

Procedures for Obtaining Graph-Theoretical Resonance Energies

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A graph-theoretical method for obtaining a characteristic polynomial of a secular matrix is reformulated, and a definition of graph-theoretical resonance energy is reviewed. Several procedures for simplifying the obtaining of these resonance energies are outlined.

Hückel molecular orbital theory has been reexamined and redefined in terms of graph theory.¹ This reexamination has confirmed the essential topological and structural basis of HMO theory, but has not provided much in the way of new ideas that can be tested experimentally or theoretically. One exception is the concept of "isospectral molecular graphs", i.e., nonisomorphic molecular graphs whose HMO Hamiltonian matrices give identical eigenvalues.²⁻¹⁰ This topic has been discussed extensively in connection with the problem of coding or storing molecular structures using information obtained from the characteristic polynomial of the adjacency matrix of the molecular graph.²⁻⁶ Experimental examinations of molecular systems of this type have also been carried out.^{11,12a}

A second very useful result is a graph-theoretical definition of resonance energy for unsaturated π systems obtained as follows.¹³⁻¹⁶ The coefficients of HMO secular polynomials can be written using graph theory,^{16,18-20} since each coefficient is a prescribed function of the number of bonds and cyclic components of the molecular graph. The polynomial for the resonance free reference system is obtained by deleting the cyclic component contributions to the coefficients. This polynomial refers to a hypothetical structure in which all structural details of the original system are present except for cyclic substructures. Solutions of HMO secular polynomials give the π energy levels, so the resonance energy can then be defined as the difference between the total energy of the original molecular π system and that of the hypothetical acyclic reference structure. The justifications for this abstract definition lie in the numerous, precise parallels of the calculated resonance energies^{14-16,20-22} with those found by other methods.

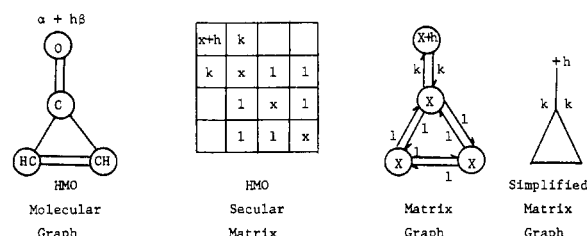
Obtaining the characteristic polynomials for parent and reference systems has previously been judged the crucial step in evaluating graph theoretical resonance energies.¹³⁻²⁰ We disagree, and believe that the main objective is to obtain the roots of the polynomials, which then correspond to energy levels. In the course of our studies on graph theory applied to organic chemistry,^{6-8,12,22-27} we have developed some systematic procedures that facilitate this process. Methods that incorporate the decomposition or factorization of graphs are particularly useful. We have also discovered that for many types of cyclic systems one can draw acyclic molecular graphs that have characteristic polynomials identical with those of the hypothetical reference structures. This allows one to use the standard available MO computer programs to obtain a reference system energy, by-passing the more difficult²¹ construction of the acyclic reference polynomial. This paper gives examples of these procedures.

GENERAL RULES FOR CONSTRUCTING CHARACTERISTIC POLYNOMIALS

This section restates the well-known procedure¹⁸⁻²⁰ for constructing characteristic polynomials from the topological properties of molecular graphs. The mathematical equivalencies of graphs, secular matrices, and characteristic polynomials are emphasized in this new approach. The polynomial itself is visualized as a set of graphs that can be derived from

the original molecular graph. One advantage of this approach is that heteroatom Coulomb and exchange parameters can be introduced directly into the molecular graphs, and subsequently into the polynomial graphs, to finally yield the desired polynomials. The following description is pictorial, but more rigorous algebraic justifications can be given and are available from the authors.^{12b}

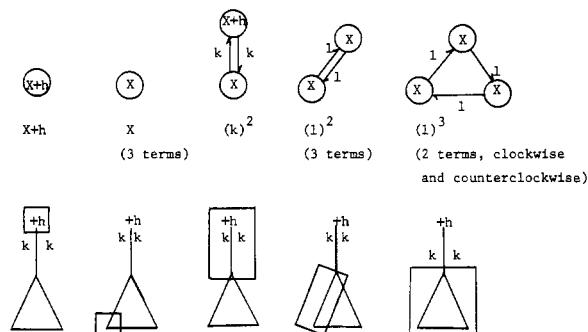
Within the HMO formalism,²³ a molecular graph will be composed of vertices represented as circles (p orbitals) and lines (π bonds). The secular matrix in **1** for cyclopropenone



1

incorporates the usual HMO definitions; $x = (\alpha - E)/\beta$, $\alpha(O) = \alpha(C) + h\beta$, $\beta(CO) = k\beta(CC)$. The matrix graph is a weighted directed graph with a one-to-one correspondence of the weighting terms to element entries of the secular matrix. Vertices are labeled with diagonal elements, and the directed lines are weighted with the off-diagonal terms. The simplified matrix graph incorporates only the weighting parameters for heteroatoms with the remaining line and vertex weights assumed to be understood.

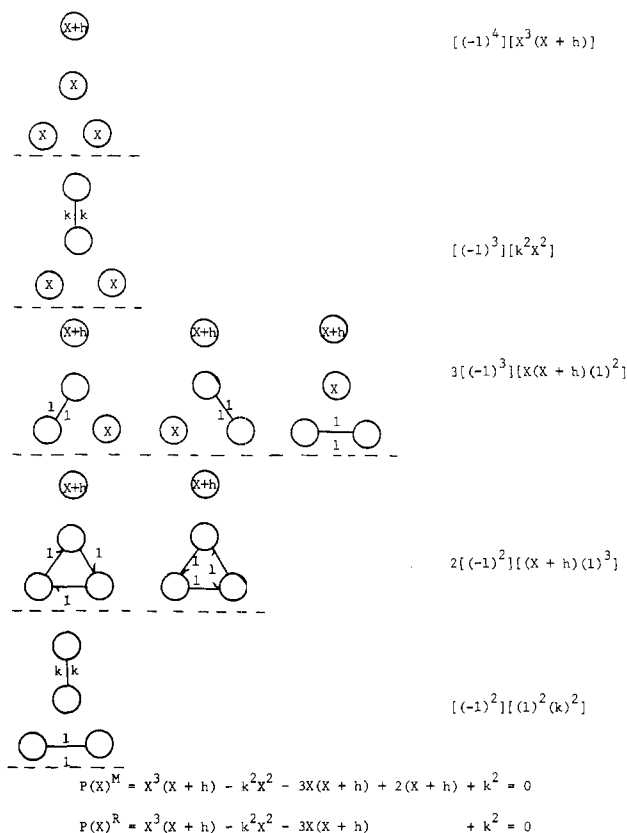
To show the further correspondence to a characteristic polynomial, the concept of an allowable subgraph of the matrix graph must now be defined. An allowable subgraph is a single vertex, two vertices and connecting lines, or a cycle of vertices and connecting lines as shown in **2**.³⁰ Each subgraph has an



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associated algebraic term. The entry in the appropriate diagonal element of the secular matrix is the term characterizing an allowed subgraph consisting of a single vertex. The term corresponding to an allowed subgraph with lines is simply the product of the line weights. These terms can be read easily from the simplified matrix graph as shown in the bottom row of **2**. The proper power for each parameter is indicated.

A vertex covering of the matrix graph is a collection of subgraphs that includes every vertex exactly once. We define an algebraic function for a vertex covering which is the product of the constituent subgraphs algebraic terms. The characteristic polynomial is just the sum of all functions corresponding to vertex coverings using only allowed subgraphs. Each vertex covering function also has a parity, $(-1)^a$, where a is the number of allowed subgraphs in the vertex covering. Vertex coverings, associated algebraic terms, and parities for cyclopropenone are listed in 3.

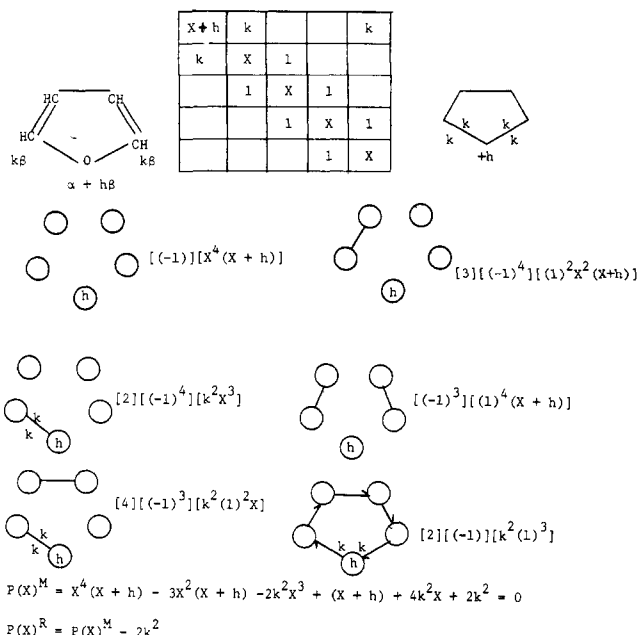


3

The polynomial for the resonance-free reference system $P(x)^R$ is defined to be the molecular system polynomial $P(x)^M$ with cyclic components deleted. The method for obtaining this reference polynomial is obvious from the example given in 3. Previous graph-theoretical descriptions of heteroatom systems have used a formulation which does not allow the reference polynomial to be easily obtained.^{16,20,31-34} It should also be noted that the present reformulation is not limited to the Hückel formalism for MO calculations. The characteristic polynomials for any Hamiltonian matrix using any basis functions can be obtained using this approach, and corresponding resonance energy characteristics can be defined. Applications of this idea are under investigation.

An additional example may help to clarify the procedures, so characteristic and reference polynomials for heterocyclic molecules of the furan type are derived in 4. One helpful hint to use in writing the terms of the characteristic polynomial is to realize that every term is a product of line weights and vertex functions, the total degree of each term being the degree of the polynomial. For this system the degree of the polynomial is 5, and five factors are therefore included in each term. Note also that the sign of every term has been changed in $P(X)^M$ and $P(X)^R$.

Comparison of the derived characteristic polynomials with a previous derivation²⁰ shows some differences in relative signs of the polynomial terms. This is because the method described



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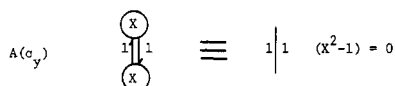
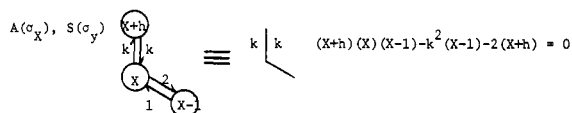
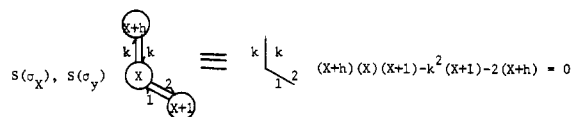
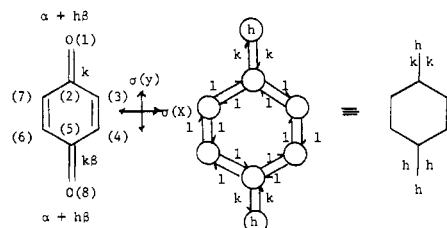
here gives the values $X = (\alpha - E)/\beta$ in the usual HMO theory form, negative X referring to a bonding energy level. All previous descriptions of graphical methods for obtaining characteristic polynomials have signs of X reversed from the usual definition. If not carefully noted, this fact can lead to some confusion in the treatment of nonalternant and heterocyclic systems.

FACTORED SECULAR EQUATIONS FROM SYMMETRY-REDUCED GRAPHS

The Hamiltonian matrix for a molecule with symmetry can be reduced to a unitary representation by a similarity transformation.³⁵ This means that one can block-diagonalize the matrix using group theory. The secular polynomial is then a product of several equations of smaller degree; i.e., the secular equation has been factored. A procedure that involves addition and subtraction of rows and columns corresponding to symmetry-related orbitals also leads to a block-diagonalized matrix, and subsequently to factored secular equations.^{36,37} Heilbronner,³⁶ McClelland,³⁸ and King³⁷ have shown that these applications of group theory can be translated directly into corresponding operations on the graph itself.

In general, the symmetry-reduced graphs are linear graphs, and the general rules for writing the corresponding characteristic polynomials are particularly easy to apply. The method is best illustrated with examples. In those given below, the elements of symmetry used to carry out the graph factorization are planes (σ_x and σ_y) perpendicular to the molecular plane. The use of other types of symmetry elements has been described by King.³⁷ Factored graphs and resulting factors of characteristic polynomials will be classified as symmetric S or antisymmetric A with respect to symmetry planes. This classification leads to a correct assignment of the characters of the irreducible representation of molecular orbitals that correspond to each obtained energy level. Benzoquinone equations and graphs are given in 5.

The symmetry reduced graphs symmetric to σ_y have only three vertices because of the symmetry equivalence of the carbon and oxygen atoms. In the factored graphs the weight of the line from vertex 2 to vertex 3 is doubled because vertex 2 is joined to both vertex 3 and its equivalent vertex 7. When a vertex is joined to a symmetrically equivalent vertex, the value of the vertex in the factored graph is $(X+1)$. A vertex connected to antisymmetrically equivalent vertex is represented

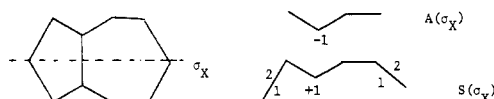


$$P(X)^M = [(X+h)(X)(X+1)-k^2(X+1)-2(X+h)][(X+h)(X)(X-1)-k^2(X-1)-2(X+h)][X^2-1] = 0$$

5

in the factored graph by the value $(X-1)$. The factored graph antisymmetric to the σ_y plane is a two-vertex graph identical with that of the ethylene molecular π system graph. It is not factored further since corresponding solutions are given directly by solving the quadratic equation, $X^2 - 1 = 0$. The resulting molecular secular polynomial is the product of the three factored polynomials. They are left in a form which is convenient for solving by the graphical bisection method.³⁹

The molecular graph of azulene is given in 6. The π system



$$P(A) = X^3(X-1)-2X^2 - X(X-1) + 1 = 0$$

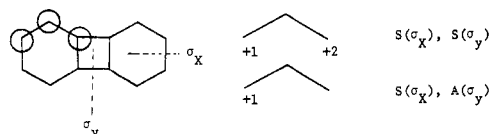
$$P(B) = X^5(X+1)-2X^4 - 5X^3(X+1) + 7X^2 + 6X(X+1) - 4 = 0$$

$$P(X)^M = [P(A)][P(B)]$$

6

has a single pertinent plane of symmetry and polynomials of the 4th and 6th degree are quickly obtainable. No further graphical reduction is possible, and the usefulness of the present method lies only in the rapid obtaining of the secular polynomial.

A final example that can be compared with a previous graph theoretical result¹⁸ demonstrates the great advantage of using factored graphs in alternant systems. In the molecular graph of biphenylene shown in 7 two planes of symmetry are shown



$$P(S(\sigma_y)) = (X+1)(X)(X+2) - (X+2) - (X+1) = 0$$

$$P(A(\sigma_y)) = (X+1)X^2 - X - (X+1) = 0$$

7

and nonredundant carbon atoms are circled. Only the factored graphs and polynomials corresponding to the $S(\sigma_x)$ roots are

shown. For alternant systems the roots occur in negative and positive conjugate pairs so only these two cubic equations have to be solved to provide all of the energy levels for the biphenylene π system. Comparing the present approach with that used previously to graphically obtain the 12th degree characteristic polynomial,¹⁸ one finds a saving of time and labor.

REFERENCE POLYNOMIAL SOLUTIONS AND REFERENCE GRAPHS

One method for obtaining the reference polynomial has already been illustrated, and consists of eliminating terms in the parent system polynomial that are derived from cyclic components of the molecular graph. We find it is more efficient to use one of the following procedures to find the reference energies.

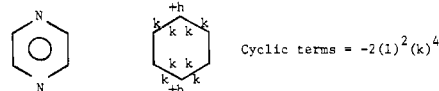
Computer programs to solve HMO secular matrices are readily available. After obtaining the eigenvalues, the characteristic polynomial can take the form

$$P(X)^M = \prod_{j=1}^n (X - X_j^M) = 0 \quad (1)$$

where the X_j^M are the numerical values of the solutions. The reference polynomial has cyclic contributions deleted and can therefore be written as

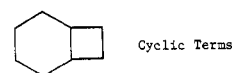
$$P(X)^R = \prod_{j=1}^n (X - X_j^M) - (\text{cyclic components}) = 0 \quad (2)$$

It is easier to enumerate only the cyclic algebraic terms that correspond to allowed vertex covering subgraphs than it is to count all of the terms that contribute to the characteristic polynomials. Then the reference polynomial can be written according to eq 2 and solved to yield the reference energy values. A pyrazine-type system and benzocyclobutadiene π system are given in 8 and 9 as examples.

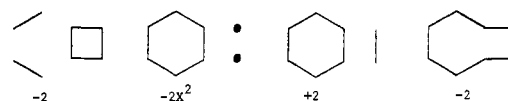
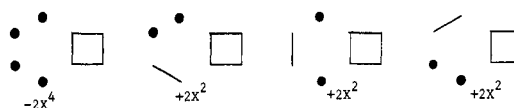


$$P(X)^R = P(X)^M + 2k^4$$

8



Cyclic Terms



$$P(X)^R = P(X)^M + 2X^4 - 4X^2 + 2$$

9

A reference polynomial can also be written in terms of linear graph polynomials¹⁶ using recurrence formulas that have been described by Heilbronner.⁴⁰ Denoting the characteristic polynomials of monocyclic and linear graphs with n vertices as C_n and L_n , respectively, these recurrence relationships are

$$L_n = XL_{n-1} - L_{n-2} \quad (3)$$

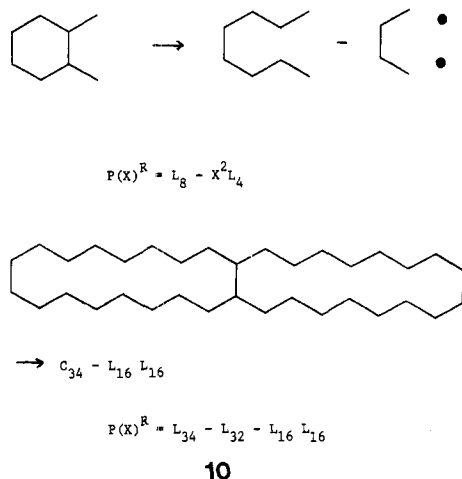
$$L_n = L_{n/2}L_{n/2} - L_{(n/2)-1}L_{(n/2)-1} \quad (4)$$

$$C_n = L_n - L_{n-2} - 2 \quad (5)$$

The last term in eq 5 is the cyclic component of the characteristic polynomial for the cyclic system so the reference polynomial is then given as

$$C_n^R = L_n - L_{n-2} \quad (6)$$

The procedure for calculation of a reference polynomial using these formulas is illustrated in **10** with the molecular graphs



of *o*-xylene and [18]annuleno[18]annulene.

The resulting complex polynomials only involve linear graph polynomials. The terms of the linear graph equations have been tabulated⁴⁰ or can be generated from a table of binomial coefficients. Our computer program to solve equations of this type requires only the number of terms and their size (*n*) to generate the reference polynomial and its solutions. The process is quite fast, and the energy for [18]annuleno[18]annulene can be obtained in ca. 3 s CPU time (IBM 360-50 system). A previous computation of the graph theoretical resonance energy of the same molecule was not completed after 30 min of CPU time (DEC 1099 system).²¹

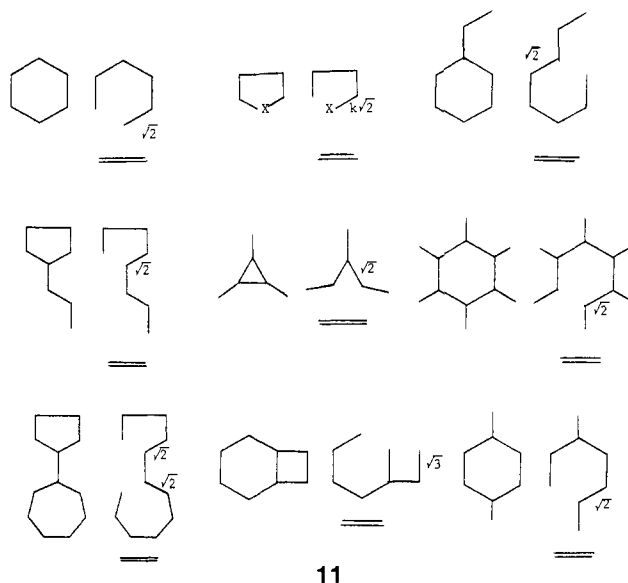
The final method for finding reference structure energies that will be described involves obtaining a molecular graph which has a characteristic polynomial identical with that of the hypothetical reference structure. That is, the secular matrix corresponding to the reference graph has the same eigenvalues as the roots of the graph-theoretically defined reference polynomial. One can then simply set up the required secular matrices for parent and reference system, and use MO computer programs to obtain eigenvalues and the consequent resonance energies.^{22,27,28}

There are several general types of π systems for which reference graphs can be drawn. Included are monocycles, monocycles with single side chains, cross-conjugated bicyclic systems, radialenes, and annelated cyclobutadienoid systems. Specific examples of each type are given in **11** with the reference graph underlined in each pair. The reference graphs for homologues and heteroatom derivatives can be constructed by making the obvious extensions and substitutions.

Expansions of the determinants of the secular matrices, or graph-theoretical calculations of the characteristic polynomials, verify that these open-chain reference graphs with heterobond parameters ($k = \sqrt{2}$ or $\sqrt{3}$) do have the correct required eigenvalues. Each one of these reference structures was obtained by trial and error, and the extension to the general case for each type of system was shown to hold by mathematical induction.

DISCUSSION

Use of the methods outlined in the previous sections will facilitate the obtaining of graph-theoretical resonance energies.



The reference graph approach is highly advantageous in this regard, but no simple ways to construct reference graphs for the completely general case have been discovered. In general, the reduction process using the Heilbronner⁴⁰ equations leads to the greatest economy of effort.

As mentioned before, graph theoretical resonance energies are in excellent agreement with nearly all recent estimates based variously on SCF-LCAO-MO calculations,^{14,42} valence-bond theory,^{43,44} or modified Hückel methods.⁴⁵⁻⁴⁷ This agreement coupled with the idea of a reference structure graph points up the very artificial nature of the concept of resonance. Resonance energies that agree with the graph-theoretical values cannot be obtained by taking the difference in HMO delocalization energies of a cyclic system and an arbitrarily chosen isoelectronic open chain analogue. Instead, the molecular graph for the acyclic reference structure must contain particular bonds with unusually high CC bond integral parameters. The π energy of the usual open chain reference structure chosen in earlier work⁴⁸ is an underestimate of the reference energy, and leads to a consequent overestimation of resonance energy for the parent cyclic system.

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REFERENCES AND NOTES

- (1) This reexamination has principally been carried out by the group at the Rugjer Bosković Institute, Zagreb, Yugoslavia. Review articles are: (a) Gutman, I.; Trinajstić, N. "Graph Theory and Molecular Orbitals", *Top. Curr. Chem.* **1973**, *42*, 49-93. (b) Graovac, A.; Gutman, I.; Trinajstić, N. "Topological Approach to the Chemistry of Conjugated Molecules", *Lect. Notes Chem.* **1977**, *4*, 1-123.
- (2) Spialter, L. "The Atom Connectivity Matrix (ACM) and Its Characteristic Polynomial (ACMCP)", *J. Chem. Doc.*, **1964**, *4*, 261-269; "The Atom Connectivity Matrix Characteristic Polynomial (ACMCP) and its Physicochemical (Topological) Significance" *Ibid.* **1964**, *4*, 269-274.
- (3) Spialter, L. "Atom Connectivity Matrix (ACM) and Its Characteristic Polynomial (ACMCP). A New Computer Oriented Chemical Nomenclature" *J. Am. Chem. Soc.* **1963**, *85*, 2012-2013.
- (4) Balaban, A. T.; Harary, F. "The Characteristic Polynomial Does Not Uniquely Determine the Topology of a Molecule" *J. Chem. Doc.* **1971**, *4*, 258-259.
- (5) Kudo, Y.; Yamasaki, T.; Sasaki, S.-I. "The Characteristic Polynomial Uniquely Represents the Topology of a Molecule" *J. Chem. Doc.* **1973**, *13*, 225-227.
- (6) Herndon, W. C. "The Characteristic Polynomial Does Not Uniquely Determine Molecular Topology" *J. Chem. Doc.* **1974**, *14*, 150-151.
- (7) Herndon, W. C. "Isospectral Molecules" *Tetrahedron Lett.* **1974**, 671-674.
- (8) Herndon, W. C.; Ellzey, M. L., Jr. "Isospectral Graphs and Molecules" *Tetrahedron*, **1975**, *31*, 99-107.

- (9) Zivković, T.; Trinajstić, N.; Randić, M. "On Conjugated Molecules with Identical Topological Spectra" *Mol. Phys.* **1975**, *30*, 517-533.
- (10) Randić, M.; Trinajstić, N.; Zivković, T. "Molecular Graphs Having Identical Spectra" *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 244-256.
- (11) Heilbronner, E.; Jones, T. B. "Spectral Differences Between 'Isospectral' Molecules" *J. Am. Chem. Soc.*, **1976**, *100*, 6506-6507. A preprint of this article was kindly supplied by Professor Heilbronner.
- (12) (a) Herndon, W. C.; Tao, F.-K., unpublished work. (b) Herndon, W. C.; Ellzey, M. L., Jr., papers submitted for publication, 1972-1974, and rejected.
- (13) Gutman, I.; Milun, M.; Trinajstić, N. "Topological Definition of Delocalisation Energy" *MATCH*, **1975**, *1*, 171-175.
- (14) Aihara, J. "A New Definition of Dewar-Type Resonance Energies" *J. Am. Chem. Soc.* **1976**, *98*, 2750-2758.
- (15) Aihara, J. "Resonance Energies of Benzenoid Hydrocarbons" *J. Am. Chem. Soc.* **1977**, *99*, 2048-2053.
- (16) Gutman, I.; Milun, M.; Trinajstić, N. "Graph Theory and Molecular Orbitals. 19. Nonparametric Resonance Energies of Arbitrary Conjugated Systems" *J. Am. Chem. Soc.* **1977**, *99*, 1692-1704.
- (17) Trinajstić, N. "New Developments in Hückel Theory" *Int. J. Quantum Chem.: Quantum Chem. Symp. II* **1977**, 469-477.
- (18) Hosoya, H. "Graphical Enumeration of the Coefficients of the Secular Polynomials of the Hückel Molecular Orbitals" *Theor. Chim. Acta* **1972**, *25*, 215-222.
- (19) Graovac, A.; Gutman, I.; Trinajstić, N.; Zivković, T. "Graph Theory and Molecular Orbitals. Application of Sachs Theorem", *Theor. Chim. Acta* **1972**, *26*, 67-78.
- (20) Aihara, J. "General Rules for Constructing Hückel Molecular Orbital Characteristic Polynomials" *J. Am. Chem. Soc.* **1976**, *98*, 6840-6844.
- (21) Hess, B. A., Jr.; Schaad, L. J.; Agranat, I. "The Aromaticity of Annulenoannulenes", *J. Am. Chem. Soc.* **1978**, *100*, 5268-5271.
- (22) Herndon, W. C.; Parkányi, C. "Perturbation-Graph Theory. I. Resonance Energies of Heteroannulene π Systems" *Tetrahedron* **1978**, *34*, 3419-3425.
- (23) Herndon, W. C. "Enumeration of Resonance Structures" *Tetrahedron* **1973**, *29*, 3-12.
- (24) Herndon, W. C.; Ellzey, M. L., Jr. "Closed-Shell Biradical Structures" *Tetrahedron Lett.* **1974**, 1399-1402.
- (25) Herndon, W. C. "Resonance Theory and the Enumeration of Kekule Structures" *J. Chem. Educ.* **1974**, *51*, 10-15.
- (26) Herndon, W. C.; Ellzey, M. L., Jr.; Raghuvver, K. S. "Topological Orbitals, Graph Theory, and Ionization Potentials of Saturated Hydrocarbons" *J. Am. Chem. Soc.* **1978**, *100*, 2645-2650.
- (27) Herndon, W. C. "Resonance Energies of Benzene and Heterobenzenes from Photoelectron Spectra" *Tetrahedron Lett.*, in press.
- (28) Herndon, W. C. "Perturbation-Graph Theory. III. Resonance Energies From Photoelectron Spectra" *Pure Appl. Chem.*, in press.
- (29) Streitwieser, A., Jr. "Molecular Orbital Theory for Organic Chemists"; Wiley: New York, 1961.
- (30) Formerly, some subgraphs of the type considered were called "Sachs graphs" referring to work of H. Sachs, cited in ref 18-20.
- (31) Mallion, R. B.; Schwenk, A. J.; Trinajstić, N. "A Graphical Study of Heteroconjugated Molecules" *Croat. Chem. Acta* **1974**, *46*, 171-182.
- (32) Mallion, R. B.; Trinajstić, N.; Schwenk, A. J. "Graph Theory in Chemistry - Generalization of Sachs's Formula" *Z. Naturforsch.* **1974**, *29a*, 1481-1484.
- (33) Graovac, A.; Polansky, O. E.; Trinajstić, N.; Tyutyulkov, N. "Graph Theory in Chemistry. II. Graph Theoretical Description of Heteroconjugated Molecules" *Z. Naturforsch.* **1975**, *30a*, 1696-1699.
- (34) Rigby, M. J.; Mallion, R. B.; Day, A. C. "Comment on a Graph-Theoretical Description of Heteroconjugated Molecules" *Chem. Phys. Lett.* **1977**, *51*, 178-182.
- (35) Hall, L. H. "Group Theory and Symmetry in Chemistry"; McGraw-Hill: New York, 1969; Chapters 5 and 6.
- (36) Heilbronner, E. "Ein graphisches Verfahren zur Faktorisierung der Sakulardeterminante aromatischer Ringsysteme in Rahmen der LCAO-MO-Theorie" *Helv. Chim. Acta* **1954**, *37*, 913-921.
- (37) King, R. B. "Symmetry Factoring of the Characteristic Equations of Graphs Corresponding to Polyhedra" *Theor. Chim. Acta* **1977**, *44*, 223-243.
- (38) McClelland, B. J. "Graphical Method for Factorizing Secular Determinants of Hückel Molecular Orbital Theory" *J. Chem. Soc., Faraday Trans 2* **1974**, 1453-1456.
- (39) Texas Instrument calculators TI58 and TI59 are preprogrammed to solve algebraic equations using this method. A Fortran computer program to solve these equations is available from the authors.
- (40) Heilbronner, E. "Das Kompositions-Prinzip: Eine anschauliche Methode zur elektronen-theoretischen Behandlung nicht oder niedrig symmetrischer Molekeln im Rahmen der MO-Theorie" *Helv. Chim. Acta* **1953**, *36*, 170-188.
- (41) Dewar, M. J. S.; Gleicher, G. J. "Ground States of Conjugated Molecules. II. Allowance for Molecular Geometry" *J. Am. Chem. Soc.* **1965**, *87*, 685-692.
- (42) Dewar, M. J. S.; de Llano, C. "Ground States of Conjugated Molecules. XI. Improved Treatment of Hydrocarbons" *J. Am. Chem. Soc.* **1969**, *91*, 789-795.
- (43) Herndon, W. C. "Resonance Energies of Aromatic Hydrocarbons. A Quantitative Test of Resonance Theory" *J. Am. Chem. Soc.* **1973**, *95*, 2404-2406.
- (44) Herndon, W. C.; M. L. Ellzey, Jr. "Resonance Theory. V. Resonance Energies of Benzenoid and Nonbenzenoid π Systems" *J. Am. Chem. Soc.* **1974**, *96*, 6631-6642.
- (45) Hess, B. A., Jr.; Schaad, L. J. "Hückel Molecular Orbital π Resonance Energies. A New Approach" *J. Am. Chem. Soc.* **1971**, *93*, 305-310.
- (46) Hess, B. A., Jr.; Schaad, L. J. "Hückel Molecular Orbital π Resonance Energies. The Benzenoid Hydrocarbons" *J. Am. Chem. Soc.* **1971**, *93*, 2413-2416.
- (47) Hess, B. A., Jr.; Schaad, L. J. "Hückel Molecular Orbital π Resonance Energies. The Nonalternant Hydrocarbons" *J. Org. Chem.* **1971**, *36*, 3418-3423.
- (48) Wheland, G. W. "Resonance in Organic Chemistry"; Wiley: New York, 1955; pp 75-121.

The Probability of Dichotomization by a Binary Linear Classifier as a Function of Training Set Population Distribution

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The dimensionality (number of descriptors per pattern) of nonparametric binary pattern classifiers has been the topic of several papers appearing in the chemical literature.¹⁻⁵ These papers have discussed the relationship between the ratio of the number of patterns being classified, N , and the number of descriptors per pattern, d , and the probability of dichotomization, P , for a binary linear classifier. The theoretical relationship

$$P = D(N, d) / 2^N \quad (1)$$

$$D(N, d) = 2 \sum_{k=0}^d \frac{(N-1)!}{(N-1-k)!k!} \quad (2)$$

is derived in many pattern recognition texts (e.g., refs 6 and 7) and has been discussed in the literature and will not be dealt with in detail here. The only constraint used in the derivation

is that the patterns be well distributed. The derivation makes no mention of the way the patterns forming the two classes are divided between the two classes. This relationship is commonly used to determine requirements upon the ratio of N to d for development of linear classifiers such that the probability of complete separation between the two classes due to mathematical artifacts is kept very small.

Several authors have proposed rules for practical application of the theoretical probability. Bender et al.⁵ recommended using three times the number of patterns as descriptors per pattern for each class, and Gray³ proposed that a threshold criterion could be imposed on the probability function. Both of these guidelines appeal directly to the theoretical probability of dichotomization.

An important and relevant consideration has been omitted from all previous treatments. The fraction of the patterns comprising each of the two classes will affect the probability