Variable Neighborhood Search for Extremal Graphs. 2. Finding Graphs with Extremal Energy

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The recently developed Variable Neighborhood Search (VNS) metaheuristic for combinatorial and global optimization is outlined together with its specialization to the problem of finding extremal graphs with respect to one or more invariants and the corresponding program (AGX). We illustrate the potential of the VNS algorithm on the example of energy E, a graph invariant which (in the case of molecular graphs of conjugated hydrocarbons) corresponds to the total π-electron energy. Novel lower and upper bounds for E are suggested by AGX and several conjectures concerning (molecular) graphs with extremal E values put forward. Moreover, most of the bounds are proved to hold.

INTRODUCTION

In theoretical chemistry, chemical informatics, and chemical computer science a vast variety of molecular-graph-based quantities is encountered. Such graph invariants, being of interest in chemistry, are often called topological indices (*TI*s). One of the aspects of their study is the finding of the extremal (maximal and minimal) values which a particular *TI* assumes within a pertinently chosen class of molecular graphs. This is usually tantamount to the identification of the graphs being extremal with respect to the given *TI*.

In this paper we describe a recently designed novel method of combinatorial and global optimization, called *Variable Neighborhood Search* (VNS), its specialization to graph theory, and the underlying computer system *AutoGraphiX* (AGX). We then apply it to the (previously much investigated) problem of finding graphs with extremal energy and estimating this energy.

VARIABLE NEIGHBORHOOD SEARCH

Numerous problems of combinatorial and global optimization have many *local optima*, *i.e.*, solutions which are best in their neighborhood but not necessarily so in the whole solution space. For large instances, exact solution is then often out of reach and one uses *heuristics*, which provide in moderate computing time a good but not necessarily optimal solution.

A simple and often used heuristic is *local search* (LS). Consider a problem P defined by $min\ f(x)$, $x \in X$ where x denotes a feasible solution, $f(x)$ the objective function, and

Initialization Choose $x \in X$

Repeat Let $x' = argmin_{y \in N(x)} f(y)$;
  If $f(x') = f(x)$ **stop;**
  Otherwise set $x \leftarrow x'$ **and iterate this step.**

Figure 1. Local search.

X the *solution space*. Then local search follows the steps described in Figure 1. Let N denote a *neighborhood structure* and $N(x)$ the *neighborhood* of x.

At each step, one finds the best solution x' in the neighborhood $N(x)$ of x, replaces x by this solution if it is better than x, and iterates until no improved solution can be found.

To illustrate use of the LS heuristic, consider the problem of finding a tree with six vertices and minimum energy E (the definition of energy is recalled in the section below on "Total π-electron energy and the energy of a graph").

Then an instance x of a tree with six vertices is that one represented on Figure 2 (x). Its energy is $E(x) = 6$. A neighborhood structure N for trees consists in associating to each tree all trees which can be obtained by moving a pending edge. The tree x has three neighbors (up to isomorphism) represented by x_1, x_2, and x_3 in Figure 2. So $N(x) = \{x_1,x_2,x_3\}$

$$x' = arg \min_{y \in N(x)} E(y) = x_1 \qquad (1)$$

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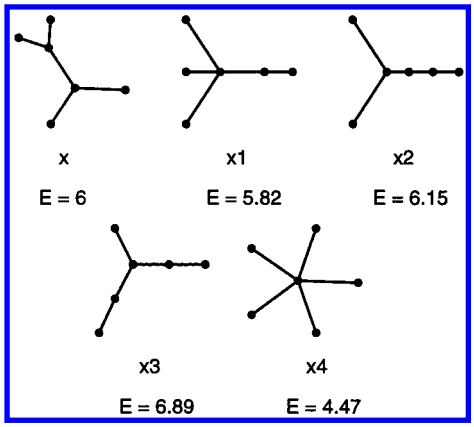

Figure 2. An example of local search: finding a tree with six vertices and minimum energy.

Initialization: Choose $x \in X$, choose stopping criterion

Repeat: until the stopping criterion is met:
Choose x' at random $\in \mathcal{N}(x)$;
If $f(x') = f(x)$ set $x \leftarrow x'$;

Figure 3. Randomized local search.

i.e., among these neighbors, x_1 has minimum energy: $E(x_1) = 5.82$. In turn, x_1 has four neighbors (up to isomorphism) *i.e.*, x, x_2, x_3, and the star x_4 also, represented in Figure 2. So $N(x_1) = \{x,x_2,x_3,x_4\}$ and

$$x' = arg \min_{y \in N(x_1)} E(y) = x_4 \qquad (2)$$

Then x_4 has a single neighbor, *i.e.*, x_1, with a higher energy. A local minimum (which is also a global one in this case as stars have minimum energy among trees on the same number of vertices) has been reached and heuristic LS stops.

The heuristic just described is a *best descent* one *i.e.*, at each iteration, one seeks the best neighbor of x. This operation may be lengthy if $N(x)$ is large and $f(x)$ long to compute. Therefore, one may prefer a randomized *first descent* version of local search (called Randomized Local Search or RLS). Such a heuristic is described in Figure 3. Solutions x' in the neighborhood of x are drawn at random and replace x as soon as a better one is found. The stopping criterion may be, *e.g.*, maximum computing time, maximum number of iterations, or maximum number of iteractions since the last improvement.

Both LS and RLS suffer from a grave defect: they stop as soon as a first local optimum is reached. The value of this optimum may be quite far from the globally optimal one. One way out is the so-called *multistart* heuristic which consists in applying LS many times from randomly drawn initial solutions $x_1, x_2, x_3, ... \in X$ and keeping the best solution found. Such an approach is adequate when there are fairly few local optima and valleys for the objective function $f(x)$ on X. But it breaks down completely when the number of local optima is large, *i.e.*, much greater than any reasonable number of descents. Then, as illustrated in ref 1 for a well-known global optimization problem, the multisource Weber problem, the solutions provided by multistart may have a value 50% or even 100% above the globally optimal one.

Other ways to overcome the problem of early termination in poor local optima have been proposed and studied a great deal in the last 15 years with the advent of *metaheuristics*. These are general frameworks for heuristics and can thus be adapted to solution of a large variety of combinatorial and global optimization problems. Among the best known metaheuristics are Variable-Depth Search,[2,3] Simulated Annealing,[4] Tabu Search,[5−9] Genetic Search,[10] Adaptive Multi-Start,[11] GRASP,[12] and Ant Colonies Optimization.[13]

A good introduction to metaheuristics is given in the book-length multiauthored survey[14] and an extensive bibliography in ref 15. Observe that several metaheuristics are based on analogies with processes occurring in physics (simulated annealing) or biology (genetic search, ant colonies). The metaheuristics cited above represent a breakthrough in the design of heuristics. Very substantial increases in performance have been witnessed for numerous problems, both theoretical and applied, in many fields. Theoretical development and application of metaheuristics is now one of the most active areas of Operations Research. However, many of the heuristics proposed (and in particular hybrid ones which rely on several metaheuristic principles) tend to have numerous parameters and sets of complicated rules. Usually, these rules are justified empirically. A clear understanding of *why* metaheuristics work as well as they do is still, for the most part, lacking. In order to partly answer this question, and also provide simpler and hopefully better heuristics, a new metaheuristic called *Variable Neighborhood Search* (VNS)[16−18] has recently been introduced. It is based on systematic use of an idea little explored up till now: change of neighborhood within the search. Thus it generalizes in a natural way both LS and RLS. Moreover, parameters are kept to a minimum and often completely avoided. Finally, in many cases, the effort to transform a LS or RLS heuristic into a VNS one is minimal.

Let us denote with N_k, ($k = 1, ..., k_{max}$), a finite set of preselected neighborhood structures and with $N_k(x)$ the set of solutions in the kth neighborhood of x. (Most local search heuristics use one neighborhood structure, *i.e.*, $k_{max} = 1$.) Steps of the basic VNS are presented in Figure 4. They make use of a local search routine discussed later.

After initialization VNS explores increasingly far neighborhoods of the current best known solution x. To this effect a point x' is generated at random in the kth neighborhood $N_k(x)$ of x. Then a local search is performed from x' leading to a new local optimum x''. If x'' is better than x it replaces it, *i.e.*, the search is recentered around x'' beginning with the first neighborhood. Otherwise one proceeds to the next neighborhood. If the last neighborhood has been reached without a better solution x'' than x being found, one begins again to explore the first neighborhood unless the stopping condition has been met.

Clearly, some ideas of VNS are similar to parts of other metaheuristics, mostly simulated annealing and tabu search. Principles of genetic search and neural networks are more remote. Note, however, that contrary to simulated annealing and tabu search, VNS is not a trajectory method *i.e.*, instead of following a single trajectory, it exploits through systematic perturbations characteristics of the best known solution and recenters the search if and only if a better solution is found, see ref 18 for a more thorough discussion.

Initialization. Select the set of neighborhood structures $\mathcal{N}_k$, $k = 1, \ldots, k_{max}$, that will be used in the search; find an initial solution x; choose a stopping condition;

Repeat the following until the stopping condition is met:
(1) Set $k \leftarrow 1$; (2) Until $k = k_{max}$, repeat the following steps:
(a) *Shaking.* Generate a point x' at random from the k^{th} neighborhood of x ($x' \in \mathcal{N}_k(x)$);
(b) *Local search.* Apply some local search method with x' as initial solution; denote with x'' the so obtained local optimum;
(c) *Move or not.* If this local optimum is better than the incumbent, move there ($x \leftarrow x''$), and continue the search with $\mathcal{N}_1$ ($k \leftarrow 1$); otherwise, set $k \leftarrow k + 1$;

Figure 4. Steps of the basic VNS.

Initialization. Select the set of neighborhood structures $\mathcal{N}'_k$, $k = 1, \ldots, k'_{max}$, that will be used in the descent; find an initial solution x;

Repeat the following until no improvement is obtained:
(1) Set $k \leftarrow 1$; (2) Until $k = k'_{max}$, repeat the following steps:
(a) *Exploration of neighborhood.* Find the best neighbor x' of x ($x' \in \mathcal{N}'_k(x)$);
(b) *Move or not.* If the solution thus obtained x' is better than x, set $x \leftarrow x'$; otherwise, set $k \leftarrow k + 1$;

Figure 5. Steps of the basic VND.

The general VNS scheme uses repeatedly a local search routine, which may itself involve several neighborhoods. In such a case it is called a Variable Neighborhood Descent (VND) routine. The basic scheme for VND is presented in Figure 5.

It uses a first neighborhood until a local minimum is attained and then switches to the next. This sequence is repeated until no better local optimum than the current one can be reached. Usually neighborhoods in VND are sorted in increasing order of computation needed to explore them.

Three types of applications of VNS have been explored up to now. First, VNS heuristics have been developed for a series of combinatorial and global optimization problems and compared with state-of-the-art heuristics. In all cases improved results were obtained. These problems include the traveling salesman problem[16,19] and a variant with precedence constraints,[16,20] the p-median problem of discrete location theory,[16,21−24] the multisource Weber problem which is the counterpart of the p-median problem in continuous location theory,[25,26] the minimum sum-of-squares clustering problem[18] of cluster analysis, and the weighted maximum satisfiability problem from logic.[17]

Second, VNS heuristics have been used *within exact algorithms* to greatly augment their efficiency. This happens in particular when using column generation methods combined with branch-and-bound to solve very large combinatial and global optimization problems. Both solutions of the subproblem of finding a column of negative reduced cost and of the initial problem, to get good estimates of dual variables at the optimum, are solved by VNS. Several breakthroughs could thus be made: exact solutions of minimum sum-of-squares clustering problem with up to 150 vertices[27] including the famous Fisher's Iris example,[28] exact solution of multisource Weber problem with up to 1060 users[29] versus 30 at most in the literature,[30] and exact solution of p-median problem with up to 3038 users[31] versus 900 at most in the literature.[32]

Third, VNS has been applied to the study of graph theory *per se* and not only of optimization problems possibly defined on graphs.[33] This endeavor is described in the next section and expanded in the remaining part of the paper.

VARIABLE NEIGHBORHOOD SEARCH FOR EXTREMAL GRAPHS

Conjectures in graph theory may be viewed as combinatorial optimization problems on an infinite family of graphs, of which only those of moderate size will be explored.[33] Then VNS can be applied. This leads to an automated system, called AutoGraphiX (or AGX for short) whose aim is to suggest, disprove, or give hints on how to prove conjectures.

Assume an objective function $f(G)$ depending on graph invariants $i_1(G)$, $i_2(G)$, ..., $i_l(G)$ is given (recall that invariants are quantities independent of edges or vertices labeling, *.e.g.*, order, size, radius, diameter, chromatic number, maximum or minimum degree, ...). Let $\mathcal{G}_n$ (respectively $\mathcal{G}_{n,m}$) denote the family of all graphs G with vertices (respectively n vertices and m edges). The problem considered is then

$$\min_{G \in \mathcal{G}_n} (\max) f(G) \quad \text{or} \quad \min_{G \in \mathcal{G}_{n,m}} (\max) f(G) \tag{3}$$

to which we apply VNS specialized to extremal graphs problems.

AGX comprises a VND component with many neighborhoods $N'_1(G)$, $N'_2(G)$, ..., $N'_{k_{max}}(G)$. In the present version there are 11 of them, defined by the following transformations on G: *deletion* of an edge; *addition* of an edge between nonadjacent vertices; *move* of an edge, *i.e.*, deletion followed by addition, but not in the same position (these three neighborhoods are used in most applications); *detour*: removal of an edge and addition of two edges between endpoints of the deleted one and a vertex not adjacent to either of these endpoints; *short cut*, *i.e.*, the reverse operation than detour; *2 opt*: removal of two nonadjacent edges and addition of two different nonadjacent edges connecting the endpoints of the removed ones; *insert pending vertex*: removal of an edge incident with a pending vertex, addition of edges between this vertex and two adjacent vertices, and

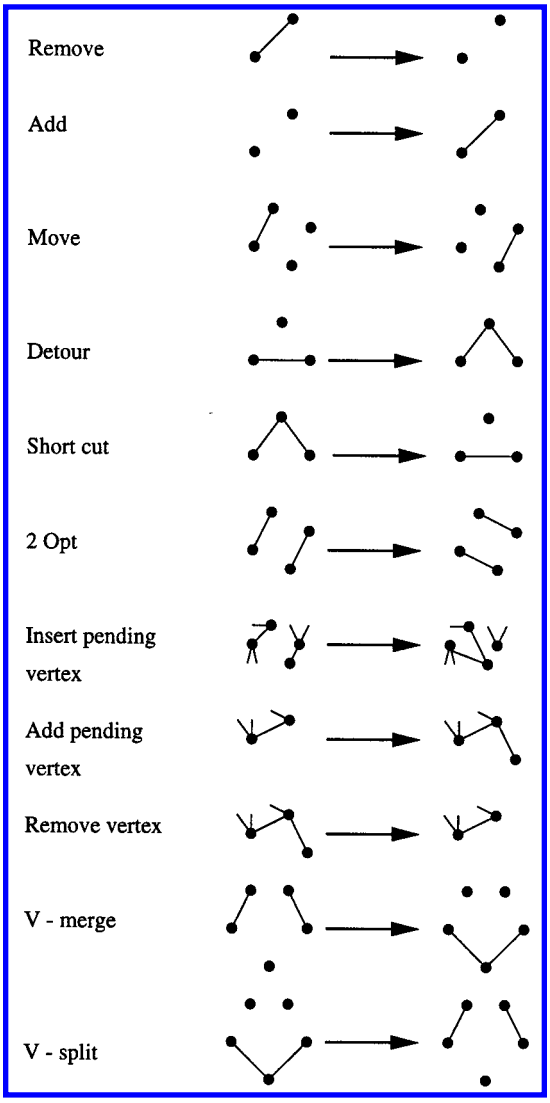

Figure 6. Neighborhoods implemented in AGX.

finally removal of the edge between them; *add pending vertex*: addition of an edge from one vertex to a new one; *delete vertex*: deletion of a vertex (possibly of bounded degree) and all edges adjacent to it; *connection*: deletion of two nonadjacent edges and addition of two adjacent ones; *v-split*: removal of two nonadjacent edges and addition of two adjacent edges having each one vertex in common with one of the removed edges; and *v-merge*: reciprocal of *v-split*. These transformations are illustrated in Figure 6.

It is up to the user to apply all transformations in turn or to select a subset of them, *e.g.* the less time-consuming ones. A learning routine can also be used. After initialization, a first descent is done to find a graph respecting the constraints (*e.g.* desired number of edges); it evaluates the best neighbor of the current solution according to each transformation. The transformations that cannot produce realizable graphs (*e.g.* those that change the number of edges) are then removed from the list, and the remaining ones are sorted by order of efficiency.

The main VNS routine uses a set of nested neighborhoods $N_1(G)$, $N_2(G)$, ... defined by the cardinality of the symmetric difference between the edge sets of two graphs $G = (V,E)$ and $G' = (V',E')$

$$\rho(G,G') = |(E \backslash E') \cup (E' \backslash E)| \tag{4}$$

i.e., $\rho(G,G') = k$ if there are exactly k pairs of vertices adjacent in G and not in G' or adjacent in G' and not in G. Then

$$G' \in N_k(G) \Leftrightarrow \rho(G,G') = k \tag{5}$$

In addition to these components, which follow the basic schemes of Figures 5 and 4, AGX comprises a routine for graph analysis which performs the following: (i) recognition of the class to which belongs the extremal graph G obtained (if it is one of the series of well known classes such as path, star, tree, complete, or bipartite graph, ...), (ii) computation of various invariants for G, (iii) visualization of G on the screen using X-Windows, with interactive modifications of position of vertices, and (iv) subroutines for interactive modifications of G by deletion or addition of edges or vertices. Moreover, AGX also has a routine for parametric analysis which obtains, stores, analyzes, and represents values of invariants and of functions corresponding to conjectures.

Variable Neighborhood Search can be used in graph theory for several purposes:

(a) Find a graph satisfying given constraints: Let $i_1(G)$, $i_2(G)$, ..., $i_l(G)$ denote l invariants of G and p_1, p_2, ..., p_l values given to them. Consider the problem

$$\min_{G \in \mathcal{G}_n} f(G) = \sum_{k=1}^{l} |i_k(G) - p_k| \tag{6}$$

Any graph such that $f(G) = 0$ satisfies these constraints. Note that constraints involving formulas on several invariants can be treated in a similar way. Expression 6 shows constrained problems can be reduced to unconstrained ones.

(b) Find optimal or near optimal values for an invariant subject to constraints: Let $i_0(G)$ denote the objective function invariant and assume constraints expressed as above. Consider the problem

$$\min_{G \in \mathcal{G}_n} f(G) = i_0(G) + M \sum_{k=1}^{l} |i_k(G) - p_k| \tag{7}$$

where M is a constant sufficiently large to ensure that for any pair of graphs G, $G' \in \mathcal{G}_n$ (or G, $G' \in \mathcal{G}_{n,m}$) such that $\sum_{k=1}^{l} |i_k(G) - p_k| = 0$ and $\sum_{k=1}^{l} |i_k(G') - p_k| > 0$, $f(G) < f(G')$. Maximum values are tackled in a similar way.

Note that some invariants take integer values and remain constant on large plateaus when G is modified a little at a time, *i.e.*, replaced sequentially by a graph in the neighborhood $N(G)$. It is then convenient to complement the objective function by adding a secondary objective, with a coefficient sufficiently small not to change the ordering of graphs according to the first objective, and orienting the transformations in the right direction.

(c) Refute a conjecture: Consider a conjecture $h(G) \leq g(G)$ where $h(G)$ and $g(G)$ are formulas depending on one or more invariants of G. It corresponds to the problem

$$\min_{G \in \mathcal{G}_n} f(G) = g(G) - h(G) \tag{8}$$

If a graph G for which $f(G) < 0$ is found, the conjecture is refuted.

(d) Suggest a conjecture (or sharpen one): This can be done in various ways, which usually use parameterization

on n or other invariants $i_1(G)$, $i_2(G)$, $i_3(G)$, ... $i_l(G)$. For instance consider

$$\min_{G \in \mathcal{G}_n} f(G) = i_2(G) - i_1(G) \tag{9}$$

If no graph G with $f(G) < 0$ is found this suggests $i_1(G) \leq i_2(G)$. If the extremal graphs found belong to a recognizable class, it may be possible to deduce a more precise inequality in $i_1(G)$, $i_2(G)$, and n.

(e) Suggest a proof: The way the extremal graphs are obtained, *e.g.* what transformations of G are used, may suggest strategies to prove conjectures for all graphs or for some classes of them.

Use of AGX in the study of graphs with extremal energy is presented in the section on "Results and Discussion" below. Statement of the problem studied and its context are first given.

There are of course other programs than AGX for computer-aided graph theory, prominent among which appear to be Graph[34,35] and Graffiti.[36,37] They are briefly discussed in part 1 of this series.[33] Note that none of these programs uses heuristic optimization to obtain extremal graphs.

TOTAL Π-ELECTRON ENERGY AND THE ENERGY OF A GRAPH

One of the most remarkable chemical applications of graph theory is based on the close correspondence between the graph eigenvalues and the molecular orbital energy levels of the π-electrons in conjugated hydrocarbons; for details see refs 38−43. If G is a molecular graph of a conjugated hydrocarbons and λ_1, λ_2, ..., λ_n are its eigenvalues, then in the Hückel molecular orbital (HMO) approximation the energy of the ith molecular orbital is given by

$$E_i = \alpha + \lambda_i \beta$$

where α and β are pertinent constants. In order to simplify the formalism, it is customary[38−43] to set $\alpha = 0$ and $\beta = 1$ in which case the π-electron orbital energies and the graph eigenvalues coincide.

The total π-electron energy (E) is equal to the sum of the energies of all π-electrons present in the respective molecule

$$E = \sum_{i=1}^{n} g_i E_i = \sum_{i=1}^{n} g_i \lambda_i$$

with g_i being the number of electrons in the ith molecular orbital. Because of restrictions coming from the Pauli exclusion principle, g_i is two, one, or zero. In the majority of chemically relevant cases, $g_i = 2$ whenever $\lambda_i > 0$ and $g_i = 0$ whenever $\lambda_i < 0$, implying

$$E = 2 \sum_{+} \lambda_i$$

with $\sum_+$ indicating summation over positive eigenvalues. Because the sum of all eigenvalues is zero, one immediately arrives at

$$E = E(G) = \sum_{i=1}^{n} |\lambda_i| \tag{10}$$

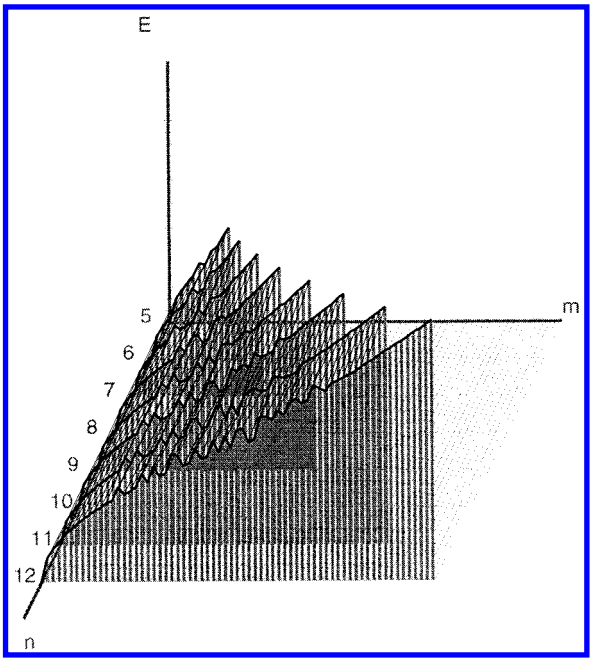

Figure 7. Conjectured minimum values of E for $n = 12$ and $m = 0-66$.

The right-hand side of eq 10 is defined for all graphs (no matter whether they represent the carbon-atom skeleton of a conjugated π-electron system or not). In view of this, if G is any graph, then by means of eq 10 one *defines* $E(G)$ and calls it *the energy of the graph G*.

Many results reported in the chemical literature for the HMO total π-electron energy of conjugated hydrocarbons are, in fact, results valid for the energy of an arbitrary graph; for a survey of the mathematical properties of E see chapter 12 of the book[41] and the review.[44]

The properties of the HMO total π-electron energy, and, in particular, its dependence on molecular structure, are attracting the attention of theoretical chemists since over half a century. Among the plethora of results obtained in this field there are many dealing with (molecular) graphs with extremal E values and/or lower and upper bounds for E.[45−71]

Most of the bounds for E pertain to special types of graphs: bipartite,[47,49,51,56,63,64,67,68] benzenoid,[52,54,55,59−61,65,66] trees,[47,58,71] and other.[48,62,69,70] There are surprisingly few results applying to all graphs.[45,46,50,53] The graphs with extremal energy have been determined only for n-vertex trees[47] and for n-vertex trees with a perfect matching.[71] Results of a computer search (but only up to $n = 6$) were reported in ref 57.

The aim of this work is to contribute toward filling this gap.

RESULTS AND DISCUSSION

In a first series of experiments, AGX was applied to the problem of finding extremal graphs with minimum energy. The numbers of vertices and m of edges were taken as parameters with values $2 \leq n \leq 12$ and $0 \leq m \leq [n(n-1)]/2$. All neighborhoods were used except those which modify n or m, and the program was run during a whole weekend on a Pentium 133 MHz.

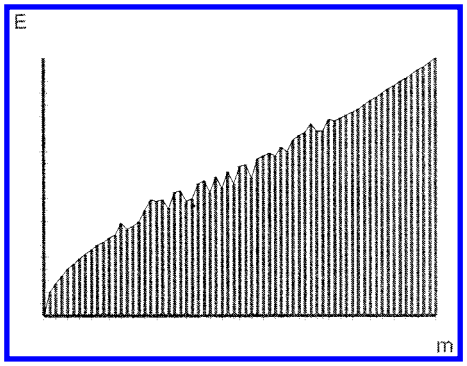

Figure 8. Smallest value of E for $n = 12$ and $m = 0-66$ found by the program.

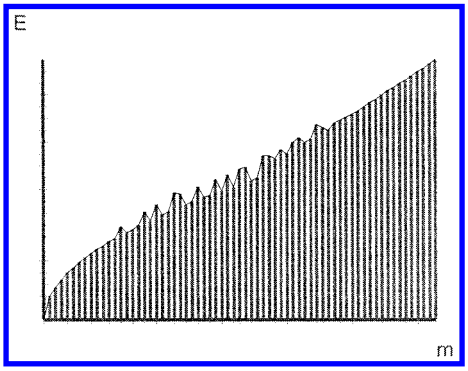

Figure 9. Smallest values of E for $n = 12$ and $m = 0-66$ after correction.

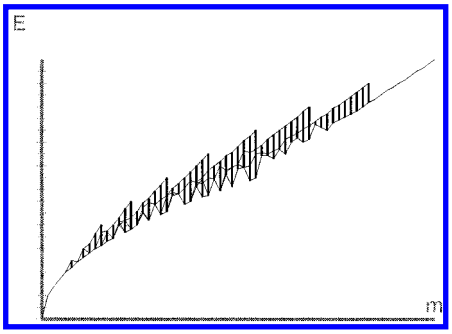

Figure 10. Superposed results for $n = 2-12$.

The surface of conjectured minimum values of E as a function of n and m is represented in Figure 7. It is easier to interpret results if one considers values for fixed n or m. The results for $n = 12$ are represented in Figure 8.

Patterns clearly arise in two parts of this figure: a curve on the left and a straight line on the right. Checking extremal graphs on the apparent curve, it was found that they correspond to complete bipartite graphs (*i.e.*, graphs whose vertices may be partitioned into two sets V_1 and V_2 such that pairs of vertices in the same set are never joined by an edge and pairs of vertices in different sets always are), possibly with some isolated vertices. This suggests that corrections might be made interactively by checking if complete bipartite graphs, when possible for given values of n and m, have lower energy than those found by AGX. This indeed led to improved results in three cases out of 67. Interactive corrections for extremal graphs on the right side along lines explained below led to improved results in two more cases.

The corrected results are presented in Figure 9.

Superposing results for $n = 2-12$, as done in Figure 10, shows that the left sides of the curves coincide in many cases. It is then easy to see that points are on or above the curve $2\sqrt{m}$. Moreover, this value is obtained whenever there is a complete bipartite graph for the given n and m. It is the case if and only if $m = a \times b$ and $a + b \leq n$ for some positive integers a and b. This happens in 27 cases for $n = 12$. Comparing results of several trials showed also that if there are several pairs of values (a,b), (a',b'), ... which satisfy these conditions, they corresponding to complete bipartite graphs with the same energy. An example, for $n = 5$, $m = 4$, is, on the one hand, the star with five vertices, and on the other hand, the bipartite graph with two vertices on each side plus one isolated vertex. Both have energy $E = 4$.

When values m and n are such that there is no pair a,b of positive integers with $m = a \times b$ and $a + b \leq n$, the extremal graphs appear to be modified bipartite graphs with $a \times b < m$ and $m - a \times b$ edges joining a vertex on the smallest side to other vertices on that side. The 10 extremal graphs for $n = 12$ which are not complete bipartite graphs possibly plus isolated vertices and for which $m \leq \lfloor n/2 \rfloor \times \lceil n/2 \rceil$, *i.e.*, the maximum number of edges in a complete bipartite graph, are represented in Figure 11.

Observe that the bipartite graph which is modified by addition of edges is not always that one which has the most edges. Indeed, in the case $n = 12$ and $m = 34$ the extremal graph with $a = 5$, $b = 6$ and 4 additional edges (the last graph on Figure 11) has $E = 12.877$, while that one with $a = 4$, $b = 8$ and 2 additional edges has $E = 13.17$ as checked interactively by modifying the previous one. Observations made up to now can be summarized in the following conjectures.

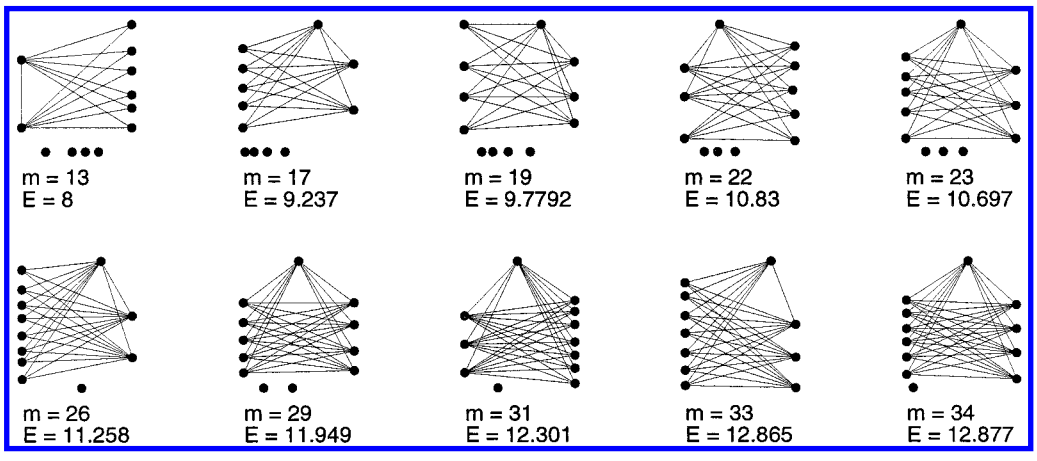

Figure 11. Extremal graphs which are not complete and bipartite.

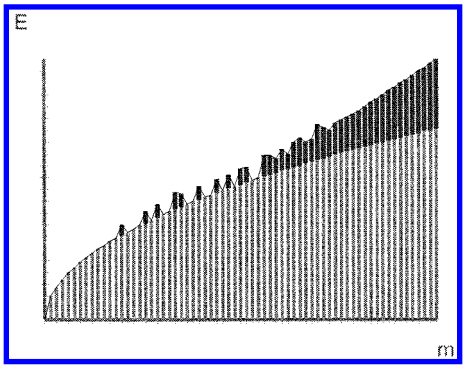

Figure 12. Smallest values of E for $n = 12$ and $m = 0-66$ compared to Conjecture 1.

Conjecture 1. *For all graphs G the energy satisfies*

$$E \geq 2\sqrt{m} \tag{11}$$

Moreover, the bound is attained if and only if G is a complete bipartite graph, plus possibly some isolated vertices.

This conjecture is proved in the Appendix.

Conjecture 2. *If G is a graph with n vertices, $m \leq [n/2]-[n/2]$ edges and minimum energy, then (i) if there exist positive integers a and b such that $a \times b = m$ and $a + b \leq n$, G is a complete bipartite graph $K_{a,b}$, plus possibly some isolated vertices; (ii) otherwise, G is a complete bipartite graph $K_{a',b'}$ with $a' \times b' \leq m$ and $a' + b' \leq n$ modified by addition of $m - a' \times b'$ edges between one vertex on the smallest side of $K_{a',b'}$ and other vertices on that side, plus possibly some isolated vertices.*

The curve (11) and the results for $n = 12$ are represented in Figure 12. It appears that coincidence on the left side (*i.e.*, for $m \leq 36$, the largest number of edges in a bipartite graph on 12 vertices) is excellent, as the bound is attained for 27 values out of 37. However, the curve is well below observed values for $m > 36$. Observe then that prolongating the linear pattern which appears on the right gives a straight line through the origin. Noting that for complete graphs on n vertices $m = [n(n-1)]/2$ and $E = 2n - 2$, (see ref 39, p 72) the slope of this line is easily computed and leads to the following conjecture.

Conjecture 3. *For all graphs G, the energy E satisfies*

$$E \geq \frac{4m}{n} \tag{12}$$

This conjecture is also proved in the Appendix.

For $n = 12$ and $m \geq 37$, the bound (12) is attained by the graphs obtained with AGX in 12 cases out of 37. Both curves (11) and (12) and the results for $n = 12$ are represented in Figure 13. Observed values appear to be reasonably close to the curves and on them in many cases.

Characterization of extremal graphs for $n = 12$ and $m \geq 37$ appears to be more difficult than for $m \leq 36$. As there are many edges it is convenient to use, rather than G itself, the complementary graph $\bar{G}$ of G, where an edge joins vertices v_k and v_l in $\bar{G}$ if and only if no edge does so in G. Complements $\bar{G}$ of some of the graphs G found by AGX for $n = 12$ are represented in Figure 14. It appears that most but not all of these graphs $\bar{G}$ are composed of disjoint cliques, plus possibly some isolated vertices. Cliques of almost equal size appear to be favored. Indeed, one case in which the values of n and m are such that there exists a decomposition in very unequal cliques (*i.e.*, $n = 12$, $m = 43$, and $\bar{m} = 23$, which decomposes into K_7, $2K_2$, and a K_1) does have a conjectured extremal graph $\bar{G}$ which is composed of a clique on five vertices and a seven vertices component composed of two cliques on five and three vertices respectively which have one common vertex.

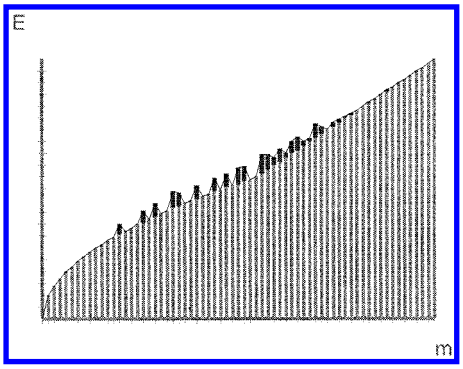

Figure 13. Smallest values of E for $n = 12$ and $m = 0-66$ compared to both Conjecture 1 and Conjecture 3.

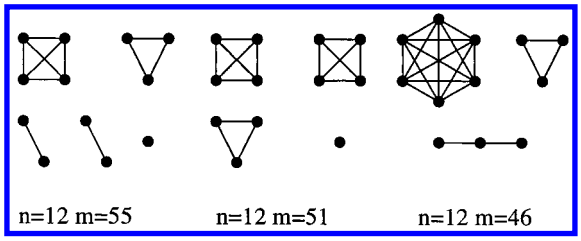

Figure 14. Complements of conjectured extremal graphs.

Turan graphs, *e.g.*, ref 68, are composed of disjoint cliques with equal or almost equal (*i.e.*, differing by 1) cardinalities. Graphs $\bar{G}$ which are Turan graphs are not necessarily complements of graph G such that the bound (12) is attained. More surprisingly, this property does not even hold when $\bar{G}$ is composed of disjoint edges. For instance if $n = 11$, $m = 52$, and $\bar{m} = 3$, $\bar{G}$ consists of three disjoint edges plus five isolated vertices and $E = 18.954$, while the bound is $4m/n = 18.909$.

In a second series of experiments, AGX was applied to the problem of finding connected graphs with minimum energy, again with n and m as parameters. Ranges considered were $2 \leq n \leq 12$ and $n - 1 \leq m \leq [n(n-1)]/2$. Computing time was similar to that of the first series of experiments. The surface of conjectured minimum values of E for connected graphs as a function of n and m is represented in Figure 15. Minimum values of E for given n are always obtained for $m = n - 1$, *i.e.*, for stars.

Conjecture 4. *For all connected graphs G*

$$E \geq 2\sqrt{n-1} \tag{13}$$

and the bound is tight if and only if G is a star.

A stronger result is proved in the Appendix.

Results for $n = 12$ are given in Figure 16. The connectedness constraint makes values of E found with AGX larger than in the unconstrained case in the left part of the curve except for values of m such that there exists a complete bipartite graph with 12 vertices and m edges. Between such values E usually increases then decreases when m increases. The curve between the two first local optima, which corresponds to the star and the complete bipartite graph $K_{2,10}$,

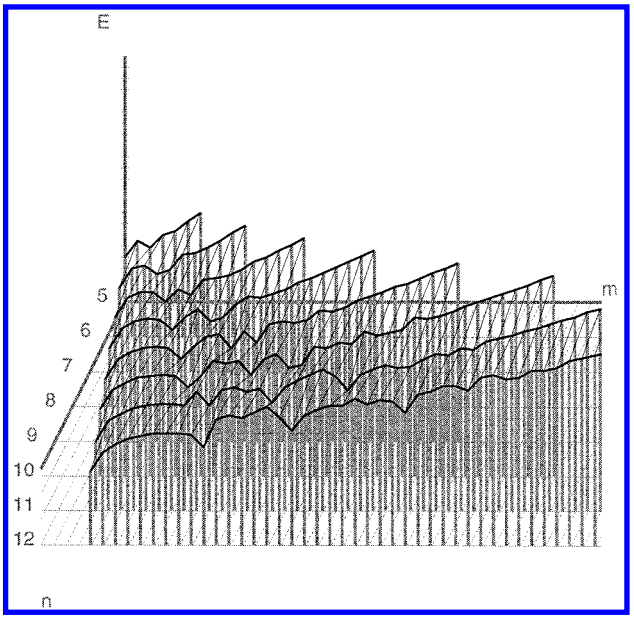

Figure 15. Minimum energy for connected graphs.

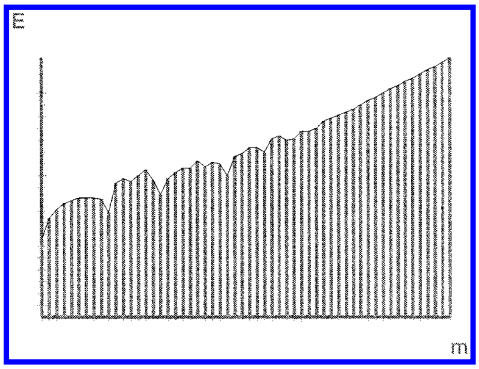

Figure 16. Minimum energy for connected graphs for $n = 12$.

is smooth. Those between the next local optima are less so, but this might be due to AGX not finding graphs with minimum energy in all cases. The sequence of graphs obtained for $n = 12$ and $11 \leq m \leq 20$ is represented in Figure 17. It appears that edges adjacent to the same vertex v_k are added one at a time until $m = 15$, then the edge joining the vertex v_l adjacent to all others to v_k is removed, and two edges adjacent to v_k are added. Then edges adjacent to v_k are added again one at a time. The value of m for which one edge is removed and two added for $n = 5-12$ are respectively 6, 7, 8, 10, 11, 13, 14, and 16. From this we obtain the following conjecture.

Conjecture 5. *Connected graphs G with $n \geq 6$ vertices, $n - 1 \leq m \leq 2(n-2)$ edges and minimum energy are stars with $m - n + 1$ additional edges all connected to the same vertex for $m \leq n + [(n-7)/2]$, and bipartite graphs with two vertices on one side, one of which is connected to all vertices on the other side otherwise.*

In a third series of experiments, AGX was applied to the problem of finding graphs with maximum energy, once more with n and m as parameters. Ranges considered are the same as in the first series of experiments and computing time was again similar. The surface of conjectured maximum values of E as a function of n and m is represented in Figure 18; values for $n = 12$ are given in Figure 19. It appears clearly that the leftmost part of the curve is a straight line segment. Moreover, similar straight lines segments with the same slope appear for the other values of n. The corresponding extremal graphs are composed of disjoint edges plus possibly some isolated vertices. This leads to the next conjecture.

Conjecture 6. *For all graphs G with m edges, the energy satisfies*

$$E \leq 2m \tag{14}$$

and the bound is attained if and only if G is composed of disjoint edges plus possibly some isolated vertices.

As pointed out by an anonymous referee, Conjecture 6 is equivalent to conjecture 146 of Graffiti,[37] i.e., "The sum of positive eigenvalues of a graph is less than or equal to its size. The bound is attained if and only if the maximum degree is 1." Not long after its announcement, in 1988, this conjecture received a short, as yet unpublished, proof by Shearer.[37,73]

This conjecture is proved in the Appendix. The line (14) and the largest values of E for $n = 12$ are presented in Figure 20. Another upper bound, due to McClelland,[45] is well known:

$$E \leq \sqrt{2mn} \tag{15}$$

This bound is attained for $m = 0$ and also for $m = n/2$ when n is even. The curve (15) and the results for $n = 12$ are

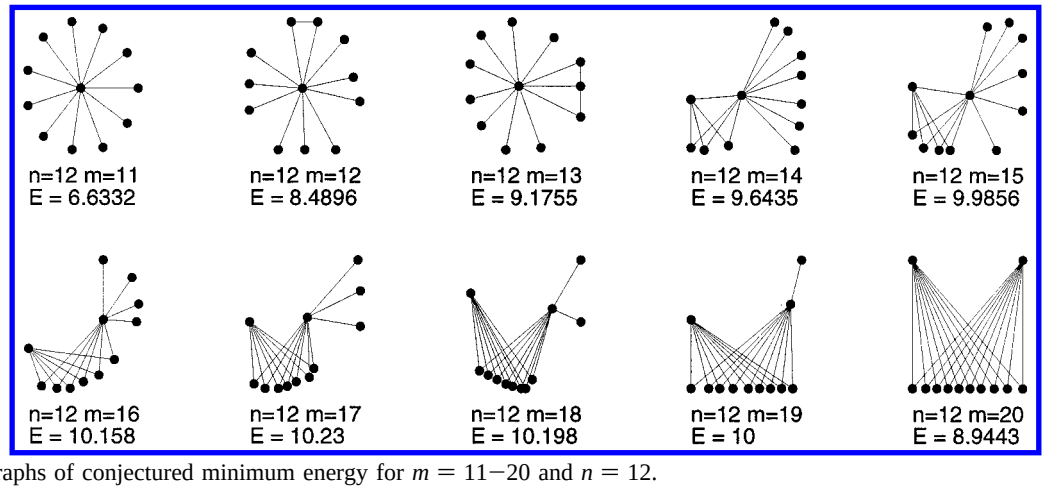

Figure 17. Graphs of conjectured minimum energy for $m = 11-20$ and $n = 12$.

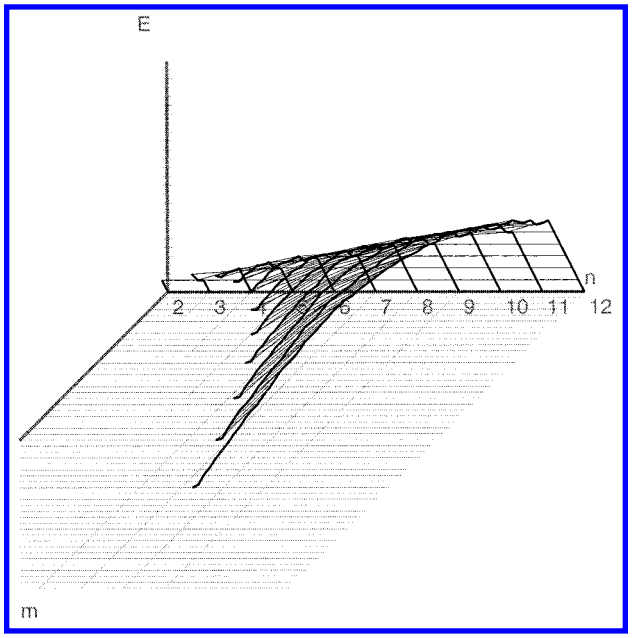

Figure 18. Largest values of E for $n = 5-12$ and $m = 0$ to $[n(n-1)]/2$.

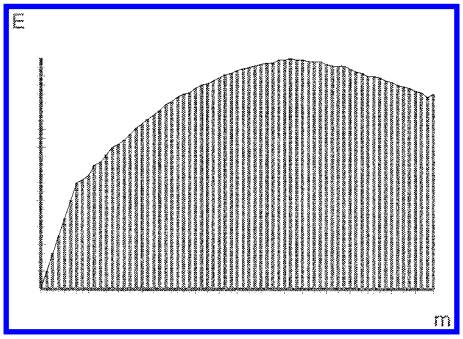

Figure 19. Largest values of E for $n = 12$ and $m = 0-66$.

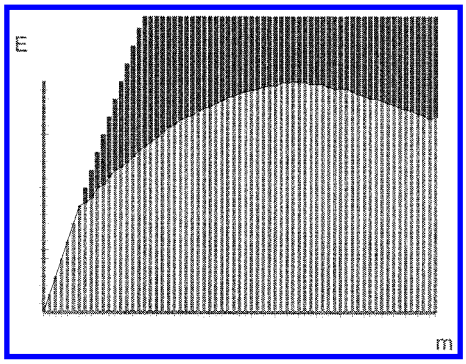

Figure 20. Largest values of E for $n = 12$ and $m = 0-66$ compared to Conjecture 6.

represented in Figure 21; both curves are compared to these values in Figure 22.

The results for maximum energy appear to be more difficult to analyze than those for minimum energy except for the bounds already described. Observe that the bound (15) increases monotonously with m, while the curve of largest values of E passes through a maximum and then decreases with m (except for a slight increase when reaching the complete graph) when $n \geq 7$. The largest values found for E for a given n are listed in Table 1. Up to $n = 7$ the graphs with maximum energy are complete and $E = 2n - 2$, *i.e.*, maximum energy increases linearly with n. Then

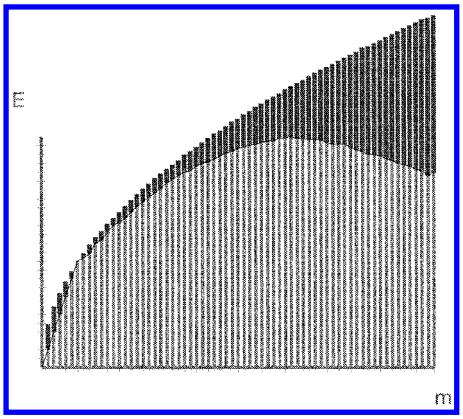

Figure 21. Largest values of E for $n = 12$ and $m = 0-66$ compared to McClelland bound.

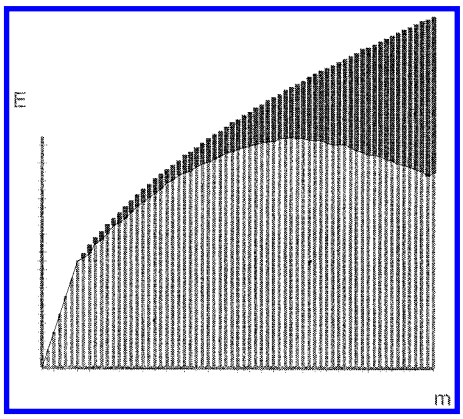

Figure 22. Largest values of E for $n = 12$ and $m = 0-66$ compared to both Conjecture 6 and McClelland bound.

Table 1. Largest Values of E for Given n

n	E	n	E
5	8	9	17.06
6	10	10	20
7	12	11	22.91
8	14.32	12	26

values increase more than linearly. It follows from $m \leq [n(n-1)]/2$ and (15) that

$$E \leq \sqrt{n^2(n-1)} < n^{3/2} \tag{16}$$

Fitting a curve of power $^3/_2$ above the differences between largest values of E and the line $2n - 2$ yields the following conjecture.

Conjecture 7. *For all graphs G with n vertices, the energy E satisfies*

$$E \leq 2n - 2 + 0.4[\max(m-7,0)]^{3/2} \tag{17}$$

This bound is attained for $n \leq 7$, $n = 9$, and $n = 10$. It is more complicated than the previous ones, and it is not likely to be attained for many values of n. The graph with largest energy for $n = 10$ has $E = 20$ and is the complement of the Petersen graph, which is represented in Figure 24.

Results for $n = 12$ are compared with all three bounds in Figure 23. Results are more clear-cut for connected graphs with few edges. For $m = n - 1$ only trees are connected, and the path has maximum energy.[47] Unicyclic graphs (with $m = n$) of largest energy are either cycles or cycles with an appended path, as represented in Figure 25. Results for

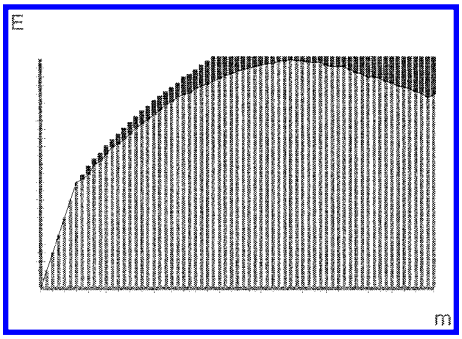

Figure 23. Largest values of E for $n = 12$ and $m = 0-66$ compared to both Conjecture 6, Conjecture 7, and McClelland bound.

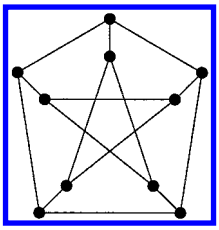

Figure 24. Petersen graph.

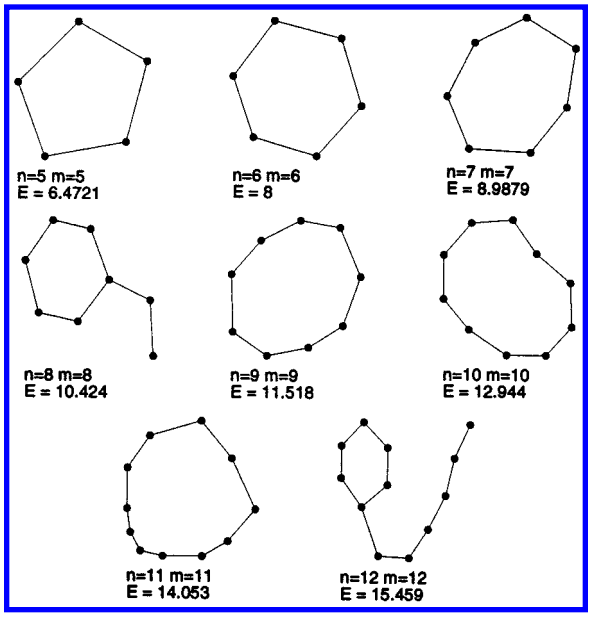

Figure 25. Unicyclic graphs with largest energy for $n = 5-12$.

connected graphs with cyclomatic number 2 (*i.e.*, $m = n + 1$) are represented in Figure 26.

Based on the results presented in Figure 25 we arrive at the following conjecture. Let P_n and C_n stand for the path and circuit on n vertices. Let $C_k(h)$ be the graph obtained by connecting a vertex of the circuit C_k with a terminal vertex of the path P_h.

Conjecture 8. *Among unicyclic graphs on n vertices the circuit C_n has maximal energy if $n \leq 7$ and $n = 9, 10, 11, 13$ and 15. For all other values of n the unicyclic graph with maximum energy is $C_6(n-6)$.*

The results shown in Figures 25 and 26 deserve the particular attention of chemists. Our analysis reveals that, provided the number of edges is not too large, the graphs with maximum energy possess many hexagons. In other words, a hexagon is a structural detail preferred by (molecular) graphs having large energy. This is in good agreement

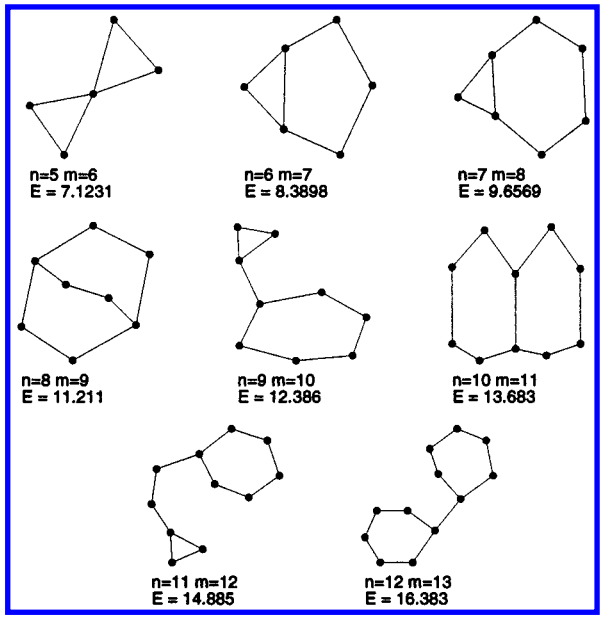

Figure 26. Bicyclic graphs with largest energy for $n = 5-12$.

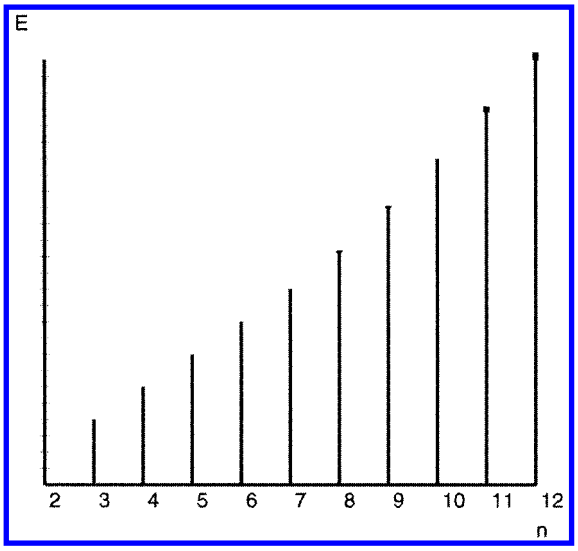

Figure 27. Maximum energy as a function of n.

with the empirically known fact that conjugated molecules with many hexagons (benzenoid hydrocarbons) possess a particularly high thermodynamic stability.

CONCLUDING REMARKS

In this paper we briefly outlined the Variable Neighborhood Search metaheuristic and exemplified its application on a long-time-open chemical problem. Although we were not able to fully characterize graphs and molecular graphs with extremal energy, we nevertheless arrived at some interesting results and recognized a few hitherto unnoticed regularities. Our results made it possible to formulate several conjectures, some of which have eventually been proven in a rigorous mathematical manner (see Appendix).

The opportunities which the Variable Neighborhood Search approach offers in mathematical chemistry, and chemical graph theory in particular, go much beyond the examination of energy. The method can be applied to any of the numerous currently studied topological indices (*TI*s). With a few exceptions, the molecules/molecular graphs with

extremal values of these *TI*s have not been identified, although the knowledge of the structure of such extremal systems would be of great value for understanding the physicochemical meaning of each particular *TI*.

Results obtained along these lines are expected to be communicated in the near future.

ACKNOWLEDGMENT

The proof of inequality (30) was proposed by Dr. Mirko Lepović (Kragujevac). One of the authors (D.C.) thanks GERAD for the hospitality during a visit when a part of the research reported in this paper was being done. The first and fourth authors were supported by NSERC Grant OGPOO 39682, FCAR Grant 32EQ 1048, and a Grant from CETAI-HEC.

APPENDIX: PROOFS OF SOME CONJECTURES

In this Appendix, we prove most of the conjectures stated above, thus obtaining several bounds for the energy of graphs. Perhaps surprisingly, Theorems 1−4 are, to the authors' best knowledge, novel, hitherto unpublished results, not to be found in any of the (otherwise quite numerous) chemical and/or mathematical papers[45−71] devoted to this topic.

Let G be an arbitrary graph on n vertices, possessing m edges. As before, $\lambda_1, \lambda_2, ..., \lambda_n$ are the eigenvalues of G. Three well-known relations for the eigenvalues are

$$\sum_{i=1}^{n}\lambda_i = 0 \tag{18}$$

$$\sum_{i=1}^{n}(\lambda_i)^2 = 2m \tag{19}$$

$$\sum_{i<j}\lambda_i\lambda_j = -m \tag{20}$$

If G has isolated vertices (*i.e.*, vertices to which no other vertex is adjacent), then each isolated vertex results in an eigenvalue equal to zero. Adding isolated vertices to G will thus change neither m nor E.

From eq 10 we have

$$E(G)^2 = \sum_{i=1}^{n}|\lambda_i|^2 + 2\sum_{i<j}|\lambda_i||\lambda_j| \tag{21}$$

Because of (19) the first sum of the right-hand side of (21) is equal to $2m$. In view of (20)

$$\sum_{i<j}|\lambda_i||\lambda_j| \geq |\sum_{i<j}\lambda_i\lambda_j| = m \tag{22}$$

Consequently,

$$E(G) \geq 4m$$

that is

$$E(G) \geq 2\sqrt{m} \tag{23}$$

which is Conjecture 1.

From (22) we see that equality in (23) will occur if and only if the graph G has exactly one positive and exactly one negative eigenvalue. This, in turn, is the case if and only if one component of G is a complete bipartite graph and all its other components are isolated vertices (see ref 39, p 163).

By direct expansion and by using eqs 10 and 19 we verify that[41]

$$\sum_{i=1}^{n}\sum_{j=1}^{n}(|\lambda_i| - |\lambda_j|)^2 = 4nm - 2E(G)^2$$

Because the left-hand side of the above identity is obviously non-negative, we arrive at the long-known McClelland upper bound:[41]

$$E(G) \leq \sqrt{2mn} \tag{24}$$

Equality in (24) is attained if and only if the absolute values of all eigenvalues are equal.

Consider, for a moment, graphs having m edges and no isolated vertices. The maximum number of vertices of such graphs is $2m$, which happens if $G = mK_2$, *i.e.*, if the graph G consists of m isolated edges. For all other graphs, $n < 2m$. Bearing this in mind, we have

$$\sqrt{2mn} \leq \sqrt{2m(2)} = 2m \tag{25}$$

which combined with (24) yields

$$E(G) \leq 2m \tag{26}$$

which is Conjecture 6.

The spectrum of mK_2 consists of numbers $+1$ (m times) and -1 (m times), hence the absolute values of all eigenvalues are equal. Therefore, for $G = mK_2$ we have equality in both (24) and (25), and therefore we have equality also in (26). Clearly, equality in (26) will hold also if in addition to m isolated edges, the graph G contains any number of isolated vertices.

By this we proved Theorem 1.

Theorem 1. *If G is an arbitrary graph containing m edges, then*

$$2\sqrt{m} \leq E(G) \leq 2m \tag{27}$$

where $E(G) = 2\sqrt{m}$ *if and only if G is a complete bipartite graph plus arbitrarily many isolated vertices, and where* $E(G) = 2m$ *holds if and only if G consists of m isolated edges and of arbitrarily many isolated vertices.*

Among lower and upper bounds for E, depending solely on m, those given by eq 27 are the best possible. Although being of very simple form, the lower bound in (27) has not been noticed so far.

At this point the natural question is to find bounds for E, depending solely on n. Then, of course, the consideration has to be restricted to graphs without isolated vertices. We have Theorem 2.

Theorem 2. *If G is an n-vertex graph without isolated vertices, then*

$$E(G) \geq 2\sqrt{n-1} \tag{28}$$

with equality if and only if G is the n-vertex star.

Proof. If G is a connected graph, then $m = n - 1 + c$ where c is the cyclomatic number, $c \geq 0$. Consequently, m

$\geq n - 1$ and (28) follows from (23). Equality is attained if G is a complete bipartite graph with $c = 0$, which is the star.

Thus let G be a graph composed of $p > 1$ components, $G_1, G_2, ..., G_p$, having $n_1, n_2, ..., n_p$ vertices, respectively, $n_1 + n_2 + ... + n_p = n$. Note that since G has no isolated vertices, for all values of i it must be $n_i \geq 2$ and therefore $\sqrt{n_i-1} \geq 1$.

Then

$$E(G) = E(G_1) + E(G_2) + ... + E(G_p)$$

and for $i = 1, 2, ..., p$

$$E(G_i) \geq 2\sqrt{n_i-1}$$

Therefore,

$$E(G) \geq 2(\sqrt{n_1-1} + \sqrt{n_2-1} + ... + \sqrt{n_p-1}) =$$
$$2\sqrt{(\sqrt{n_1-1} + \sqrt{n_2-1} + ... + \sqrt{n_p-1})^2} =$$
$$2\sqrt{(n_1-1) + (n_2-1) + ... + (n_p-1) + 2\sum_{i<j}\sqrt{n_i-1}\sqrt{n_j-1}} \geq$$
$$2\sqrt{n - p + p(p-1)} = 2\sqrt{n - 1 + (p-1)^2}$$

because there are $p(p-1)/2$ summands of the form $\sqrt{n_i-1}\sqrt{n_j-1}$, each being greater than or equal to unity.

We thus proved a stronger result, from which Theorem 2 follows immediately.

Theorem 3. *If G is an n-vertex graph without isolated vertices and with p components, $p \geq 1$, then*

$$E(G) \geq 2\sqrt{n - 1 + (p-1)^2} \qquad (29)$$

If $p = 1$, then equality in (29) occurs for G being the n-vertex star. If $p > 1$, then $E(G) = 2\sqrt{n-1+(p-1)^2}$ holds if and only if $G = pK_2$, *i.e.*, if $n_1 = n_2 = ... = n_p = 2$, which can happen only if n is even. eq 29 implies Conjecture 4.

For graphs with a large number of edges, the inequality (23) can be improved as follows.

It is known (see ref 39, p 85) that the greatest eigenvalue of a graph cannot be less than the average vertex degree. On the other hand, the average vertex degree is just $2m/n$. Thus,

$$\frac{2m}{n} \leq \lambda_1 \leq \sum_{+}\lambda_1 = \frac{1}{2}E(G)$$

i.e.,

$$E(G) \geq \frac{4m}{n} \qquad (30)$$

which is Conjecture 3.

The idea for the above proof of inequality (30) was given by Dr. Mirko Lepović.

It is easy to show that the upper bound (30) is better than (23) if $n^2/4 < m \leq n(n-1)/2$. Equality in (30) occurs if (a) G is a regular graph and (b) if G has exactly one positive eigenvalue. Conditions (a) and (b) are simultaneously obeyed only by multipartite graphs, *i.e.*, graphs in which the vertices can be divided in several groups, such that vertices within each group are not adjacent, whereas any two vertices from different groups are (see ref 35, p 163). Recall that the complete graph and the complete bipartite graphs are special cases of multipartite graphs.

The above considerations can be summarized as Theorem 4.

Theorem 4. *If G is an arbitrary graph containing n vertices and m edges, then*

$$\max\left(\frac{4m}{n}, 2\sqrt{m}\right) \leq E(G) \leq \min(2m, \sqrt{2mn}) \qquad (31)$$

The (m,n)-type estimates given in Theorem 4 are all attained but are not the best possible for all values of m and n. They, however, are the best that we know of at the moment.

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