound (8).

Proof. Consider the expression

$$\sum_{i=1}^n \sum_{j=1}^n (|x_i - \bar{x}| - |x_j - \bar{x}|)^2. \quad (13)$$

whose value is evidently greater than or equal to zero. Expanding (13) we obtain

$$\begin{aligned} & \sum_{i=1}^n \sum_{j=1}^n [(x_i - \bar{x})^2 + (x_j - \bar{x})^2 - 2|x_i - \bar{x}||x_j - \bar{x}|] \\ &= n \sum_{i=1}^n (x_i - \bar{x})^2 + n \sum_{j=1}^n (x_j - \bar{x})^2 \\ & \quad - 2 \sum_{i=1}^n |x_i - \bar{x}| \sum_{j=1}^n |x_j - \bar{x}| \\ &= 2n^2 \text{Var}(x) - 2(E_X)^2 \geq 0, \end{aligned}$$

and inequality (12) follows.

Equality in (12) is attained if and only if all summands in (13) are equal to zero, which will happen

if and only if all $|x_i - \bar{x}|$, $i = 1, 2, \dots, n$, are mutually equal. The remaining consideration is then same as in the proof of Theorem 1. \square

4. Discussion and Concluding Remarks

What remains to be done is to demonstrate that the bounds

$$\begin{aligned} & \sqrt{n \text{Var}(x) + n(n-1)|P(\bar{x})|^{2/n}} \\ & \leq E_X \leq n \sqrt{\text{Var}(x)} \end{aligned} \quad (14)$$

reduce to the McClelland inequalities (2) in the case when the x_i 's coincide with the ordinary eigenvalues of a (molecular) graph.

We already pointed out that in this case $P(\bar{x}) = \det \mathbf{A}$.

Because the sum of the graph eigenvalues is equal to zero, $\bar{\lambda} = 0$,

$$\text{Var}(\lambda) = \frac{1}{n} \sum_{i=1}^n (\lambda_i)^2,$$

and therefore

$$\text{Var}(\lambda) = \frac{2m}{n}.$$

Substituting this latter relation back into (14) we straightforwardly arrive at McClelland's result (2).

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