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Dedicated to Professor Mircea Diudea on the Occasion of His 65th Anniversary

APPROXIMATING THE ENERGY OF NANOTUBES

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ABSTRACT. The eigenvalues of a graph are the eigenvalues of its adjacency matrix and the energy of a molecular graph is defined as the sum of absolute values of its eigenvalues. In this paper, some classical methods are used to evaluate the energy of nanotubes.

Keywords: *Eigenvalue, energy, nanotube.*

INTRODUCTION

A molecular graph G(M) is called the pair (V(M),E(M)) of the sets V(M) and E(M) of atoms and chemical bonds of the molecule M. Throughout this paper we consider only simple molecular graphs, without multiple bonds and loops [1]. Suppose $V(M) = \{v_1,v_2,\ldots,v_n\}$. Then the adjacency matrix $A(M) = [a_{ij}]$ is an $n \times n$ {0,1}–matrix in which for all integers i and j, $1 \leq i , j \leq n$, $a_{ij} = 1$ if and only if there is a chemical bond between v_i and v_j. The spectrum of a molecular graph G(M) (simply denoted by M) is a multiset containing all numbers which are eigenvalues of A(G), together with their multiplicities. Here, a multiset is a generalization of the concept of a set in which multiple instances of elements are allowed [2,3].

A molecular graph M is called bipartite if its vertex set can be partitioned into two disjoint sets R and S such that every edge connects a vertex in R and a vertex in S. The energy of a molecular graph, $\bar{E}(M)$, is defined as the sum of

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absolute values of eigenvalues of M. In chemistry, the energy of a conjugated hydrocarbon is computed by the Hückel theory. Ivan Gutman [4,5] proved that if the molecular graph is bipartite then the two different concepts for energy will coincides. In [6], the dependence of energy on the size of the molecule and the number of Kekulé structures are studied in details, and in [7], the connection between the energy and the total electron energy of a class of organic molecules together with some basic mathematical properties of graph energy are presented.

Gutman et al. [8] proved that if F is a fullerene or nanotube with n carbon atoms, then $1.34n \leq \bar{E}(F) \leq 1.73n$; in [9] an infinite sequence of fullerene containing 10n vertices is considered. They proved that all terms of this sequence have a centrosymmetric adjacency matrix and by properties of centrosymmetric matrices and Key–Fan theorem, a better lower bound to the energy of the fullerene may be obtained for $n \in \{10\times2\times5, 10\times2\times7, 10\times2\times11, 10\times2\times13\}$. In [10], the centrosymmetricity of another infinite series of fullerene graphs is proved and its upper bound is given.

John and Sachs [11] developed an elementary method to factor the characteristic polynomial of (3,6)–fullerene into smaller polynomials, all of the same size and in [12] the authors applied this result to compute the energy of a nanotorus and that of a (3, 6)–fullerene. In [13], some numerical methods are given in view of estimating the energy of nanohorns. In this paper, we continue [13] to approximate the energies of some nanotubes.

MAIN RESULTS

The Mathematical Nanoscience is a new branch of science that considers mathematical properties of nano-objects. The symmetry and topology are two important subjects in mathematics used for study of these new materials. For more information in this topic, we refer to innovating works of Diudea [14–18]. This section is concerned with the use of numerical techniques in the study of energy of the molecular graph of nanotubes. An approximation for the energy of the molecular graphs of a class of nanotubes (Figure 1) is presented. In Table 1, we search for the best of such a function to fit data listed in this table. Our main method applies a combination of two computer packages TopoCluj [19] and DataFit [20].

Suppose we have a data set $A = \{(x_1,y_1), ..., (x_n,y_n)\} \subseteq \mathbb{C} \times \mathbb{C}$, where $\mathbb{C}$ denotes the set of all complex numbers. This data set is usually based on an experiment or a measurement. It is easy to see that it is possible to find a sequence $\{\alpha_t\}_{t \geq n}$ such that $\alpha_t(x_i) = y_i$, for each i and t with $1 \leq i \leq n$ and $t \geq n$.

However, the function that fits data set A is not unique. By this reason finding a curve β with a given property to fit data set A is an important question in numerical analysis. In an exact phrase, the curve fitting is a curve that has the best fit to a series of data points and allows other constrains.

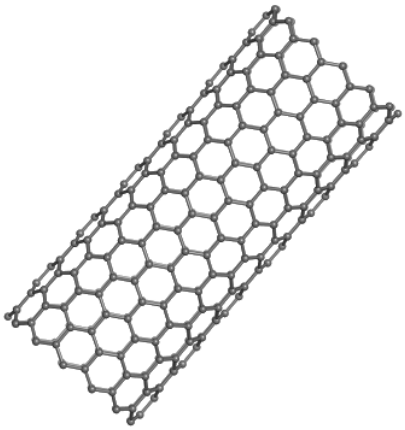

Figure 1. The Molecular Graph of a Nanotube.

Let C: y = f(x) is a curve. We say that a point (a,b) belongs to this curve, if b = f(a). This curve is called linear if for points (x_1,y_1) and (x_2,y_2) on C, we have $y_1 + y_2 = f(x_1 + x_2)$. For evaluating the energy of a sequence of nanotubes, we are interested in curve fitting by elementary functions containing polynomials, exponential and logarithmic functions.

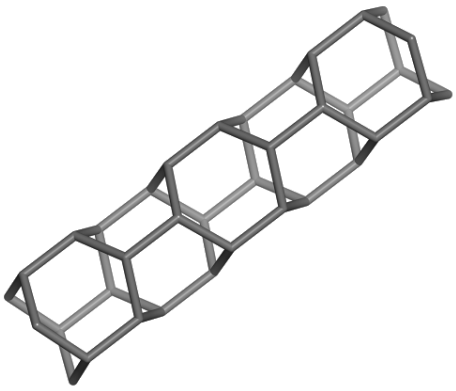

Figure 2. The Molecular Graph of E[6].

In what follows, the eigenvalues of a sequence $\{E[n]\}_{n\geq 1}$ of zig-zag nanotubes with exactly 6n + 12 vertices is considered (Figure 2). We have to note that the molecular graph of the open nanotubes is bipartite. A well-known result in algebraic graph theory states that the eigenvalues of every bipartite graph are symmetric about zero. Thus, the Energy of E[n] is two times the summation of positive eigenvalues.

Recall that since the molecular graph of a nanotube is bipartite its graph and Hückel energies are the same. In Table 1, the positive eigenvalues of E[n], $1 \leq n \leq 7$, together with their graph energies are given.

Table 1. The Positive Eigenvalues of E[n], $1 \leq n \leq 7$.

Nano-tubes	Positive Eigenvalues	Energy
E[1]	2.7616, 2.1249, 1.8019, 1.8019, 1.3633, 1.2470, 1.2470, 0.4450, 0.4450	26.4752
E[2]	2.8512, 2.4329, 1.8794, 1.8794, 1.8372, 1.5321, 1.5321, 1.2555, 1.0000, 1.0000, 0.3473, 0.3473	35.7888
E[3]	2.8986, 2.6067, 2.1636, 1.9190, 1.9190, 1.6825, 1.6825, 1.6453, 1.3097, 1.3097, 1.1898, 0.8308, 0.8308, 0.2846, 0.2846	45.1144
E[4]	2.9265, 2.7123, 2.3770, 1.9565, 1.9419, 1.9419, 1.7709, 1.7709, 1.5120, 1.4971, 1.4970, 1.1466, 1.1361, 1.1361, 0.7092, 0.7092, 0.2411, 0.2411	54.4468
E[5]	2.9443, 2.9443, 2.5204, 2.1823, 1.9563, 1.9563, 1.8271, 1.8271, 1.7976, 1.6180, 1.6180, 1.4159, 1.3383, 1.3383, 1.1167, 1.0000, 1.0000, 0.6180, 0.6180, 0.2091, 0.2091	63.7832
E[6]	2.9564, 2.8276, 2.6203, 2.3458, 2.0215, 1.9659, 1.9659, 1.8650, 1.8649, 1.7004, 1.7004, 1.6740, 1.4780, 1.4780, 1.3443, 1.2053, 1.2053, 1.0951, 0.8915, 0.8915, 0.5473, 0.5473, 0.1845, 0.1845	73.1214
E[7]	2.9649, 2.8610, 2.6924, 2.4663, 2.1934, 1.9727, 1.9727, 1.8916, 1.8909, 1.8899, 1.7589, 1.7589, 1.5783, 1.5775, 1.5772, 1.3546, 1.3546, 1.2897, 1.0939, 1.0939, 1.0790, 0.8034, 0.8034, 0.4910, 0.4910, 0.1652, 0.1652	82.4630

Suppose $\lambda_1 \leq \lambda_2 \leq ... \leq \lambda_{6n+12}$ are eigenvalues of the molecular graph of E[n]. From our calculations given in Table 1, we can suggest the following observations:

1. If n > m then $\lambda_{6n+12}(E[n]) > \lambda_{6m+12}(E[m])$. As a consequence, $\lim_{n\to\infty}\lambda_{6n+12}(E[n]) = 3$.
2. There is no zero eigenvalue, but $\lim_{n\to\infty}\lambda_{3n+6}(E[n]) = 0$.
3. The function $a + b \times \ln(x)+c \times \exp(-x)$ is the best approximation model for energy.

Next we consider another sequence $\{F[n]\}_{n\geq 1}$, of armchair nanotubes (Figure 3), with exactly 6n + 6 vertices. In Table 2, the positive eigenvalues of F[n], $1 \leq n \leq 8$, and their energies are listed.

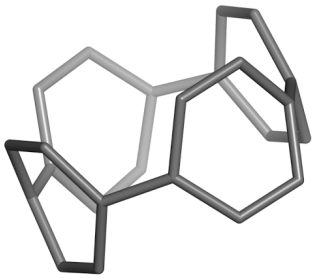

Figure 3. The Molecular Graph of F[3].

Table 2. The Positive Eigenvalues of F[n], $1 \leq n \leq 8$.

Nano-tubes	Positive Eigenvalues	Energy
F[1]	2.4142, 1.7321, 1.7321, 1, 1, 0.4142	16.5852
F[2]	2/4142, 2/101, 2/101, 1/2593**,** 1/2593, 1, 1, 1, 0.4142	25.098
F[3]	2.4142, 2.2361, 2.2361, 1.7321**,** 1.7321, 1, 1, 1, 1, 1, 1, 0.4142	33.5296
F[4]	2.4142, 2.2996, 2.2996, 1.9683, 1.9683, 1.4581, 1.4581, 1, 1, 1, 1, 1, 0.8437, 0.4142	41.9356
F[5]	2.4142, 2.3344, 2.3344, 2.1010, 2.1010, 1.7320, 1.7320, 1.2593, 1.2593, 1, 1, 1, 1, 1, 0.7420, 0.7420, 0.4142	50.3316
F[6]	2.4142, 2.3555, 2.3555, 2.1825, 2.1825, 1.9051, 1.9051, 1.5397, 1.5397, 1.1120, 1.1120, 1, 1, 1, 1, 1, 1, 1, 0.6721, 0.6721, 0.4142	58.7244
F[7]	2.4142, 2.3692, 2.3692, 2.2361, 2.2361, 2.0205, 2.0205, 1.7320, 1.7320, 1.3848, 1.3848, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 0.6220, 0.6220, 0.4142	67.1152
F[8]	2.4142, 2.3786, 2.3786, 2.2730, 2.2730, 2.1010, 2.1010, 1.8685, 1.8685, 1.5839, 1.5839, 1.2593, 1.2593, 1, 1, 1, 1, 1, 1, 1, 1, 1, 0.9129, 0.9129, 0.5849, 0.5849, 0.4142	75.5052

We now assume that $\sigma_1 \leq \sigma_2 \leq ... \leq \sigma_{6n+12}$ are eigenvalues of the molecular graph of F[n]. From our calculations given Table 2, we can draw the following observations:

1. The maximum eigenvalue of F[n] , $n \geq 1$, is $\sqrt{2} + 1$.
   This eigenvalue is simple.
2. The minimum positive eigenvalues of F[n], $n \geq 1$, is $\sqrt{2} - 1$.
   This eigenvalue is simple.

3. If $n > m$ then $\sigma_{6n+5}(F[n]) > \sigma_{6m+5}(F[m])$. As a consequence, $\lim_{n\to\infty}\sigma_{6n+5}(F[n]) = 1 + \sqrt{2}$.
4. If n is even then the multiplicity of 1 is n + 1 and for odd n, the multiplicity is 2n.
5. The function $a + b \times \ln(x)+c \times \exp(-x)$ is the best approximation model for energy.

CONCLUSION

In this paper the power of numerical methods for investigation of energy of armchair and zig-zag nanotubes are investigated. Some results obtained by our numerical investigation can be proved in general, but evaluation of energy for nanotubes of arbitrary length and diameter is an open question for future study.

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