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ORIGINAL PAPER

Towards a definition of almost–equienergetic graphs

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Abstract The energy $E(G)$ of a graph G, a quantity closely related to total π-electron energy, is equal to the sum of absolute values of the eigenvalues of G. Two graphs G_a and G_b are said to be equienergetic if $E(G_a) = E(G_b)$. In 2009 it was discovered that there are pairs of graphs for which the difference $E(G_a) - E(G_b)$ is non-zero, but very small. Such pairs of graphs were referred to as *almost equienergetic*, but a precise criterion for almost–equienergeticity was not given. We now fill this gap.

Keywords Total π-electron energy · Energy of graph · Equienergetic graphs · Almost–equienergetic graphs

AMS Classification Primary: 05C50 · Secondary: 05C90

1 Introduction

The total π-electron energy (E_π), as calculated within the simple tight–binding approximation, is one of the most precious pieces of information that can be obtained from the spectrum of the molecular graph [1–4]. In the case of the most interesting conjugated π-electron systems (in particular, benzenoids and fullerenes), E_π is quantitatively related with the experimentally determined heats of formation and other measures of thermodynamic stability [3,5–8].

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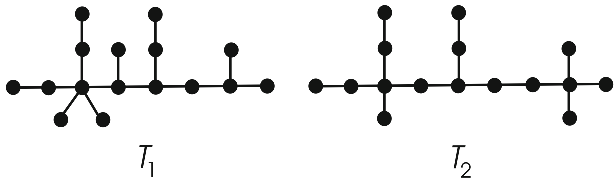

Fig. 1 Two almost–equienergetic trees: $E(T_1) = 18.090756640280765\ldots$, $E(T_2) = 18.0907\text{-}56641775140\ldots$

The graph–spectral expression for total π-electron energy was the motivation for the introduction of the concept of *graph energy*, defined as

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

where G is a general graph of order n, whose eigenvalues (i.e., the eigenvalues of its (0,1)-adjacency matrix) are $\lambda_1, \lambda_2, \ldots, \lambda_n$. For the vast majority of chemically relevant graphs (but not always [9]), E and E_π coincide. In the last 10–15 years, graph energy became a popular topic of mathematical research, resulting in hundreds of published papers. For details on graph energy, see the book [10] and the references cited therein. Some of the results thus obtained have direct chemical applicability.

A noteworthy discovery made in the theory of graph energy was that there are non-isomorphic and non-cospectral graphs with equal E-values. This was done practically simultaneously in 2004 by Balakrishnan [11] and Brankov et al. [12]. Such pairs of graphs are referred to as *equienergetic*. Eventually, numerous pairs, triplets, and larger families of equienergetic graphs were discovered and/or constructed [10].

Within a computer–aided search for equienergetic trees [13], it was noticed that there exist pairs of trees T_a, T_b, for which the difference $E(T_a) - E(T_b)$ is non-zero, but remarkably small. An example of this kind is displayed in Fig. 1.

Pairs of graphs with such property were named *almost–equienergetic* [13]. However, a rigorous definition of almost–equienergeticity has not be given. In [13] we read:

> …We tentatively and to a great degree arbitrarily call two graphs G_a and G_b almost–equienergetic if $0 < |E(G_a) - E(G_b)| < 10^{-8}$.

We now offer an analysis, leading to a more rational and theoretically better founded criterion for almost–equienergeticity.

2 Preparatory considerations

Throughout this paper we restrict our considerations to bipartite graphs. By this, the generality of the approach will be only slightly diminished, whereas the mathematical formalism will be significantly simplified.

The characteristic polynomial of a bipartite graph G with n vertices is of the form [14]

$$\phi(G,\lambda) = \sum_{k=0}^{\lfloor n/2 \rfloor} (-1)^k \, b(G,k) \, \lambda^{n-2k} \tag{1}$$

where $b(G,0) = 1$ and $b(G,k) \geq 0$ for all k, $1 \leq k \leq \lfloor n/2 \rfloor$.

Let thus G_a and G_b be two bipartite graphs, both possessing n vertices. Without loss of generality, in what follows we assume that n is even. According to a classical result by Coulson and Jacobs [15],

$$E(G_a) - E(G_b) = \frac{2}{\pi} \int_0^{+\infty} \ln \frac{\phi(G_a, \, ix)}{\phi(G_b, \, ix)} \, dx$$

where $i = \sqrt{-1}$. In view of Eq. (1),

$$E(G_a) - E(G_b) = \frac{2}{\pi} \int_0^{+\infty} \ln \frac{\sum_{k \geq 0} b(G_a,k) \, x^{n-2k}}{\sum_{k \geq 0} b(G_b,k) \, x^{n-2k}} \, dx. \tag{2}$$

Bearing in mind Eq. (2), we will focus our attention to the integral

$$\mathbf{J} = \int_0^{+\infty} \ln \frac{P(x)}{Q(x)} \, dx \tag{3}$$

where $P(x)$ and $Q(x)$ are polynomials:

$$P(x) = x^n + a_2 \, x^{n-2} + a_4 \, x^{n-4} + \ldots + a_n$$
$$Q(x) = x^n + b_2 \, x^{n-2} + b_4 \, x^{n-4} + \ldots + b_n$$

with conveniently chosen coefficients (see below), and examine what is the smallest possible non-zero value of $|\mathbf{J}|$.

3 Main result

Let n be an even positive integer, and

$$P(x) = \sum_{k=0}^{n/2} a_{2k} \, x^{n-2k} \quad ; \quad a_0 = 1$$

$$Q(x) = \sum_{k=0}^{n/2} b_{2k} \, x^{n-2k} \quad ; \quad b_0 = 1$$

be polynomials whose coefficients are non-negative integers. Let the integral $\mathbf{J}$ be given by Eq. (3).

In an earlier work [16], we have shown that by choosing the coefficients of $P(x)$ and $Q(x)$ sufficiently large, the integral $\mathbf{J}$ achieves arbitrarily small positive values. This property of $\mathbf{J}$ is independent of the actual value of n.

On the other hand, if the polynomials $P(x)$ and $Q(x)$ pertain to the characteristic polynomials of n-vertex (bipartite) graphs, then their coefficients cannot be boundlessly large. It is easy to recognize that in the case of acyclic graphs (including trees), the greatest possible value of these coefficients is $\binom{n/2}{k}$, achieved in the case of the graph consisting of $n/2$ isolated edges. We shall therefore require that $a_{2k}, b_{2k} \leq \binom{n/2}{k}$, $k = 1, 2, \ldots, n/2$.

It is obvious that $\mathbf{J} = 0$ if $a_{2k} = b_{2k}$ holds for all $k = 1, 2, \ldots, n/2$. If, however, $a_{2k} \geq b_{2k}$ holds for all $k = 1, 2, \ldots, n/2$, and at least one of these inequalities is strict, then $\mathbf{J} > 0$. We are interested to find out, how small $\mathbf{J}$ could be in such a case.

Let, therefore, the polynomials $P(x)$ and $Q(x)$ be chosen so that $a_{2k} = b_{2k}$ for all $k \neq (n - k_0)/2$ and $b_{n-k_0} = a_{n-k_0} - 1$, that is

$$Q(x) = P(x) - x^{k_0}. \tag{4}$$

Then

$$\begin{aligned}
\mathbf{J} &= \int_0^{+\infty} \ln\left[1 + \frac{x^{k_0}}{Q(x)}\right] dx \\
&\geq \int_0^{+\infty} \ln\left[1 + \frac{x^{k_0}}{\sum_{k=0}^{n/2} \binom{n/2}{k} x^{n-2k}}\right] dx = \int_0^{+\infty} \ln\left[1 + \frac{x^{k_0}}{(x^2+1)^{n/2}}\right] dx \\
&= \int_0^{1} \ln\left[1 + \frac{x^{k_0}}{(x^2+1)^{n/2}}\right] dx + \int_1^{+\infty} \ln\left[1 + \frac{x^{k_0}}{(x^2+1)^{n/2}}\right] dx \\
&\geq \int_0^{1} \ln\left[1 + \frac{x^{k_0}}{2^{n/2}}\right] dx + \int_1^{+\infty} \ln\left[1 + \frac{x^{k_0}}{(2x^2)^{n/2}}\right] dx.
\end{aligned}$$

Denote the integrals $\int_0^1 \ln\left(1 + \frac{x^{k_0}}{2^{n/2}}\right) dx$ and $\int_1^{+\infty} \ln\left(1 + \frac{x^{k_0}}{(2x^2)^{n/2}}\right) dx$ by $\mathbf{J}_1(n, k_0)$ and $\mathbf{J}_2(n, k_0)$, respectively, and let

$$\widehat{\mathbf{J}}(n, k_0) = \mathbf{J}_1(n, k_0) + \mathbf{J}_2(n, k_0).$$

It is clear that $\mathbf{J} \geq \widehat{\mathbf{J}}(n, k_0)$.

Consider first the integral $\mathbf{J}_1(n, k_0)$. For $k_0 = 0$, we simply have

$$\mathbf{J}_1(n, 0) = \ln\left(1 + \frac{1}{2^{n/2}}\right)$$

whereas for $k_0 > 0$, by performing integration by parts and taking into account the identity [17]

$$\int_0^u \frac{x^{\mu-1}}{1+\beta x}\,dx = \frac{u^\mu}{\mu}\;{}_2F_1(1\,,\ \mu\,;\ 1+\mu\,;\ -u\beta)$$

we obtain

$$\mathbf{J}_1(n,k_0) = \ln\left(1+\frac{1}{2^{n/2}}\right) - k_0\left[1 - {}_2F_1\left(1\,,\ \frac{1}{k_0}\,;\ 1+\frac{1}{k_0}\,;\ -\frac{1}{2^{n/2}}\right)\right].$$

In the above expressions, ${}_2F_1(a\,,\ b\,;\ c\,;\ z)$ is the Gaussian hypergeometric function defined via

$${}_2F_1(a\,,\ b\,;\ c\,;\ z) = \sum_{k=0}^{+\infty} \frac{(a)_k\,(b)_k}{(c)_k}\,\frac{z^k}{k!}$$

where

$$(q)_k = \begin{cases} 1 & \text{for}\, k = 0 \\ q(q+1)\ldots(q+k-1) & \text{for}\, k > 0. \end{cases}$$

Consider now the integral $\mathbf{J}_2(n,k_0)$, which can be written as

$$\mathbf{J}_2(n,k_0) = \int_1^{+\infty} \ln\left(1+\frac{1}{2^{n/2}\,x^{n-k_0}}\right)dx.$$

By applying integration by parts we get

$$\mathbf{J}_2(n,k_0) = x\ln\left(1+\frac{1}{2^{n/2}\,x^{n-k_0}}\right)\Bigg|_1^{+\infty} + \int_1^{+\infty} \frac{n-k_0}{1+2^{n/2}\,x^{n-k_0}}\,dx.$$

Since $n-k_0 \geq 2$, by application of l'Hospital's rule, we have

$$\lim_{x\to+\infty} x\ln\left(1+\frac{1}{2^{n/2}\,x^{n-k_0}}\right) = \lim_{x\to+\infty} \frac{\ln\left(1+\frac{1}{2^{n/2}\,x^{n-k_0}}\right)}{\frac{1}{x}}$$

$$= \lim_{x\to+\infty} \frac{\frac{k_0-n}{x+2^{n/2}\,x^{n-k_0+1}}}{-\frac{1}{x^2}} = \lim_{x\to+\infty} \frac{n-k_0}{\frac{1}{x}+2^{n/2}\,x^{n-k_0-1}} = 0$$

and therefore

$$\mathbf{J}_2(n,k_0) = -\ln\left(1+\frac{1}{2^{n/2}}\right) + \int_1^{+\infty} \frac{n-k_0}{1+2^{n/2}\,x^{n-k_0}}\,dx. \tag{5}$$

In view of the identity [17]

$$\int_u^{+\infty} \frac{x^{\mu-1}}{(1+\beta\,x)^{\nu}}\,dx = \frac{u^{\mu-\nu}}{(\nu-\mu)\beta^{\nu}}\ {}_2F_1\left(\nu\,,\ \nu-\mu\,;\ \nu-\mu+1\,;\ -\frac{1}{u\beta}\right)$$

the integral on the right–hand side of (5) is equal to

$$\frac{n-k_0}{2^{n/2}\,(n-k_0-1)}\ {}_2F_1\left(1\,,\ 1-\frac{1}{n-k_0}\,;\ 2-\frac{1}{n-k_0}\,;\ -\frac{1}{2^{n/2}}\right)$$

and therefore

$$\begin{aligned}\mathbf{J}_2(n,k_0) &= -\ln\left(1+\frac{1}{2^{n/2}}\right)\\ &\quad+\frac{n-k_0}{2^{n/2}\,(n-k_0-1)}\ {}_2F_1\left(1\,,\ 1-\frac{1}{n-k_0}\,;\ 2-\frac{1}{n-k_0}\,;\ -\frac{1}{2^{n/2}}\right).\end{aligned}$$

For $k_0=0$, this finally yields

$$\widehat{\mathbf{J}}(n,0) = \frac{n}{2^{n/2}\,(n-1)}\ {}_2F_1\left(1\,,\ 1-\frac{1}{n}\,;\ 2-\frac{1}{n}\,;\ -\frac{1}{2^{n/2}}\right) \tag{6}$$

whereas for $k_0>0$, we get

$$\begin{aligned}\widehat{\mathbf{J}}(n,k_0) &= \frac{n-k_0}{2^{n/2}\,(n-k_0-1)}\ {}_2F_1\left(1\,,\ 1-\frac{1}{n-k_0}\,;\ 2-\frac{1}{n-k_0}\,;\ -\frac{1}{2^{n/2}}\right)\\ &\quad-k_0\left[1-{}_2F_1\left(1\,,\ \frac{1}{k_0}\,;\ 1+\frac{1}{k_0}\,;\ -\frac{1}{2^{n/2}}\right)\right].\end{aligned}$$

In Fig. 2 is shown the dependence of the integral $\widehat{\mathbf{J}}(n,k_0)$ on the variable k_0 , $k_0 \in [0, n-2]$, for a few selected values of n. The greatest value of $\widehat{\mathbf{J}}(n,k_0)$ is always achieved at $k_0=n-2$, in which case

$$\begin{aligned}\widehat{\mathbf{J}}(n,n-2) &= 2^{1-n/4}\arctan\left(2^{-n/4}\right)\\ &\quad-(n-2)\left[1-{}_2F_1\left(1\,,\ \frac{1}{n-2}\,;\ 1+\frac{1}{n-2}\,;\ -\frac{1}{2^{n/2}}\right)\right]. \end{aligned}\tag{7}$$

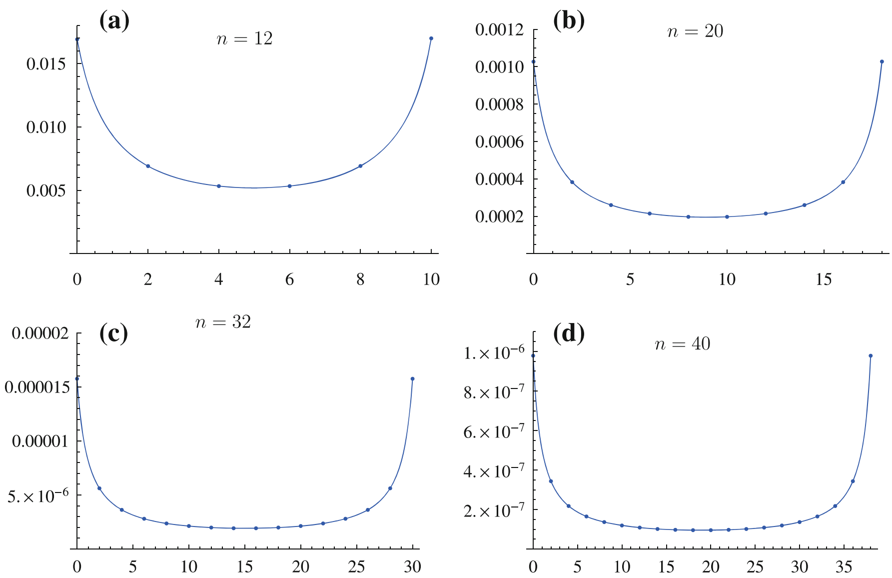

Fig. 2 The integrals $\widehat{\mathbf{J}}(n, k_0)$ for $k_0 \in [0, n-2]$, $n = 12, 20, 32, 40$

Table 1 The integral $\widehat{\mathbf{J}}(n, n-2)$ for $n = 6, 8, \ldots, 60$

n	$\widehat{\mathbf{J}}(n, n-2)$	n	$\widehat{\mathbf{J}}(n, n-2)$
6	1.47×10^{-1}	8	7.06×10^{-2}
10	3.45×10^{-2}	12	1.70×10^{-2}
14	8.40×10^{-3}	16	4.16×10^{-3}
18	2.07×10^{-3}	20	1.03×10^{-3}
22	5.11×10^{-4}	24	2.55×10^{-4}
26	1.27×10^{-4}	28	6.33×10^{-5}
30	3.16×10^{-5}	32	1.58×10^{-5}
34	7.86×10^{-6}	36	3.92×10^{-6}
38	1.96×10^{-6}	40	9.78×10^{-7}
42	4.88×10^{-7}	44	2.44×10^{-7}
46	1.22×10^{-7}	48	6.09×10^{-8}
50	3.04×10^{-8}	52	1.52×10^{-8}
54	7.59×10^{-9}	56	3.79×10^{-9}
58	1.90×10^{-9}	60	9.47×10^{-10}

Numerical values of $\widehat{\mathbf{J}}(n, n-2)$ for the first few values of n are given in Table 1, whereas the corresponding values of $\widehat{\mathbf{J}}(n, 0)$ are found in Table 2. It can be noticed that the numerical values of these two integrals differ insignificantly. Therefore, since the form of the expression (6) is somewhat simpler than that of (7), the former should be preferred with regard to the definition of almost–equienergeticity.

Table 2 The integral $\widehat{\mathbf{J}}(n, 0)$ for $n = 6, 8, \ldots, 60$

n	$\widehat{\mathbf{J}}(n, 0)$	n	$\widehat{\mathbf{J}}(n, 0)$
6	1.42×10^{-1}	8	6.94×10^{-2}
10	3.42×10^{-2}	12	1.69×10^{-2}
14	8.38×10^{-3}	16	4.16×10^{-3}
18	2.07×10^{-3}	20	1.03×10^{-3}
22	5.11×10^{-4}	24	2.55×10^{-4}
26	1.27×10^{-4}	28	6.33×10^{-5}
30	3.16×10^{-5}	32	1.58×10^{-5}
34	7.86×10^{-6}	36	3.92×10^{-6}
38	1.96×10^{-6}	40	9.78×10^{-7}
42	4.88×10^{-7}	44	2.44×10^{-7}
46	1.22×10^{-7}	48	6.09×10^{-8}
50	3.04×10^{-8}	52	1.52×10^{-8}
54	7.59×10^{-9}	56	3.79×10^{-9}
58	1.90×10^{-9}	60	9.47×10^{-10}

4 Discussion

The integral $\frac{2}{\pi}\,\mathbf{J}$, calculated according to the model (4), and its estimates $\frac{2}{\pi}\,\widehat{\mathbf{J}}$, are certainly not the smallest non-zero value that the energy difference of two graphs may assume. Even smaller values of $|E(G_a) - E(G_b)|$ must be encountered if some coefficients of $Q(x)$ are set smaller and some other greater than the respective coefficients of $P(x)$. Therefore, $\frac{2}{\pi}\,\widehat{\mathbf{J}}(n, n-2)$ may be viewed as the greatest energy difference within a setup that is far from both the best possible and the worst possible, but which—from an algebraic point of view—is the simplest possible.

It is intuitively clear that whatever the criterion for almost–equienergeticity would be, it should be a (moderately) decreasing function of the number n of vertices. As seen from Tables 1 and 2, the behavior of $\widehat{\mathbf{J}}$ satisfies this requirement. In addition, the actual numerical values of $\frac{2}{\pi}\,\widehat{\mathbf{J}}(n, n-2)$ are in good agreement with the smallest observed (non-zero) energy differences encountered in the earlier computer–aided study [13].

Therefore, we propose that two n-vertex graphs G_a and G_b be referred to as almost–equienergetic if the condition

$$0 < |E(G_a) - E(G_b)| \leq \frac{2}{\pi}\,\widehat{\mathbf{J}}(n, n-2)$$

is obeyed, which in practice is identical to the condition

$$0 < |E(G_a) - E(G_b)| \leq \frac{2}{\pi}\,\widehat{\mathbf{J}}(n, 0)$$

where $\widehat{\mathbf{J}}(n, n-2)$ and $\widehat{\mathbf{J}}(n, 0)$ are given by Eqs. (7) and (6), respectively, and where the needed numerical values can be taken from Tables 1 and 2.

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References

1. A. Graovac, I. Gutman, N. Trinajstić, *Topological Approach to the Chemistry of Conjugated Molecules* (Springer, Berlin, 1977)
2. N. Trinajstić, *Chemical Graph Theory* (CRC, Boca Raton, 1983)
3. I. Gutman, O.E. Polansky,*Mathematical Concepts in Organic Chemistry, chapter 8* (Springer, Berlin, 1986)
4. J.R. Dias, *Molecular Orbital Calculations Using Chemical Graph Theory* (Springer, Berlin, 1993)
5. L.J. Schaad, B.A. Hess, J. Am. Chem. Soc. **94**, 3068 (1972)
6. I. Gutman, Top. Curr. Chem. **162**, 29 (1992)
7. S.J. Austin, P.W. Fowler, P. Hansen, D.E. Manolopoulos, M. Zheng, Chem. Phys. Lett. **228**, 478 (1994)
8. I. Gutman, J. Serb. Chem. Soc. **70**, 441 (2005)
9. D.J. Klein, V.R. Rosenfeld, J. Math. Chem. **49**, 1238 (2011)
10. X. Le, Y. Shi, I. Gutman, *Graph Energy* (Springer, New York, 2012)
11. R. Balakrishnan, Linear Algebra Appl. **387**, 287 (2004)
12. V. Brankov, D. Stevanović, I. Gutman, J. Serb. Chem. Soc. **69**, 549 (2004)
13. O. Miljković, B. Furtula, S. Radenković, I. Gutman, MATCH Commun. Math. Comput. Chem. **61**, 451 (2009)
14. D. Cvetković, P. Rowlinson, S. Simić, *An Introduction to the Theory of Graph Spectra* (Cambridge University Press, Cambridge, 2010)
15. C.A. Coulson, J. Jacobs, J. Chem. Soc., 2805 (1949)
16. M.P. Stanić, I. Gutman, MATCH Commun. Math. Comput. Chem. **70**, 681 (2013)
17. I.S. Gradshteyn, I.M. Ryzhik, *Tables of Integrals, Series, and Products* (Academic Press, London, 2000)