

APPROXIMATE ENERGY OF DENDRIMERS¹

DRAGAN STEVANOVIĆ

*University of Primorska—FAMNIT, Glagoljaška 8, 6000 Koper, Slovenia,
University of Niš—PMF, Višegradska 33, 18000 Niš, Serbia
e-mail: dragance106@yahoo.com*

(Received June 19, 2009)

Abstract

The characteristic polynomials of monodendrons is shown to be related to the Dickson polynomials of the second kind. This relation is then used to derive the characteristic polynomials and approximate the total π -electron energy of dendrimers and bidendrons.

1 Introduction

Dendrimers are highly branched macromolecules with a regular tree-like structure made up of repeating units arranged in a hierarchical and self-similar fashion [1]. We recall that a tree is a connected acyclic graph. The balanced tree is an unweighted rooted tree \mathcal{T} such that in each level the vertices have equal degree. Let the root vertex be at level 1 and let \mathcal{T} has k levels, such that the vertices in the level k have degree 1. For $j = 1, \dots, k$, the numbers d_j and n_j denote the degree of the vertices and the number of vertices in the level j , respectively. Then $n_2 = d_1 n_1$ and for $j = 2, \dots, k - 1$,

$$n_{j+1} = (d_j - 1)n_j.$$

¹This work was supported by the research program P1-0285 of Slovenian Agency for Research, the research grant 144015G of Serbian Ministry of Science.

The total number of vertices in the tree is

$$n = \sum_{j=1}^k n_j.$$

The *dendrimer* $D_{d,k}$ is now a balanced tree for which $d_1 = d_2 = \dots = d_{k-1} = d + 1$, where vertices represent the dendrimer building blocks. A *monodendron* $D'_{d,k-1}$ is any largest connected subtree of $D_{d,k}$ that does not contain the root of $D_{d,k}$. In other words, monodendron $D'_{d,k}$ is a k -level balanced tree for which $d_1 = d$ and $d_2 = \dots = d_{k-1} = d + 1$. Note that the path on n vertices is a monodendron $D'_{1,n}$. We shall exclude this trivial case by assuming that $d \geq 2$ in the sequel.

Let G be a simple molecular graph with the adjacency matrix $A(G)$ having the eigenvalues $\lambda_1, \dots, \lambda_n$. The characteristic polynomial $\phi(G, \lambda)$ of the graph G is the characteristic polynomial of $A(G)$, $\phi(G, \lambda) = \det(\lambda I - A(G))$, and the eigenvalues of G are the solutions of the equation $\phi(G, \lambda) = 0$.

We are concerned here with the eigenvalues of monodendrons and dendrimers, and their total π -electron energy E , as calculated within the simple Hückel molecular orbital (HMO) model [2, 3]. According to the standard procedure in the theory of the HMO total π -electron energy (see, for instance, [2]–[9]), E is expressed in the units of the carbon-carbon resonance integral β , using as an origin the Coulomb integral pertaining to C atoms, $\alpha = 0$. In order to further simplify calculations, we shall treat dendrimer building blocks as if they were single atoms, and assume that h and k values corresponding to non-carbon atoms are all equal to one (although these assumptions hold only in a hypothetical carbon dendrimer). The quantity E can be calculated from the eigenvalues of the graph G , representing the respective molecule [4, 5]:

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

2 Spectra and energy of monodendrons

Let $\Phi = \{1, \dots, k - 1\}$ and

$$\Omega = \{j \in \Phi : n_{k-j} < n_{k-j+1}\}.$$

Rojo and Soto proved the following theorem in [10]:

Theorem 1 Let $S_0(\lambda) = 1$, $S_1(\lambda) = \lambda$ and

$$S_j(\lambda) = \lambda S_{j-1}(\lambda) - \frac{n_{k-j+2}}{n_{k-j+1}} S_{j-2}(\lambda)$$

for $j = 2, \dots, k$. Then

(a) If $S_j(\lambda) \neq 0$ for all $j = 1, \dots, k-1$, then

$$\phi(A(\mathcal{T}), \lambda) = S_k(\lambda) \prod_{j \in \Omega} S_j^{n_{k-j+1} - n_{k-j}}(\lambda).$$

(b) The distinct eigenvalues of $A(\mathcal{T})$ are given by

$$(\cup_{j \in \Omega} \{\lambda \in \mathbb{R} : S_j(\lambda) = 0\}) \cup \{\lambda \in \mathbb{R} : S_k(\lambda) = 0\}.$$

Consider now a monodendron $D'_{d,k}$. Then $\Omega = \Phi$ and $\frac{n_{k-j+2}}{n_{k-j+1}} = d$ is constant for all $j = 2, \dots, k$. Thus,

$$S_j(\lambda) = \lambda S_{j-1}(\lambda) - d S_{j-2}(\lambda)$$

for $j = 2, \dots, k$, which together with $S_0(\lambda) = 1$, $S_1(\lambda) = \lambda$ defines Dickson polynomials [11] of the second kind

$$S_j(\lambda) \equiv E_j(\lambda, d) = \sum_{p=0}^{\lfloor j/2 \rfloor} \binom{j-p}{p} (-d)^p \lambda^{j-2p}.$$

Dickson polynomial $E_j(\lambda, d)$ is related to Chebyshev polynomial of the second kind $U_j(\lambda)$ by

$$E_j(\lambda, d) = \sqrt{d}^j U_j\left(\frac{\lambda}{2\sqrt{d}}\right).$$

Recall that $U_j(\lambda)$ is defined by

$$U_j(\cos \theta) = \frac{\sin(j+1)\theta}{\sin \theta}$$

and that the zeros of $U_j(\lambda)$ are of the form

$$\cos \frac{i\pi}{j+1}, \quad i = 1, \dots, j.$$

Thus, the zeros of $S_j(\lambda)$ are of the form

$$2\sqrt{d} \cos \frac{i\pi}{j+1}, \quad i = 1, \dots, j$$

and the entire spectrum of monodendron $D'_{d,k}$, representing multiplicities as bracketed exponents, is given by

$$\begin{aligned} & \bigcup_{j=1}^{k-1} \left\{ 2\sqrt{d} \cos \frac{i\pi}{j+1} \right. \\ & \quad \left. : i = 1, \dots, j \right\} \\ & \cup \left\{ 2\sqrt{d} \cos \frac{i\pi}{k+1} : i = 1, \dots, k \right\}. \end{aligned}$$

The relation $\phi(P_j, \lambda) = U_j(\lambda/2)$, telling us that the values

$$2 \cos \frac{i\pi}{j+1}, \quad i = 1, \dots, j$$

form the spectrum of the path P_j with j vertices, has been recognized already in [12]. Therefore, we see that the spectrum of the monodendron $D'_{d,k}$ is formed from an appropriate number copies of the spectra of paths P_1, \dots, P_k , multiplied by \sqrt{d} . This observation may be used to represent $E(D'_{d,k})$ as

$$\begin{aligned} & \sum_{j=1}^{k-1} d^{k-j-1} (d-1) \sum_{i=1}^j \left| 2\sqrt{d} \cos \frac{i\pi}{j+1} \right| \\ & + \sum_{i=1}^k \left| 2\sqrt{d} \cos \frac{i\pi}{k+1} \right| \\ & = \sqrt{d} \left(\sum_{j=1}^{k-1} d^{k-j-1} (d-1) E(P_j) + E(P_k) \right) \\ & = \sqrt{d} \left(\sum_{j=1}^{k-1} d^{k-j} E(P_j) - \sum_{j=2}^k d^{k-j} E(P_{j-1}) + E(P_k) \right) \\ & = \sqrt{d} \sum_{j=2}^k d^{k-j} (E(P_j) - E(P_{j-1})) \end{aligned}$$

since $E(P_1) = 0$. Thus, the energy of a monodendron is a product of \sqrt{d} and a polynomial in d , whose coefficients are differences of energies of two consecutive paths. The first few coefficients are given in Table 1. In fact, for $j \rightarrow \infty$ we have that $E(P_j) \approx 4j/\pi$, so that $E(P_j) - E(P_{j-1}) \approx 4/\pi \approx 1.27323954$ is the limit value of the coefficients.

3 Energy of dendrimers

Let T be a tree, $e = uv$ its edge and T_1, T_2 the connected components of $T - e$ (such that $u \in T_1, v \in T_2$). Then the following relation holds [12, p. 59]

$$\phi(T, \lambda) = \phi(T_1, \lambda)\phi(T_2, \lambda) - \phi(T_1 - u, \lambda)\phi(T_2 - v, \lambda). \quad (1)$$

j	$E(P_j) - E(P_{j-1})$	j	$E(P_j) - E(P_{j-1})$
2	2	16	1.36956212
3	0.82842712	17	1.18420171
4	1.64370883	18	1.35902657
5	0.99196566	19	1.19327830
6	1.52381680	20	1.35057053
7	1.06676057	21	1.20067391
8	1.46286198	22	1.34363318
9	1.10996207	23	1.20681629
10	1.42584534	24	1.33783884
11	1.13815986	25	1.21199931
12	1.40095140	26	1.33292639
13	1.15803133	27	1.21643158
14	1.38305352	28	1.32870862
15	1.17279631	29	1.22026527

Table 1: Differences of energies of two consecutive paths.

If T is the dendrimer $D_{d,k}$ and the edge $e = uv$ is incident to its root (see Figure 1),

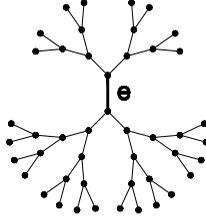


Figure 1: Dendrimer $D_{2,5}$.

then T_1 is the monodendron $D'_{d,k}$, T_2 is the monodendron $D'_{d,k-1}$, and $T_1 - u$ and $T_2 - v$ consist of d copies of monodendrons $D'_{d,k-1}$ and $D'_{d,k-2}$, respectively. Then, denoting $S_j(\lambda)$ shortly by S_j ,

$$\begin{aligned}
 & \phi(D_{d,k}, \lambda) \\
 = & \phi(D'_{d,k}, \lambda)\phi(D'_{d,k-1}, \lambda) - \phi^d(D'_{d,k-1}, \lambda)\phi^d(D'_{d,k-2}, \lambda) \\
 = & S_k \prod_{j=1}^{k-1} S_j^{d^{k-j-1}(d-1)} S_{k-1} \prod_{j=1}^{k-2} S_j^{d^{k-j-2}(d-1)} \\
 - & S_{k-1}^d \prod_{j=1}^{k-2} S_j^{d^{k-j-1}(d-1)} S_{k-2}^d \prod_{j=1}^{k-3} S_j^{d^{k-j-2}(d-1)}
 \end{aligned}$$

$$\begin{aligned}
 &= S_{k-1}(S_k - S_{k-2}) \prod_{j=1}^{k-1} S_j^{d^{k-j-1}(d-1)} \prod_{j=1}^{k-2} S_j^{d^{k-j-2}(d-1)} \\
 &= S_{k-1}^d(S_k - S_{k-2}) \prod_{j=1}^{k-2} S_j^{d^{k-j-2}(d^2-1)}.
 \end{aligned}$$

So, the spectrum of $D_{d,k}$ consists of

$$\begin{aligned}
 &\bigcup_{j=1}^{k-2} \left\{ 2\sqrt{d} \cos \frac{i\pi^{[d^{k-j-2}(d^2-1)]}}{j+1} : i = 1, \dots, j \right\} \\
 &\cup \left\{ 2\sqrt{d} \cos \frac{i\pi^{[d]}}{k} : i = 1, \dots, k-1 \right\}
 \end{aligned}$$

and k roots of $S_k(\lambda) - S_{k-2}(\lambda)$. However, we know of no closed-form formula for the roots of this polynomial, and we cannot give an exact formula for the energy of dendrimer $D_{d,k}$. Instead, we may use the results of Day and So ([13, Corollary 4.3] and [14, Corollary 2.7]) to estimate the energy of $D_{d,k}$:

$$E(D_{d,k} - e) < E(D_{d,k}) \leq E(D_{d,k} - e) + 2.$$

Since $D_{d,k} - e$ consists of $D'_{d,k}$ and $D'_{d,k-1}$, from previous section we have that

$$\begin{aligned}
 &E(D_{d,k} - e) \\
 &= \sqrt{d} \sum_{j=2}^k d^{k-j} (E(P_j) - E(P_{j-1})) \\
 &+ \sqrt{d} \sum_{j=2}^{k-1} d^{k-1-j} (E(P_j) - E(P_{j-1})) \\
 &= \sqrt{d} \left(2d^{k-2} + \sum_{j=3}^k d^{k-j} (E(P_j) - E(P_{j-2})) \right).
 \end{aligned}$$

This estimate produces an easily calculable interval of length two containing the true value of $E(D_{d,k})$. As an example, Table 2 contains the approximate value of $E(D_{d,k})$, the lower bound $E(D'_{d,k}) + E(D'_{d,k-1})$ and their difference for $d = 2$ and $k \leq 11$. We can see from the table that the difference oscillates roughly around 0.548, so we can propose an approximate formula for $d = 2$:

$$E(D_{2,k}) \approx \sqrt{2} \left(2^{k-1} + \sum_{j=3}^k 2^{k-j} (E(P_j) - E(P_{j-2})) \right) + 0.548.$$

k	$E(D'_{d,k}) + E(D'_{d,k-1})$	$E(D_{d,k})$	difference
3	9.65685425	10.12899020	0.47213595
4	22.80983669	23.38426086	0.57442417
5	49.34708000	49.86588464	0.51880464
6	102.25201367	102.81377581	0.56176214
7	208.16765700	208.70096090	0.53330390
8	419.91274051	420.46975221	0.55701170
9	843.46400369	844.00367659	0.53967290
10	1690.51418059	1691.06889461	0.55471402
11	3384.65441210	3385.19744391	0.54303181

Table 2: The values of $E(D_{d,k})$ for $d = 2$, $k \leq 11$ and its bounds.

4 Energy of bidendrons

Bidendron $B_{d,k}$ is formed from two monodendrons $D'_{d,k}$ by joining their roots with an edge (see Figure 2). Applying the relation (1) to this edge, we get

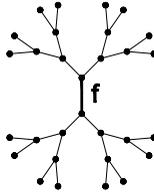


Figure 2: Bidendron $B_{2,4}$.

$$\begin{aligned}
 & \phi(B_{d,k}, \lambda) \\
 = & \phi(D'_{d,k}, \lambda)\phi(D'_{d,k}, \lambda) - \phi^d(D'_{d,k-1}, \lambda)\phi^d(D'_{d,k-1}, \lambda) \\
 = & S_k^2 \prod_{j=1}^{k-1} S_j^{2d^{k-j-1}(d-1)} - S_{k-1}^{2d} \prod_{j=1}^{k-2} S_j^{2d^{k-j-1}(d-1)} \\
 = & (S_k^2 - S_{k-1}^2) \prod_{j=1}^{k-1} S_j^{2d^{k-j-1}(d-1)}.
 \end{aligned}$$

So, the spectrum of $B_{d,k}$ consists of

$$\bigcup_{j=1}^{k-1} \left\{ 2\sqrt{d} \cos \frac{i\pi}{j+1} \right\}_{[2d^{k-j-1}(d-1)]} : i = 1, \dots, j$$

and $2k$ roots of $S_k^2(\lambda) - S_{k-1}^2(\lambda)$. Again, we can estimate the energy of $B_{d,k}$ as

$$E(B_{d,k} - f) < E(B_{d,k}) \leq E(B_{d,k} - f) + 2.$$

Since $B_{d,k} - f$ consists of two copies of $D'_{d,k}$, we have that

$$0 < E(B_{d,k}) - 2\sqrt{d} \sum_{j=2}^k d^{k-j} (E(P_j) - E(P_{j-1})) \leq 2.$$

Again, we get an interval of length two containing the true value of $E(B_{d,k})$. As an example, Table 3 contains the approximate value of $E(B_{d,k})$, the lower bound $2E(D'_{d,k})$ and the upper bound $2E(D'_{d,k}) + 2$ for $d = 2$ and $k \leq 10$. The difference again oscillates

k	$2E(D'_{d,k})$	$E(B_{d,k})$	difference
2	5.65685425	6.00000000	0.34314575
3	13.65685425	14.91128026	1.25442601
4	31.96281914	32.38523287	0.42241373
5	66.73134086	67.74899789	1.01765703
6	137.77268649	138.23020400	0.45751751
7	278.56262751	279.46299871	0.90037120
8	561.26285352	561.74029669	0.47744317
9	1125.66515385	1126.49537971	0.83022586
10	2255.363207329	2255.85351433	0.49030700

Table 3: The values of $E(B_{d,k})$ for $d = 2$, $k \leq 10$ and its bounds.

about its limit value, but this time the convergence is much slower and we cannot easily approximate the limit value.

Acknowledgement. The author is grateful to the referee for pointing out an older reference [15], whose results may be used as a starting point in Section 2 instead of Theorem 1, which comes from [10].

References

- [1] D.A. Tomalia, A.M. Naylor, W.A. Goddard III, *Angew. Chem. Int. Ed. Engl.* 29 (1990) 138.
- [2] C.A. Coulson, B. O'Leary, R.B. Mallion, *Hückel Theory for Organic Chemists*, Academic Press, London, 1978.

- [3] K. Yates, Hückel Molecular Orbital Theory, Academic Press, New York, 1978.
- [4] N. Trinajstić, Chemical Graph Theory, CRC Press, Boca Raton, FL, 1992.
- [5] I. Gutman, O.E. Polansky, Mathematical Concepts in Organic Chemistry, Springer, Berlin, 1986.
- [6] I. Gutman, Topics Curr. Chem. 162 (1992) 29.
- [7] I. Gutman, J. Serb. Chem. Soc. 70 (2005) 441.
- [8] I. Gutman, X. Li, J. Zhang, Graph energy, in: M. Dehmer, F. Emmert–Streib (Eds.), Analysis of Complex Networks. From Biology to Linguistics, Wiley–VCH, Weinheim, 2009, pp. 145.
- [9] S. Majstorović, A. Klobučar, I. Gutman, Selected topics from the theory of graph energy: hypoenergetic graphs, in: D. Cvetković, I. Gutman (Eds.), Applications of Graph Spectra, Math. Inst., Belgrade, 2009, pp. 65.
- [10] O. Rojo, R. Soto, Linear Algebra Appl. 403 (2005) 97.
- [11] M. Hazewinkel, Encyclopedia of Mathematics, Springer, 2000.
- [12] D. Cvetković, M. Doob, H. Sachs, Spectra of Graphs—Theory and Applications, Academic Press, New York, 1980.
- [13] J. Day, W. So, Linear Algebra Appl. 428 (2008) 2070.
- [14] J. Day, W. So, Electronic J. Linear Algebra 16 (2007) 291.
- [15] I. Gutman, Publ. Inst. Math. (Beograd) 27 (1980) 61.