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Hückel Energy Of A Graph: Its Evolution From Quantum Chemistry To Mathematics

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HÜCKEL ENERGY OF A GRAPH: ITS EVOLUTION FROM QUANTUM CHEMISTRY TO MATHEMATICS

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ABSTRACT

The energy of a graph began with German physicist, Erich Hückel's 1931 paper, Quantentheoretische Beiträge zum Benzolproblem. His work developed a method for computing the binding energy of the π-electrons for a certain class of organic molecules. The vertices of the graph represented the carbon atoms while the single edge between each pair of distinct vertices represented the hydrogen bonds between the carbon atoms. In turn, the chemical graphs were represented by an $n \times n$ matrix used in solving Schrödinger's eigenvalue/eigenvector equation. The sum of the absolute values of these graph eigenvalues represented the total π-electron energy. The criteria for constructing these chemical graphs and the chemical interpretations of all the quantities involved made up the Hückel Molecular Orbital theory or HMO theory. In this paper, we will show how the chemical interpretation of Hückel's graph energy evolved to a mathematical interpretation of graph energy that Ivan Gutman provided for us in his famous 1978 definition of the energy of a graph. Next, we will present Charles Coulson's 1940 theorem that expresses the energy of a graph as a contour integral and prove some of its corollaries. These corollaries allow us to order the energies of acyclic and bipartite graphs by the coefficients of their characteristic polynomial. Following Coulson's theorem and its corollaries we will look at McClelland's first theorem on the bounds for the energy of a graph. In the corollaries that follow McClelland's 1971 theorem, we will prove the corollaries that show a direct variation between the energy of a graph and the number of its vertices and edges. Finally, we will see how this relationship led to Gutman's conjecture that the complete graph on n vertices has maximal energy. Although this was disproved by Chris Godsil in 1981, we will provide an independent counterexample with the help of the software, Maple 13.

I dedicate this work to my mother, Pat Neff for her support and long suffering.

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CHAPTER ONE: INTRODUCTION

1.0.1 Assumptions on the graph G

A graph G is a family of two sets. The first is a set of points or nodes, called a vertex set, denoted by V_G, and the other set is an edge set, E_G. The edge set defines the relationships between pairs of not necessarily distinct elements from V_G. The element of E_G, denoted xy, means the edge between x and y If $xy \neq yx$ for all distinct vertices x and y, then G is called a directed graph or digraph. xy is the directed edge from x to y and yx is the directed edge from y to x. We say that two vertices v_i and v_j are adjacent if v_i and v_j are joined by an edge, (i.e. v_iv_j belongs to E_G). Vertex adjacency is a symmetric relationship for all undirected graphs. Graphs can be finite or infinite depending on the cardinality of V_G. We will focus our attention on finite undirected simple graphs. These graphs of interest have the following properties:

- The graph G has no loops.
- G has no multiple edges between any distinct pair of vertices x and y.
- G has no directed edges.

Here are some basic graph-theoretical notions that will be mentioned throughout. We begin with some special simple graphs. We say that G is empty, if $V_G = \emptyset$; trivial, if $|V_G| = 1$, and null, if $E_G = \emptyset$ [1]. G is called a complete graph on n vertices, denoted K_n, if every vertex is joined to the remaining $n-1$ vertices. If two sets X and Y partition V_G and every element of E_G consists of a vertex from X and a vertex from Y, then we say that G is bipartite. If X has m vertices and Y has n vertices then $K_{m,n}$ denotes the bipartite graph with mn edges.

P_n and C_n denote the path and cycle on n vertices, respectively. A graph G with no cycles is a forest. If G is connected and without cycles then G is a tree [1]. The complement of G, denoted $\overline{G}$, over n vertices has the properties $V_G = V_{\overline{G}}$, $E_G \cap E_{\overline{G}} = \emptyset$, and $E_G \cup E_{\overline{G}} = E_{K_n}$. Any other simple graphs not mentioned will be introduced later in this work when necessary. If H is a graph having all of its vertices and edges in G then we say that H is a subgraph of G [23]. If $V_H = V_G$ then H is a spanning subgraph of G [23]. For any set S of vertices of G, the induced subgraph is the maximal subgraph of G with vertex set S [23]. An elementary subgraph of G is any edge or cycle contained in G [1].

Let $\mathbf{A} = \mathbf{A}(G)$ be the adjacency matrix of G. $\mathbf{A}$(G) is $n \times n$; n is the number of vertices in G, and each (i,j)-entry is determined by the following rule:

$$(\mathbf{A}(G))_{ij} = \begin{cases} 1 & v_i \text{ and } v_j \text{ are joined by an edge,} \\ 0 & \text{otherwise.} \end{cases}$$

The characteristic polynomial of a graph G is the characteristic polynomial of $\mathbf{A}$(G) which is given by the equation:

$$\phi(G, x) = \det|\mathbf{I}x - \mathbf{A}(G)| = x^n - \sigma_1 x^{n-1} + \sigma_2 x^{n-2} - \ldots + (-1)^n \sigma_n.$$

In 1962, Harary published the following theorem which computes the determinant of the adjacency matrix of a graph G. [1] provides a proof to this theorem.

Theorem 1 ([1])**.** *If G is a graph with n vertices and adjacency matrix $\boldsymbol{A}(G)$, then*

$$\det(\boldsymbol{A}(G)) = (-1)^n \sum_{H \in \mathcal{H}} (-1)^{p(H)} (2)^{c(H)},$$

where $\mathcal{H}$ is the set of all spanning subgraphs of G, p(H) denotes the number of components of H and c(H) denotes the number of cycles in H.

We will use this theorem to prove this useful corollary which will determine the coefficients of the characteristic polynomial of G.

Corollary 1 (Sachs' Coefficient Theorem[1])**.** *Let*

$$\phi(G,x) = x^n - \sigma_1 x^{n-1} + \sigma_2 x^{n-2} - \ldots + (-1)^n \sigma_n,$$

and let $\mathcal{H}_i$ *be the set of elementary subgraphs of* G *with* i *vertices. Then*

$$\sigma_i = \sum_{H \in \mathcal{H}_i} (-1)^{p(H)} (2)^{c(H)}, (i = 1, \ldots, n).$$

Proof [1]: The number $(-1)^i \sigma_i$ is the sum of all $i \times i$ principal minors of $\mathbf{A}$(G), and each such minor is the determinant of the adjacency matrix of an induced subgraph on i vertices. An elementary subgraph with i vertices is contained in exactly one of such subgraph, and so the result follows by applying Theorem 1 to each minor. □

By the Fundamental Theorem of Algebra, $\phi(G,x) = 0$ has n complex roots $\lambda_1, \lambda_2, \ldots, \lambda_n$, and has factorization

$$\phi(G,x) = (x - \lambda_1)(x - \lambda_2) \ldots (x - \lambda_n) = 0.$$

The roots satisfying the equation $\phi(G,x) = 0$ are the eigenvalues of $\mathbf{A}$(G). The next section will prove some basic theorems we will need to establish useful properties of $\mathbf{A}$(G) and its eigenvalues.

1.0.2 Essential Results

From the definition of $\mathbf{A}$(G) and for all simple undirected graphs G, it follows that $\mathbf{A}$(G) has entries, either 0 or 1, and remains unchanged when we interchange its rows and columns. That is, $\mathbf{A}$(G) is symmetric. Here are two results from the book [24] that we will use to prove our main result, Theorem 4 which states the essential properties of $\mathbf{A}$(G).

Theorem 2. *Symmetric matrices have real eigenvalues.*

Two matrices $\mathbf{A}$ and $\mathbf{B}$ are said to be similar if there exists a nonsingular matrix $\mathbf{P}$ such that

$$\mathbf{A} = \mathbf{P}^{-1}\mathbf{B}\mathbf{P}$$

Theorem 3. *Similar matrices have the same eigenvalues.*

Theorem 4. *Let G be a simple graph with n vertices and m edges having adjacency matrix $\boldsymbol{A}(G)$, eigenvalues $\lambda_1, \lambda_2, \ldots, \lambda_n$, and nth degree characteristic polynomial $\phi(G, x) = |\boldsymbol{I}\boldsymbol{x} - \boldsymbol{A}(G)| = x^n - \sigma_1 x^{n-1} + \sigma_2 x^{n-2} - \ldots + (-1)^n \sigma_n$. Then we have:*

(i) $\lambda_1 \geq \lambda_2 \geq \ldots \geq \lambda_n$, *and* $\lambda_1 + \lambda_2 + \ldots + \lambda_n = 0$.

(ii) *The coefficient of x^{n-1} in $\phi(G, x)$ is 0, and the coefficient of x^{n-2} in $\phi(G, x)$ is* $\sum_{1 \leq i < j \leq n} \lambda_i \lambda_j = -m$.

(iii) $trace(\boldsymbol{A}^2(G)) = \sum_{i=1}^{n} \lambda_i^2 = 2m$.

Proof: The adjacency matrix of the simple graph G, $\mathbf{A}$(G), is symmetric with zeros down the principle diagonal.[2, page 6] By Theorem 2, the eigenvalues of $\mathbf{A}$(G) are real and, therefore, we can order the eigenvalues in the manner shown in statement (i). Also, $\mathbf{A}$(G) is similar to the matrix $\mathbf{D} = \text{diag}(\lambda_1, \lambda_2, \ldots, \lambda_n)$, and for an orthogonal matrix $\mathbf{P}$, $\mathbf{A}(G) = \mathbf{P}'\mathbf{D}\mathbf{P}$

because of the symmetry of $\mathbf{A}$(G). Theorem 3 tells us that the eigenvalues of $\mathbf{A}$(G) are also the eigenvalues of $\mathbf{D}$. When we use the fact that for any square matrices $\mathbf{X}$ and $\mathbf{Y}$, trace($\mathbf{XY}$) = trace($\mathbf{YX}$), we get

$$\begin{aligned} 0 &= \text{trace}(\mathbf{A}(G)) \\ &= \text{trace}(\mathbf{P'DP}) \\ &= \text{trace}(\mathbf{PP'D}) \\ &= \text{trace}(\mathbf{ID}) \\ &= \text{trace}(\mathbf{D}) \\ &= \lambda_1 + \lambda_2 + \ldots + \lambda_n. \end{aligned}$$

This proves (i).

We now consider the proof of statement (ii) by directing out attention to the factorization of $\phi(G, x) = (x - \lambda_1)(x - \lambda_2)\ldots(x - \lambda_n)$. To solve for σ_1, we must combine all x^{n-1} terms. The coefficient of x^{n-1} is $\sum_{i=1}^{n} -\lambda_i$, and there are a total of $\binom{n}{1}$ terms. Combining all terms of x^{n-1}, we have minus one times the sum of the eigenvalues of $\mathbf{A}$(G). By (i), that sum is zero. Hence, $\sigma_1 = 0$. Now we turn our attention to σ_2. Upon observing the expansion of the factors of $\phi(G, x)$, each coefficient of x^{n-2} is the product of $\binom{n}{2}$ pairs of distinct factors, λ_i and λ_j, where $i < j$. Thus,

$$\sigma_2 = \sum_{1 \le i < j \le n} \lambda_i \lambda_j.$$

By [4], we also have

$$\sum_{1 \le i < j \le n} \lambda_i \lambda_j = \sum_{i<j} \begin{vmatrix} a_{ii} & a_{ij} \\ a_{ji} & a_{jj} \end{vmatrix}.$$

The right - hand sum is the sum of all diagonal minors of order 2 of $\mathbf{A}$(G) and we observe straight away that the diagonal elements are zero. Now G is a simple graph having m edges.

So there are m ones above the main diagonal and m ones below the diagonal of $\mathbf{A}$(G). So of the $\binom{n}{2}$ determinants, only m will have a nonzero contribution to the sum and we have, whenever $a_{ij} = a_{ji} = 1$,

$$\begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix} = -1.$$

Therefore, the coefficient of x^{n-2} is $-m$. This proves (ii).

Finally, we turn our attention to the trace($\mathbf{A}^2(G)$). We claim that the eigenvalues of $\mathbf{A}^2(G)$ are $\lambda_1^2, \lambda_2^2, \ldots, \lambda_n^2$. To see this, observe that

$$\begin{aligned} \mathbf{A}^2(G)\mathbf{x} &= \mathbf{A}(G)\mathbf{A}(G)\mathbf{x} \\ &= \mathbf{A}(G)(\lambda\mathbf{x}) \\ &= \lambda(\mathbf{A}(G)\mathbf{x}) \\ &= \lambda^2\mathbf{x} \end{aligned}$$

Hence, trace($\mathbf{A}^2(G)$) $= \sum_{i=1}^{n} \lambda_i^2$. The jth diagonal element of $\mathbf{A}^2(G)$ represents the number of vertices adjacent to v_j. For example, if there are k ones that appear in the row or column corresponding to v_j, then the degree of v_j is k. Therefore, the trace of $\mathbf{A}^2(G)$ is the sum of the degrees of all n vertices. But G is a simple graph having m edges. So (iii) follows.
By proving statements (i) through (iii), our proof is complete. □

CHAPTER TWO: GRAPH ENERGY'S BEGINNING IN QUANTUM CHEMISTRY

2.1 HMO THEORY

The energy of a graph began in the 1930's with German physicist, Erich Hückel. He developed a method for finding approximate solutions to the Schrödinger wave equation of "unsaturated conjugated hydrocarbons", a class of organic molecules. The solutions from the time-independent Schrödinger wave equation measures the binding energy of the π-electrons. Sadly, Hückel never enjoyed the recognition his contribution merited. The details of this method, now known as the Hückel Molecular Orbital Theory, (HMO) theory, are found in books[5] and [6].

Hückel's energy computation begins with the consideration of Schrödinger's equation

$$\hat{\mathbf{H}}\Psi = \mathcal{E}\Psi, \tag{2.1.1}$$

where $\hat{\mathbf{H}}$ is the Hamiltonian operator of the system under consideration, Ψ represents the wave functions satisfying equation of the system considered, and $\mathcal{E}$ is the energy of that system. If our system under consideration is a molecule from the class of unsaturated conjugated hydrocarbons, we can use equation (2.1.1) to describe that molecule's behavior and energy of its π-electrons. Clearly, (2.1.1) is an eigenvalue/eigenvector equation in terms of the operator $\hat{\mathbf{H}}$. In order to find a feasible (not necessarily exact) solution to this equation, one needs to find a suitable set of basis functions, say, $\psi_1, \psi_2, \ldots, \psi_n$, so that Ψ is in the span$\{\psi_1, \psi_2, \ldots, \psi_n\}$. Doing so allows us to obtain solutions for (2.1.1) by solving the matrix equation

$$\mathbf{H}\Psi = \mathbf{E}\Psi, \tag{2.1.2}$$

where $\mathbf{H}$ is a square matrix having dimension n known as the Hamiltonian Matrix. [8]

According to the HMO model, the wave functions of a conjugated hydrocarbon with n carbon atoms are linear combinations of n orthogonal basis functions while the Hamiltonian Matrix $\mathbf{H}$ has this definition:

$$(\mathbf{H})_{ij} = \begin{cases} \alpha & \text{i = j,} \\ \beta & \text{if the atoms i and j are chemically bonded,} \\ 0 & \text{if there is no chemical bond between the atoms i and j.} \end{cases}$$

The parameters of α and β are constants, equal for all conjugated molecules. Their physical nature and numerical value are not relevant in our mathematical consideration.[8] Details about these parameters are found in these books [5][6]. From the definition of $\mathbf{H}$, we see that the size of $\mathbf{H}$ is equal to the number of carbon atoms in our molecule. If there is a bond between a particular pair of carbon atoms, we can think of them as vertices joined by an edge. If we assume that no carbon atom is chemically bonded to itself, no vertex has a loop. So we can form a simple graph using the carbon atoms as vertices and their chemical bonds as the edges. In the HMO theory, the physical considerations of the molecules place many restrictions on the construction of these simple graphs. Two examples of such restrictions are:

1. Every vertex must have degree at most three; [8]
2. All cycles within the graph must be the same size. [12]

Graphs that meet the HMO criteria will be denoted G_{HMO}. The specifics on how G_{HMO} is constructed are also found in the books by Coulson and Yates [5][6]. We also have from the definition of $\mathbf{H}$ this equation

$$\mathbf{H} = \alpha \mathbf{I}_n + \beta \mathbf{A}(G_{HMO}).$$

If the eigenvalues of $\mathbf{A}(G_{HMO})$ are $\lambda_1, \lambda_2, \ldots, \lambda_n$ then the energy eigenvalues of $\mathbf{H}$, denoted $E_1, E_2, \ldots, E_n$, are given by the equation

$$E_i = \alpha + \beta\lambda_i, \tag{2.1.3}$$

where $i = 1, 2, \ldots, n$. Moreover, the molecular orbitals, describing electron movement within the π-orbital, coincide with the eigenvectors ψ_i of the graph G_{HMO}.[8]

In the HMO theory, the approximation for the total energy is given by

$$E_\pi = \sum_{i=1}^{n} g_i E_i,$$

where g_i represents the quantum number of the molecular orbital ψ_i. By the Pauli Exclusion Principle, every molecular orbital has at most two electrons.[11] So g_i only takes on values 0, 1, or 2.

For what follows, we direct our attention to the fact that there are n electrons in the π-orbitals of the hydrocarbon under consideration. Then $g_1 + g_2 + \ldots + g_n = n$. So

$$\begin{aligned} E_\pi &= \sum_{i=1}^{n} g_i E_i \\ &= \sum_{i=1}^{n} g_i(\alpha + \beta\lambda_i) \\ &= n\alpha + \beta \sum_{i=1}^{n} g_i \lambda_i. \end{aligned} \tag{2.1.4}$$

If we formally set $\alpha = 0$, $\beta = 1$ and use the fact that the total number of electrons in the π-orbitals is constant, then the non-trivial part of (2.1.4) is given by

$$E = \sum_{i=1}^{n} g_i \lambda_i. \tag{2.1.5}$$

The right-hand side of equation (2.1.5) is called the "total π-electron energy", or the "total π-electron energy in β-units".[8]

Moreover, by setting $\alpha = 0$, $\beta = 1$, the Hamiltonian Matrix $\mathbf{H}$, is now the adjacency matrix $\mathbf{A}(G_{HMO})$. So the π-electron energy levels E_i are the eigenvalues of $\mathbf{A}(G_{HMO})$. By theorem 2 of Section 1 the π-electron energy levels are real eigenvalues, and therefore, can be ordered in a non-decreasing order $E_1 \leq E_2 \leq \ldots \leq E_n$. If we require that the total π-electron energy levels to be as low as possible, then, by [8] we have for even n,

$$g_i = \begin{cases} 2, & \text{for i = 1,2,. . . ,n/2} \\ 0, & \text{for i = n/2+1,n/2+2, . . . , n} \end{cases}$$

and for odd n

$$g_i = \begin{cases} 2, & \text{for i = 1,2,. . . ,(n-1)/2,} \\ 1, & \text{for i = (n+1)/2,} \\ 0, & \text{for i = (n+1)/2 +1, (n+1)/2 +2,. . . , n.} \end{cases}$$

Moreover, [8] also gives us a definition of g_i that depends on the eigenvalues of $\mathbf{A}(G_{HMO})$ which holds for the majority of our chemically relevant cases.

$$g_i = \begin{cases} 2, & \text{if } \lambda_i > 0 \\ 0, & \text{if } \lambda_i < 0 \end{cases}$$

Using this definition of g_i, equation (2.1.5) becomes

$$E = E(G_{HMO}) = 2 \sum \{\lambda_i : \lambda_i > 0\}.$$

Now, by Theorem 3(i), the sum of the eigenvalues of a simple graph is zero. So, the previous equation becomes

$$E = E(G_{HMO}) = \sum_{i=1}^{n} |\lambda_i|. \tag{2.1.6}$$

In the 1970's, Ivan Gutman noticed that many of the earlier results, pertaining to either the computation or a property of the total π-electron energy tacitly assume the validity of equation (2.1.6). [13], [14], [15], and [16] are examples of such papers that [8] mentions.

This means that the energy computation of equation (2.1.6) holds for all simple graphs, not just the Hückel molecular graphs. Gutman's observation led to his famous 1978 definition that begins every graph energy discussion.

Definition 1 ([7]). *If G is graph on n vertices, and $\lambda_1, \lambda_2, \ldots, \lambda_n$ are its eigenvalues, then the* ***energy*** *of G is*

$$E = E(G) = \sum_{i=1}^{n} |\lambda_i|. \tag{2.1.7}$$

CHAPTER THREE: GRAPH ENERGY

3.1 GRAPH ENERGY

From Gutman's definition, we observe that the energy of the empty graph and the null graph is zero. So, isolated vertices do not affect the energy of a graph G. Assuming that G has no isolated vertices gives us $m \geq n/2$, recalling that m is the number of edges of G. Also, if G has multiple components then the energy of G is the sum of the energy of each of its components. This means that we can assume, without loss of generality, that G is connected.

Moreover, Definition 1 frees us from all of the chemical-based restrictions we had to put on the graph G; thus giving us a mathematical interpretation of graph energy to every simple graph.

In the section that follows, we apply some basic properties of complex integration to establish a very useful integral formula developed by Coulson and Longuet-Higgins. This formula establishes the dependence of the energy of a graph on the characteristic polynomial of this graph. In other words, this integral makes it possible to compute the sum, as stated in Definition 1, without knowing the zeros of its characteristic polynomial. [17] However, the numerical implementation of this formula proved difficult.

In 1951, Frank Sumner, a PhD student of Christopher Longuet-Higgins, attempted to apply the integral technique to solve the HMO eigenvalue problem using the latest computing machine, Ferranti Mk I [**?**]. Soon after he began this project, his advisor, Longuet-Higgins left for another position. Frustrated with his progress on the project, he consulted with Alan Turing who advised him to "to forget the contour integrals and attack the eigenvalue problem head-on" [**?**].

Despite the numerical difficulties of this contour formula, the mathematical value of the Coulson Integral Theorem lies in its corollaries which gives us a way to establish an order of energies between acyclic graphs and bipartite graphs.

3.2 THE COULSON INTEGRAL FORMULA

In 1940, Charles Alfred Coulson gave another eigenvalue formulation of the energy of a graph. This formula establishes the dependence of the energy of a graph on the characteristic polynomial of this graph. In other words, this integral makes it possible to compute the sum, as stated in Definition 1, without knowing the zeros of its characteristic polynomial. [17]

For the integral theorem and the corollaries that follow, all integrals of the form $\int_{-\infty}^{\infty} F(x)dx$ mean the principal value of the respective integral. That is, $\int_{-\infty}^{\infty} F(x)dx = \lim_{r\to\infty} \int_{-r}^{r} F(x)dx$.

Theorem 5 (Coulson, 1940 [7])**.** *If G is a graph on n vertices, then*

$$\begin{aligned} E(G) &= \frac{1}{\pi}\int_{-\infty}^{\infty}\left[n - \frac{ix\phi'(G,ix)}{\phi(G,ix)}\right]dx \\ &= \frac{1}{\pi}\int_{-\infty}^{\infty}\left[n - \frac{d}{dx}\log\phi(G,ix)\right]dx \end{aligned}$$

where $\phi'(G,x) = \frac{d}{dx}\phi(G,x)$ and $i = \sqrt{-1}$.

Proof: [7] Since G is a graph on n vertices, G has n eigenvalues $\lambda_1 \geq \lambda_2 \geq \ldots \geq \lambda_n$. Consider only the p ($p \leq n$) distinct eigenvalues of G, $\xi_1 \geq \xi_2 \geq \ldots \geq \xi_p$ and $\mu_1, \mu_2, \ldots, \mu_p$, the corresponding algebraic multiplicity of each distinct eigenvalue such that $\sum_{j=1}^{p} \mu_j = n$. Let z be a complex variable, $z = x + iy$. Since

$$\phi(G,z) = \prod_{j=1}^{p}(z - \xi_j)^{\mu_j},$$

it follows that

$$\frac{\phi'(G,z)}{\phi(G,z)} = \sum_{j=1}^{p} \frac{\mu_j}{z-\xi_j}. \tag{3.2.1}$$

Now, $\frac{\phi'(G,z)}{\phi(G,z)}$ is a meromorphic function with simple poles at $\xi_1, \xi_2, \ldots, \xi_p$. The eigenvalues of G that influence its energy are the nonzero eigenvalues, so we will consider two possible contours and note that neither contour has a pole at $z = 0$. To this end, let Γ^+ be the semi-circular contour of radius r, centered at $z = 0$, where $r > \max\{\xi_1, |\xi_p|\}$. The contour goes along the imaginary axis from ri to $-ri$ and then returns to ri along the arc of the semi-circle of radius r. All positive eigenvalues lie on the real axis in the open interval from 0 to r. Furthermore, define

$$f(z) = z\frac{\phi'(G,z)}{\phi(G,z)}. \tag{3.2.2}$$

Observe that

$$\begin{aligned} z\frac{\phi'(G,z)}{\phi(G,z)} &= \sum_{j=1}^{p} \mu_j \frac{z}{z-\xi_j} \\ &= \sum_{j=1}^{p} \mu_j \left(1 + \frac{\xi_j}{z-\xi_j}\right) \qquad (3.2.3) \\ &= \sum_{j=1}^{p} \mu_j + \sum_{j=1}^{p} \frac{\mu_j \xi_j}{z-\xi_j} \\ &= n + \sum_{j=1}^{p} \frac{\mu_j \xi_j}{z-\xi_j}. \qquad (3.2.4) \end{aligned}$$

Therefore,

$$f(z) - n = \sum_{j=1}^{p} \frac{\mu_j \xi_j}{z-\xi_j}. \tag{3.2.5}$$

Applying the Cauchy formula to equation (3.2.1),

$$\frac{1}{2\pi i} \oint_{\Gamma^+} f(z)dz = \sum_{\xi_j \geq 0} \mu_j \xi_j = \sum_{\lambda_i \geq 0} \lambda_i = \frac{E(G)}{2}. \tag{3.2.6}$$

where Γ^+ is the aforementioned contour. Since n is a constant and Γ^+ is a closed contour, $\oint_{\Gamma^+} n dz = 0$ which means

$$\frac{1}{2\pi i}\oint_{\Gamma^+} f(z)dz = \frac{1}{2\pi i}\oint_{\Gamma^+}[f(z)-n]dz. \tag{3.2.7}$$

By equation (3.2.5),

$$\lim_{|z|\to\infty}[f(z)-n] = 0.$$

From that, it follows that if $r \to \infty$ then the integrand $[f(z)-n]$ vanishes everywhere on Γ^+, except on the imaginary axis. This change of Γ^+ will not affect the value of the contour integral itself. Hence, for $r \to \infty$,

$$\frac{1}{2\pi i}\oint_{\Gamma^+}[f(z)-n]dz = \frac{1}{2\pi i}\int_{\infty}^{-\infty}[f(iy)-n]d(iy) = \frac{1}{2\pi}\int_{-\infty}^{\infty}[n-f(iy)]dy = \frac{E(G)}{2}.$$

Recalling the definition of f, we see that our equation is equivalent to our desired result.

Lastly, we turn our attention to the second possible contour of integration, Γ^-. This contour is also semi-circular centered at z = 0 and having the same radius r as before. The contour begins at ri on the imaginary axis and traverses the semi-circular arc through the point $-r$ on the real axis and completing the arc at $-ri$. From there, we continue on the imaginary axis from $-ri$ to ri. The negative eigenvalues of G lie on the real axis in the interior of the open interval from $-r$ to 0. Using a similar argument as before and the same definition for f, but integrating over Γ^- we have

$$\frac{1}{2\pi i}\oint_{\Gamma^-}[f(z)-n]dz = \sum_{\lambda_i<0}\lambda_i$$

or

$$-\sum_{\lambda_i<0}\lambda_i = -\frac{1}{2\pi i}\oint_{\Gamma^-}[f(z)-n]dz \tag{3.2.8}$$

following from equations (3.2.6) and (3.2.7). As $r \to \infty$, we have

$$\frac{1}{2\pi i}\oint_{\Gamma^-}[f(z)-n]dz = \frac{1}{2\pi i}\int_{-\infty}^{\infty}[f(iy)-n]d(iy). \tag{3.2.9}$$

So,

$$\begin{aligned}
-\sum_{\lambda_i<0}\lambda_i &= -\frac{1}{2\pi i}\oint_{\Gamma^-}[f(z)-n]dz \\
&= -\frac{1}{2\pi i}\int_{-\infty}^{\infty}[f(iy)-n]d(iy) \\
&= -\frac{1}{2\pi}\int_{-\infty}^{\infty}[f(iy)-n]dy \\
&= \frac{1}{2\pi}\int_{-\infty}^{\infty}[n-f(iy)]dy \\
&= \sum_{\lambda_i\geq 0}\lambda_i \\
&= \frac{E(G)}{2}
\end{aligned}$$

Hence,

$$E(G)=\sum_{i=1}^{n}|\lambda_i|=\sum_{\lambda_i\geq 0}\lambda_i-\sum_{\lambda_i<0}\lambda_i=\frac{1}{\pi}\int_{-\infty}^{\infty}[n-f(iy)]dy,$$

where $f(iy)=iy\frac{\phi'(G,iy)}{\phi(G,iy)}$. □

Gutman and Mateljević point out that Coulson's theorem is not valid for graphs whose eigenvalue sum is nonzero [17]. The statement of the theorem does not require it nor do they use that fact in the details of the original proof. In their paper [17] they prove a proposition that states that the graph in which the Coulson integral formula can be applied is logically equivalent to saying that the sum of that graph's eigenvalues is zero. Furthermore, they give and prove a new integral formula that extends to graphs having a nonzero sum of its eigenvalues. No other work prior to that 2006 paper challenged the validity of that 1940 result.

From Coulson's Theorem, we have some useful corollaries as we shall see in the next section.

3.3 COROLLARIES FROM COULSON'S THEOREM

Corollary 2 ([7]). *If G_1 and G_2 are two graphs with equal number of vertices, then*

$$E(G_1) - E(G_2) = \frac{1}{\pi}\int_{-\infty}^{\infty} \log \frac{\phi(G_1, ix)}{\phi(G_2, ix)} dx.$$

Proof: By Coulson's theorem,

$$\begin{aligned} E(G_1) - E(G_2) &= \frac{1}{\pi}\int_{-\infty}^{\infty} \left[(n - x\frac{d}{dx}\log\phi(G_1, ix)) - (n - x\frac{d}{dx}\log\phi(G_2, ix)) \right] dx \\ &= \frac{1}{\pi}\int_{-\infty}^{\infty} \left[x\frac{d}{dx}\log\phi(G_2, ix) - x\frac{d}{dx}\log\phi(G_1, ix) \right] dx \\ &= \frac{1}{\pi}\int_{-\infty}^{\infty} x\frac{d}{dx}\left[\log\phi(G_2, ix) - \log\phi(G_1, ix)\right] dx \\ &= \frac{1}{\pi}\int_{-\infty}^{\infty} x\frac{d}{dx}\left[\log\frac{\phi(G_2, ix)}{\phi(G_1, ix)}\right] dx. \end{aligned}$$

Integrating by parts, we obtain

$$\begin{aligned} E(G_1) - E(G_2) &= \frac{1}{\pi}\lim_{r\to\infty}\left[x\log\frac{\phi(G_2, ix)}{\phi(G_1, ix)} \right]_{-r}^{r} - \frac{1}{\pi}\int_{-\infty}^{\infty}\log\frac{\phi(G_2, ix)}{\phi(G_1, ix)} dx \\ &= -\frac{1}{\pi}\int_{-\infty}^{\infty}\log\frac{\phi(G_2, ix)}{\phi(G_1, ix)} dx \\ &= \frac{1}{\pi}\int_{-\infty}^{\infty}\log\frac{\phi(G_1, ix)}{\phi(G_2, ix)} dx. \end{aligned}$$

To complete our proof, we need to show that

$$\frac{1}{\pi}\lim_{r\to\infty}\left[x\log\frac{\phi(G_2, ix)}{\phi(G_1, ix)} \right]_{-r}^{r} = 0.$$

This is equivalent to showing that

$$\lim_{|ix|\to\infty}\left[x\log\frac{\phi(G_2, ix)}{\phi(G_1, ix)} \right] = 0. \tag{3.3.1}$$

Observe that the characteristic polynomial of any simple graph of n vertices is monic. So the leading terms of $\phi(G_1, ix)$ and $\phi(G_2, ix)$ are identical which means their ratio tends to 1 as $|ix|$ increases without bound. So $\log\frac{\phi(G_2,ix)}{\phi(G_1,ix)} \to 0$ as $|ix| \to \infty$. Because we also have a

factor of x involved in our limit, we apply L'Hospital's Rule to verify (3.3.1). Indeed,

$$\begin{aligned}\lim_{|ix|\to\infty}\left[x\log\frac{\phi(G_2,ix)}{\phi(G_1,ix)}\right] &= \frac{\lim_{|ix|\to\infty}\frac{d}{dx}\log\frac{\phi(G_2,ix)}{\phi(G_1,ix)}}{\lim_{|ix|\to\infty}\frac{d}{dx}\left(\frac{1}{x}\right)} \\ &= \lim_{|ix|\to\infty}\left[\frac{\frac{\phi'(G_2,ix)\phi(G_1,ix)-\phi(G_2,ix)\phi'(G_1,ix)}{\phi(G_2,ix)\phi(G_1,ix)}}{\frac{-1}{x^2}}\right] \\ &= \lim_{|ix|\to\infty}(-x^2)\frac{\phi'(G_2,ix)\phi(G_1,ix)-\phi(G_2,ix)\phi'(G_1,ix)}{\phi(G_2,ix)\phi(G_1,ix)}.\end{aligned}$$

By theorem 3(ii),

$$\phi(G_2,ix) = (ix)^n - m_2(ix)^{n-2} + \ldots + \det(\mathbf{A}(G_2))$$

$$\phi(G_1,ix) = (ix)^n - m_1(ix)^{n-2} + \ldots + \det(\mathbf{A}(G_1)),$$

where m_2 and m_1 represent the number of edges in the graphs G_2 and G_1, respectively. Also,

$$\phi'(G_2,ix) = ni(ix)^{n-1} - im_2(n-2)(ix)^{n-3} + \text{remaining terms},$$

and

$$\phi'(G_1,ix) = ni(ix)^{n-1} - im_1(n-2)(ix)^{n-3} + \text{remaining terms}.$$

Now, the leading terms of $\phi'(G_2,ix)\phi(G_1,ix)$ and $\phi'(G_1,ix)\phi(G_2,ix)$ are identical and so they cancel out in the subtraction that takes place in the numerator of the limit in expression. The next highest order term is the product of $(ix)^n and \frac{d}{dx}m_{1,2}(ix)^{n-2}$ multiplied by $(-x^2)$ which makes the numerator of the limit of order $(ix)^{2n-1}$. The denominator is the product of $\phi(G_1,ix)\phi(G_2,ix)$ which is of order $(ix)^{2n}$. Hence, the expression in (3.11) is of order $\frac{1}{ix}$ and tends to zero as $|ix|$ increases without bound. This proves the corollary. □

Corollary 3 ([7]). *If G is a graph on n vertices, then*

$$E(G) = \frac{1}{\pi}\int_{-\infty}^{\infty}\frac{dx}{x^2}\log|x^n\phi(G,i/x)|.$$

Recall that all integrals of the form $\int_{-\infty}^{\infty} F(x)dx$, $\int_{-\infty}^{0} F(x)dx$, and $\int_{0}^{\infty} F(x)dx$ stand for the principal value of each integral.

Proof: By Theorem 4,

$$\begin{aligned} E(G) &= \frac{1}{\pi}\int_{-\infty}^{\infty}\left[n - iy\frac{\phi'(G,iy)}{\phi(G,iy)}\right]dy \\ &= \frac{1}{\pi}\int_{-\infty}^{0}\left[n - iy\frac{\phi'(G,iy)}{\phi(G,iy)}\right]dy + \frac{1}{\pi}\int_{0}^{\infty}\left[n - iy\frac{\phi'(G,iy)}{\phi(G,iy)}\right]dy. \end{aligned}$$

Using the change of variables $y = \frac{1}{x}$, we have

$$\begin{aligned} E(G) &= \frac{1}{\pi}\int_{0}^{-\infty}\left[n - (i/x)\frac{\phi'(G,i/x)}{\phi(G,i/x)}\right]\left(\frac{-1}{x^2}\right)dx + \frac{1}{\pi}\int_{\infty}^{0}\left[n - (i/x)\frac{\phi'(G,i/x)}{\phi(G,i/x)}\right]\left(\frac{-1}{x^2}\right)dx \\ &= \frac{1}{\pi}\int_{-\infty}^{\infty}\left[n - (i/x)\frac{\phi'(G,i/x)}{\phi(G,i/x)}\right]\left(\frac{1}{x^2}\right)dx \end{aligned}$$

Let $u = \frac{1}{x}$ and $dv = \left[\frac{n}{x} - \frac{i/x^2\phi'(G,i/x)}{\phi(G,i/x)}\right]dx$ so that
$du = -\frac{dx}{x^2}$ and $v = n\log|x| + \log|\phi(G,i/x)| = \log|x^n\phi(G,i/x)|$. Integrating by parts gives

$$\begin{aligned} E(G) &= \frac{1}{\pi}\lim_{r\to\infty}\left(\frac{1}{x}\log|x^n\phi(G,i/x)|\right)_{-r}^{r} + \frac{1}{\pi}\int_{-\infty}^{\infty}\frac{dx}{x^2}\log|x^n\phi(G,i/x)| \\ &= \frac{1}{\pi}\int_{-\infty}^{\infty}\frac{dx}{x^2}\log|x^n\phi(G,i/x)| \end{aligned}$$

because

$$\lim_{x\to\infty}\frac{\log|x^n\phi(G,i/x)|}{x} = 0$$

by applying L'Hospital's rule. This proves the corollary. □

We now turn our attention to two established characteristic polynomials of a graph on n vertices. Let F be a forest (or a tree if F is connected) with n vertices, and characteristic polynomial [21]

$$\phi(F,x) = \sum_{k=0}^{\lfloor\frac{n}{2}\rfloor}(-1)^k m(F,k)x^{n-2k}, \tag{3.3.2}$$

where m(F,k) is the number of k-matchings in F. On the other hand, if B is bipartite then its characteristic polynomial is [7], [21]

$$\phi(B,x) = \sum_{k=0}^{\lfloor \frac{n}{2} \rfloor} \sigma_{2k} x^{n-2k} = \sum_{k=0}^{\lfloor \frac{n}{2} \rfloor} (-1)^k b(B,k) x^{n-2k}, \tag{3.3.3}$$

where $\sigma_{2k} = (-1)^k b(B,k)$ and $b(B,k) \geq 0$ for all $k = 1, 2, ...\lfloor \frac{n}{2} \rfloor$. Moreover, when $k = 0$, $\sigma_0 = b(B,0) = 1$. If n_+ represents the number of positive eigenvalues then n_+ is also the number of negative eigenvalues and $b(B,k) = 0$ whenever $k > n_+$ [7]. Our next corollary, which we will state without proof, follows from equations (3.3.2), (3.3.3) and Corollary 2.

Corollary 4 ([7])**.** *If F and B are a forest and a bipartite graph, respectively on n vertices, then*

$$E(F) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{dx}{x^2} \log \left[1 + \sum_{k=1}^{\lfloor \frac{n}{2} \rfloor} m(F,k) x^{2k} \right]$$

$$E(B) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{dx}{x^2} \log \left[1 + \sum_{k=1}^{\lfloor \frac{n}{2} \rfloor} b(B,k) x^{2k} \right].$$

Corollary 3 establishes that the energy of a forest and that the energy of a bipartite graph are monotonically increasing functions of their respective coefficients of x^{2k}. [7]. The next corollary, also stated without proof, provides us with a criteria for ordering the energies of forests and the energies of bipartite graphs.

Corollary 5 ([7])**.** *The energy of two bipartite graphs and the energy of two forests are ordered in the following manner:*

(a) *If for two bipartite graphs B_1 and B_2 (not necessarily with equal number of vertices), the relation*

$$b(B_1,k) \leq b(B_2,k) \tag{3.3.4}$$

is satisfied for all $k \geq 1$, then $E(B_1) \leq E(B_2)$. If, in addition, $b(B_1, k) < b(B_2, k)$ for at least one value of k, then $E(B_1) < E(B_2)$.

(b) *If for two forests F_1 and F_2 (not necessarily with equal number of vertices), the relation*

$$m(F_1, k) \leq m(F_2, k) \tag{3.3.5}$$

is satisfied for all $k \geq 1$, then $E(F_1) \leq E(F_2)$. If, in addition, $m(F_1, k) < m(F_2, k)$ for at least one value of k, then $E(F_1) < E(F_2)$.

Relations (3.3.4) and (3.3.5) were proved by [19] and [20] for numerous pairs of graphs implying the inequalities between their energies.

Denote $\overline{K_n}$, S_n and P_n to represent the graph without edges, the star graph and the path graph, respectively, each having n vertices. Then, if F_n is a forest on n vertices different from $\overline{K_n}$ and P_n we have

$$E(\overline{K_n}) < E(F_n) < E(P_n)$$

according to [7]. Also, if T_n is a tree on n vertices differing from both S_n and P_n we also have

$$E(S_n) < E(T_n) < E(P_n)$$

by [7] as well.

The consequences of Coulson's integral formulae of Theorem 4 not only allows us to compute the energy without computing each individual eigenvalue but also we can order the energies of all members of any set of bipartite graphs as well as the energy of every element of any set of forests because of their respective characteristic polynomials. Furthermore, for the

aforementioned graphs on n vertices, we have a way to compare them with different trees or different forests also having n vertices.

One can use Theorem 6 and its corollaries to give upper and lower bounds for the energy of specific graphs. For applications such bounds may be useful to provide insight into why different molecules behave differently. The next chapter gives us some useful inequalities for E(G).

CHAPTER FOUR: BOUNDS FOR THE ENERGY OF A GRAPH

4.1 MCCLELLAND INEQUALITIES

In this chapter we mention about the bounds for energy of a graph. Of several known results we chose the work of MCClelland[16].

Theorem 6 (McClelland, 1971 [16]). *If G is a graph with n vertices, m edges and adjacency matrix $\boldsymbol{A}(G)$, then*

$$\sqrt{2m + n(n-1)|\det \boldsymbol{A}(G)|^{2/n}} \leq E(G) \leq \sqrt{2mn}. \tag{4.1.1}$$

In the following proof, we will use the notation from[7] for the geometric mean of the product of all index-distinct eigenvalue pairs

$$GM\{|\lambda_j||\lambda_k|\} = \left(\prod_{1 \leq j < k \leq n} |\lambda_j||\lambda_k| \right)^{2/(n^2-n)}. \tag{4.1.2}$$

Similarly, the notation from [7] for the arithmetic mean of the product of all index-distinct eigenvalue pairs is given by

$$AM\{|\lambda_j||\lambda_k|\} = \frac{\sum_{1 \leq j < k \leq n} |\lambda_j||\lambda_k|}{(n^2-n)/2} \tag{4.1.3}$$

Proof [7]: We begin by proving the lower bound relation. Since G is a graph on n vertices, it has n (not necessarily distinct), eigenvalues: $\lambda_1, \lambda_2, \ldots, \lambda_n$. We have by Theorem 3 (iii)

$$\sum_{i=1}^{n} \lambda_i^2 = 2m. \tag{4.1.4}$$

Indeed,

$$\begin{aligned} E^2(G) &= \left(\sum_{i=1}^{n} |\lambda_i|\right)^2 \\ &= \sum_{i=1}^{n} |\lambda_i|^2 + 2 \sum_{1\le j<k\le n} |\lambda_j||\lambda_k| \\ &= 2m + n(n-1)AM\{|\lambda_j||\lambda_k|\} \text{by equation 4.3.} \end{aligned}$$

Since $GM\{|\lambda_j||\lambda_k|\} \le AM\{|\lambda_j||\lambda_k|\}$, $2m + n(n-1)GM\{|\lambda_j||\lambda_k|\} \le E^2(G)$ follows.

Observe that

$$\begin{aligned} GM\{|\lambda_j||\lambda_k|\} &= \left(\prod_{1\le j<k\le n} |\lambda_j||\lambda_k|\right)^{2/(n(n-1))} \\ &= \left(\prod_{i=1}^{n} |\lambda_i|^{(n-1)}\right)^{2/(n(n-1))} \\ &= \left(\prod_{i=1}^{n} |\lambda_i|\right)^{2/n} \\ &= |\det\mathbf{A}(G)|^{2/n}. \end{aligned}$$

because $\prod_{i=1}^{n} |\lambda_i| = |\det\mathbf{A}(G)|$.

Therefore,

$$\sqrt{2m + n(n-1)|\det\mathbf{A}(G)|^{2/n}} \le E(G).$$

This completes the argument for the lower bound of the energy of G. Finally, we turn our attention to establishing the upper bound of E(G). To this end, we observe that the variance of the eigenvalues of G is a nonnegative quantity denoted by $VAR\{|\lambda_i|\}$ for $i = 1, 2, \ldots, n$, and its relationship with $AM\{|\lambda_i|\}$ is given by the equation

$$\begin{aligned} VAR\{|\lambda_i|\} &= AM\{|\lambda_i|^2\} - (AM\{|\lambda_i|\})^2 \\ &= \frac{1}{n}\sum_{i=1}^{n} |\lambda_i|^2 - \left(\frac{1}{n}\sum_{i=1}^{n} |\lambda_i|\right)^2 \\ &= \frac{2m}{n} - \frac{E^2(G)}{n^2} \end{aligned}$$

Therefore,

$$\frac{2m}{n} - \frac{E^2(G)}{n^2} \geq 0 \tag{4.1.5}$$

which establishes our upper bound. □

From this theorem, we have the following corollary.

Corollary 6 ([7]). *If* $\det \boldsymbol{A}(G) \neq 0$*, then* $E(G) \geq \sqrt{2m + n(n-1)} \geq n$.

Proof: Since we have $\det\mathbf{A}(G) \neq 0$, the simple graph G has no zero eigenvalues. From that it follows that G has at least one edge and at least two vertices. That is, $m \geq \frac{n}{2}$. Now, from the proof of Theorem 5, we also have

$$|\det\mathbf{A}(G)|^{2/n} = \left(\prod_{1 \leq j < k \leq n} |\lambda_j||\lambda_k| \right)^{2/(n^2-n)} = |-m|^{2/(n^2-n)}.$$

So $|-m|^{2/n^2-n} \geq 1$ means that $|\det\mathbf{A}(G)|^{2/n} \geq 1$. Hence, by Theorem 5, we have

$$\sqrt{2m + n(n-1)} \leq \sqrt{2m + n(n-1)|\det\mathbf{A}(G)|^{2/n}} \leq E(G).$$

This proves

$$E(G) \geq \sqrt{2m + n(n-1)}.$$

Finally, we want to prove that $\sqrt{2m + n(n-1)} \geq n$. Since $m \geq \frac{n}{2}$, we have $\sqrt{2m + n(n-1)} \geq \sqrt{2\left(\frac{n}{2}\right) + n(n-1)} = \sqrt{n + n(n-1)} = n$. This completes our proof of the corollary. □

Corollary 7 ([7]). *If* G *is a graph containing* m *edges, then*

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

Proof [7]: Applying the definition of $E(G)$ and the triangle inequality, we have

$$
\begin{aligned}
E^2(G) &= \left(\sum_{i=1}^{n} |\lambda_i|\right)^2 \\
&= \sum_{i=1}^{n} |\lambda_i|^2 + 2 \sum_{1\le i<j\le n} |\lambda_i||\lambda_j| \\
&\geq 2m + 2\left|\sum_{1\le i<j\le n} \lambda_i\lambda_j\right| \\
&= 2m + 2|-m| \\
&= 4m.
\end{aligned}
$$

So $E^2(G) \geq 4m$ implies $2\sqrt{m} \leq E(G)$.

If G has isolated vertices then each isolated vertex yields an eigenvalue equal to zero and each isolated vertex does not contribute to the number of edges because G has no loops. So isolated vertices contribute neither to the energy of G nor the number of edges in G. If G consists of m isolated edges and no isolated vertices then the number of vertices, n is equal to $2m$. Otherwise, the number of vertices is less than $2m$. Therefore, if $n \leq 2m$ then $\sqrt{2mn} \leq \sqrt{(2m)^2} = 2m$. By Theorem 6, we have $E(G) \leq 2m$. This proves the upper bound and the corollary is proved. □

CHAPTER FIVE: GUTMAN'S CONJECTURE

5.1 Disproving Gutman's Conjecture By Counterexample

Various empirical and statistical studies, performed on graphs of chemical interest, point towards a simple regularity: The energy of a graph is directly proportional to the number of edges and vertices. McClelland's inequality confirms this. These chemical graphs of interest were connected, but possessed a minimal number of edges. Therefore, the energies of these graphs were less than the energy of a complete graph with the same number of vertices. Gutman conjectured that the energy of the complete graph was maximal for all simple graphs having the same number of vertices. Although a very reasonable conjecture, Chris Godsil was the first to disprove this conjecture in 1981.

Using Maple 13, we will also disprove Gutman's conjecture by finding a simple graph whose energy exceeds the energy of a complete graph with the same number of vertices. The Petersen graph, a graph on ten vertices has been a standard counterexample used to disprove many conjectures and so we will see if this conjecture holds up to the Petersen graph. Since the Petersen graph is a simple graph on ten vertices and fifteen edges, we will compare its energy to the energy of the complete graph on ten vertices and 45 edges. Recall that K_{10} denotes the complete graph. Here is the adjacency matrix for K_{10}.

$$\mathbf{A}(K_{10}) = \begin{bmatrix} 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 0 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 0 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 & 0 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 & 1 & 0 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & 0 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 0 & 1 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 0 \end{bmatrix}$$

With the help of Maple 13, we have its characteristic polynomial

$$\phi(K_{10}, \lambda) = \lambda^{10} - 45\lambda^8 - 240\lambda^7 - 630\lambda^6 - 1008\lambda^5 - 1050\lambda^4 - 720\lambda^3 - 315\lambda^2 - 80\lambda - 9$$

and the eigenvalues to the equation $\phi(K_{10}, \lambda) = 0$ are $\lambda = 9$ and $\lambda = -1$ (multiplicity of 9). Therefore, $E(K_{10}) = |9| + 9| - 1| = 18$. We must find a graph whose energy exceeds $E(K_{10})$.

Consider the Petersen graph. The adjacency matrix is

$$\mathbf{A}(Petersen) = \begin{bmatrix} 0 & 1 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 1 & 0 \end{bmatrix}$$

and characteristic polynomial

$$\phi(Petersen, \lambda) = \lambda^{10} - 15\lambda^8 + 75\lambda^6 - 24\lambda^5 - 165\lambda^4 + 120\lambda^3 + 120\lambda^2 - 160\lambda + 48.$$

The eigenvalues of the Petersen graph are: $\lambda = 3$, $\lambda = -2$ (multiplicity of 4), and $\lambda = 1$ (multiplicity of 5). $E(Petersen) = |3| + 4| - 2| + 5|1| = 16$ shows that Gutman's conjecture holds up to the Petersen graph. We will now turn our attention to complement of the Petersen graph, $\overline{Petersen}$.

Starting with the adjacency matrix of the graph $\overline{Petersen}$,

$$\mathbf{A}(\overline{Petersen}) = \begin{bmatrix} 0 & 0 & 1 & 1 & 0 & 0 & 1 & 1 & 1 & 1 \\ 0 & 0 & 0 & 1 & 1 & 1 & 1 & 1 & 0 & 1 \\ 1 & 0 & 0 & 0 & 1 & 1 & 0 & 1 & 1 & 1 \\ 1 & 1 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 & 0 & 1 & 1 & 0 & 1 & 1 \\ 0 & 1 & 1 & 1 & 1 & 0 & 0 & 1 & 1 & 0 \\ 1 & 1 & 0 & 1 & 1 & 0 & 0 & 0 & 1 & 1 \\ 1 & 1 & 1 & 1 & 0 & 1 & 0 & 0 & 0 & 1 \\ 1 & 0 & 1 & 1 & 1 & 1 & 1 & 0 & 0 & 0 \\ 1 & 1 & 1 & 0 & 1 & 0 & 1 & 1 & 0 & 0 \end{bmatrix}$$

and characteristic polynomial,

$$\phi(\overline{Petersen}, \lambda) = \lambda^{10} - 30\lambda^8 - 60\lambda^7 + 105\lambda^6 + 276\lambda^5 - 180\lambda^4 - 480\lambda^3 + 240\lambda^2 + 320\lambda - 192$$

we solve $\phi(\overline{Petersen}, \lambda) = 0$ to get $\lambda = 6$, $\lambda = 1$ (multiplicity 4), and $\lambda = -2$ (multiplicity 5). Therefore, $E(\overline{Petersen}) = 20$. From this energv calculation, we conclude that the graph $\overline{Petersen}$ is our desired counterexample.

Can we generalize this result? Yes. We first observe that both the Petersen graph and the complement of the Petersen graph are connected (or primitive) strongly regular graphs with parameters n, d, μ, and ν denoting the number of vertices, the degree of each vertex, the number of neighbors between all pairs of adjacent vertices, and the neighbors between all pairs of non-adjacent vertices, respectively. For example, the Petersen graph is srg(10,3,0,1) and the complement of the Petersen graph is srg(10,6,3,4), which can easily be verified from their respective adjacency matrices. When a graph on n vertices exceed the energy of the complete graph on n vertices, we call such graphs hyperenergetic. In 2011, [25] proved that only four primitive strongly regular graphs are not hyperenergetic: srg(10, 3, 0, 1),

srg(9,4,1,2), srg(5,2,0,1) and srg(16,5,0,2). Since srg(10,6,3,4) is not among the four graphs listed, the complement of the Petersen graph is one of many counter examples to Gutman's conjecture.

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