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 $E_X = \sum_{i=1}^{n} |x_i - \overline{x}|$, where $x_1, x_2, \ldots, x_n$ are any real numbers, and $\overline{x}$ is their arithmetic mean. In particular, if $x_1, x_2, \ldots, x_n$ 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]

$$E_\pi = \sum_{i=1}^{n} |\lambda_i|, \tag{1}$$

where $\lambda_1, \lambda_2, \ldots, \lambda_n$ 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]

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

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]

$$E_\mathrm{A} = E_\mathrm{A}(G) = \sum_{i=1}^{n} |\lambda_i|, \tag{3}$$

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]

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

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

$$\sum_{i=1}^{n} \mu_i = 2m, \tag{4}$$

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

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

where $\rho_1, \rho_2, \ldots, \rho_n$ 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,

$$E_X = \sum_{i=1}^{n} |x_i - \overline{x}|, \tag{5}$$

where $x_1, x_2, \ldots, x_n$ are some real numbers, and $\overline{x}$ 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 $x_1, x_2, \ldots, x_n$ be arbitrary real numbers. Then their arithmetic mean and variance are

$$\overline{x} = \frac{1}{n} \sum_{i=1}^{n} x_i \tag{6}$$

and

$$\mathrm{Var}(x) = \frac{1}{n} \sum_{i=1}^{n} (x_i - \overline{x})^2 . \tag{7}$$

2. The Generalized Lower Bound

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

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

Note that if $x_1, x_2, \ldots, x_n$ 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

$$E_X \geq \sqrt{n\,\mathrm{Var}(x) + n(n-1)|P(\overline{x})|^{2/n}}. \tag{8}$$

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):

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

Now, by (7),

$$\sum_{i=1}^{n} (x_i - \overline{x})^2 = n\,\mathrm{Var}(x). \tag{10}$$

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,

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

Therefore

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

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

$$(E_X)^2 \geq n\,\mathrm{Var}(x) + n(n-1)|P(\overline{x})|^{2/n}$$

and inequality (8) follows.

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

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

This completes the proof of Theorem 1. □

If $\overline{x} = 0$, which happens in the case of the eigenvalues of the adjacency and distance matrices, then the term $|P(\overline{x})|$ 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

$$E_X \leq n\sqrt{\mathrm{Var}(x)}. \tag{12}$$

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

Proof. Consider the expression

$$\sum_{i=1}^{n}\sum_{j=1}^{n}\left(|x_i-\overline{x}|-|x_j-\overline{x}|\right)^2, \tag{13}$$

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

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

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 $|x_i-\overline{x}|$, $i=1,2,\ldots,n$, are mutually equal. The remaining consideration is then same as in the proof of Theorem 1. □

4. Discussion and Concluding Remarks

What remains to be done is to demonstrate that the bounds

$$\begin{aligned}&\sqrt{n\,\mathrm{Var}(x)+n(n-1)|P(\overline{x})|^{2/n}}\\&\leq E_X\leq n\sqrt{\mathrm{Var}(x)}\end{aligned} \tag{14}$$

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 $P(\overline{x}) = \det \mathbf{A}$.

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

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

and therefore

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

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

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