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How to Persuade Undergraduates to Use Chemical Graph Theory

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Abstract: New techniques are presented that permit the use of chemical graph theory to obtain secular equations for small molecules. The new techniques significantly accelerate manual calculations. A previously unrecognized relationship between the characteristic polynomial for a Hückel annulene and the secular equation for the corresponding Mobius annulene is deduced. The power of the graph-theoretical approach to illuminate chemically useful generalizations at the Hückel level is exemplified.

Introduction

Hückel Theory. In 1931, Hückel described a very simple molecular orbital approach to the π-electronic structure of planar molecules [1]. Since then, many textbooks (e.g., [2–4]) have been written to introduce Hückel theory to undergraduate students and apply it, primarily, to planar hydrocarbons. The manual application of Hückel theory to a hydrocarbon with *n* carbon atoms requires one to: (a) write a set of *n* homogeneous linear equations, (b) generate an *n* × *n* secular determinant, (c) diagonalize the determinant to generate an *n*th order polynomial (the secular equation), (d) obtain *n* roots for the secular equation (the set of *n* roots is called the spectrum of the polynomial) [5], (e) calculate the *n* molecular orbital energies (the eigenvalues) using the numbers in the spectrum, and (f) obtain *n* molecular orbitals (the eigenfunctions) for the molecule by substituting the spectrum roots back into the homogeneous linear equations. This article will focus on techniques that provide polynomial spectra (end of step d). At that point, one is in a position to obtain a variety of resonance energies commonly invoked in Hückel-level discussions (e.g., lectures about aromaticity [6]).

The manual application of Hückel theory to small molecules [7], can be enormously time consuming. For example, Hückel calculations on the C_8 tricycle **1** (Figure 1) require one to draw 125 determinants, diagonalize 46 two by two determinants, and add together 21 polynomials in order to obtain the secular equation, *S*(*x*).

Such lengthy, tedious, and repetitive procedures lead to frequent errors and a great deal of frustration for undergraduate students. On the other hand, carrying out such calculations by computer leaves students with "black-box syndrome," that is, they gain little understanding of or familiarity with the mathematics that provides chemical insight.

Chemical Graph Theory. Chemical graph theory [5, 7] constitutes a completely different mathematical approach that also generates the Hückel eigenvalues and, from them, the various resonance energies referred to earlier. Using this approach, one draws Sachs graphs, which are used to obtain each polynomial coefficient independently. Sachs graphs may be composed of two types of components: edges (or σ bonds) and rings. To draw a Sachs' graph, draw the Lewis structure and delete all bonds so that only the dots remain where the carbon atoms are located. Next, some of the dots are connected to make edges (sigma bonds) or rings. The sole rule in drawing Sachs graphs is that individual components may not touch (i.e., must be nonincident). The appropriate number of carbons (or vertices) in each graph is determined by the coefficient sought. Once the graphs are drawn they are simply counted and the resultant total transformed into the target coefficient by means of the Sachs formula.

A generalized form for the polynomial (called the characteristic polynomial: $P_C(x)$) is given in equation 1.

$$P_C(x) = a_0x^n + a_1x^{n-1} + a_2x^{n-2} + \dots + a_kx^{n-k} + \dots + a_n = 0 \qquad (1)$$

By definition, $a_0 = 1$ and $a_1 = 0$. All other coefficients may be obtained by drawing Sachs graphs with the appropriate number of vertices included in their components, for example, Sachs graphs for a_2 (designated s_2) have only two vertices involved in graph components, while s_3 graphs have 3 vertices involved in components and so on. Figure 2 presents the Sachs graphs for methylene cyclopropene (**2**).

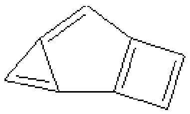
Because there are four carbons in **2**, the characteristic polynomial is fourth order. $a_0 = 1$ and $a_1 = 0$. The other coefficients are determined with the Sachs formula (see equation 2).

$$a_k = \sum_{s_k} (-1)^{c(s)} (2)^{r(s)} \qquad (2)$$

where *c*(*s*) is the number of components in each graph, *r*(*s*) is the number of rings in each graph and *k* is the number of vertices included in the graph components. Thus, for methylene cyclopropene (**2**) there are 4 s_2 graphs, for which $c(s) = 1$ and $r(s) = 0$. Applying the Sachs formula leads to $a_2 = -4$. The same procedure on the s_3 graph leads to $a_3 = -2$. Now, $a_4 = +1$. Compound **2** has the characteristic polynomial and spectrum shown in Figure 3.

When graphs have the same number of vertices but a different number of components, they must be collected and processed separately. Hence, the s_4 graphs for cyclobutadiene are drawn and processed as shown in Figure 4.

The application of graph theory to small molecules [7] can be enormously time consuming. For example, to obtain the characteristic polynomial for the C_8 tricycle **1** traditionally



1

S(x) : $x^8 - 10x^6 + 2x^5 + 27x^4 - 8x^3 - 18x^2 + 4x + 1$

Spectrum : -2.59, -1.78, -0.89, -0.15, 0.38, 1.09, 1.66, 2.28

Figure 1. Secular equation and spectrum for the tricycle (**1**).

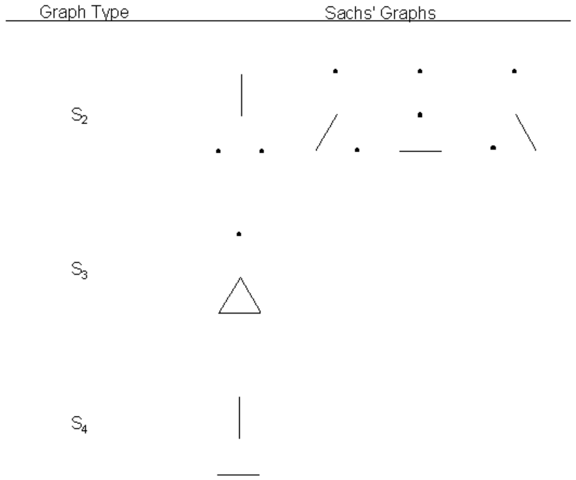
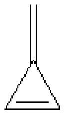


Figure 2. Sach's graphs for methylene cyclopropene (**2**).

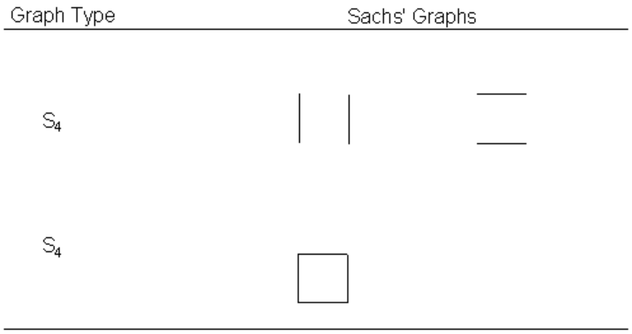


2

$P_c(x)$: $x^4 - 4x^2 - 2x + 1$

Spectrum : -1.48, -1, 0.31, 2.17

Figure 3. Characteristic polynomial and spectrum for methylene cyclopropene (**2**).



$$a_4 = 2(-1)^2(2)^0 + 1(-1)^1(2)^1 = 0$$

Figure 4. Calculating a_4 for cyclobutadiene using two types of s_4 graphs.

required one to draw 89 Sachs graphs. Determining a_4 for **1** has required drawing 29 two-edge Sachs graphs. It is very easy to inadvertently draw the same graph twice and very difficult to recognize which is the duplicate pair on a page filled with 30 graphs. To determine a_6 for the commonplace molecule, naphthalene, one must draw 63 graphs.

Furthermore, contrary to an earlier statement [7], the secular equation and the characteristic polynomial are often not identical. Imagine having a set of roots r_1, r_2, r_3 ..., which are used to construct a polynomial. Now, multiply each root by –1 and then construct a second polynomial. These polynomials would be related in exactly the same way that the secular equation and the characteristic polynomial are related. Thus, **1** has the secular equation given in Figure 1, but has the characteristic polynomial given in Figure 5.

For nonalternant hydrocarbons like **1**, the characteristic polynomial and the secular equation are not the same. The roots of the characteristic polynomial must be multiplied by –1 before they can be substituted into the homogeneous linear equations to obtain the molecular orbitals for the molecule of interest. Moreover, the eigenvalues (orbital energies) require different definitions for Hückel theory (E^H) and graph theory (E^G) as shown in equations 3 and 4.

$$E^H = \alpha - r_i\beta \tag{3}$$

$$E^G = \alpha + r_i\beta \tag{4}$$

where r_i is a root for the appropriate polynomial.

So, a student of Hückel theory, who wishes to exploit graph theory, must assume the burden of handling two closely related but different polynomials and two different but closely related definitions for energy. No matter which approach is adopted, the methods are exceedingly cumbersome and prone to copying errors. In my experience, students will invariably choose to do matrix diagonalization rather than draw Sachs graphs whenever they are given the option.

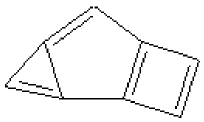
Results and Discussion

Improved Techniques. Clearly, it would be helpful if graph theory could provide secular equations directly. For a given structure, the secular equation and the characteristic polynomial have the same absolute value for corresponding coefficients but the signs are reversed for all a_{2n+1} coefficients. Consequently, it is a simple matter to modify the Sachs formula so that it provides the secular equation coefficients directly (see equation 5).

$$a_k = \sum_{s_k} (-1)^{k+c(s)} (2)^{r(s)} \tag{5}$$

where c(s) is the number of components in each graph, $r(s)$ is the number of rings in each graph, and k is the number of vertices included in the graph components. This is the modified Sachs formula.

The tedium and risk in using the graph theoretical approach for obtaining secular equations lies in drawing Sachs graphs. Drawing them is unnecessary, because one only needs to count them. To use my technique, one has to (a) draw the structure of interest, (b) number the vertices, (c) produce a list of edges (σ

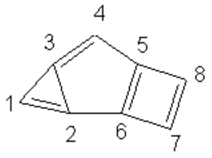


1

$P_c(x)$: $x^8 - 10x^6 - 2x^5 + 27x^4 + 8x^3 - 18x^2 - 4x + 1$

Spectrum : 2.59, 1.78, 0.89, 0.15, -0.38, -1.09, -1.66, -2.2

Figure 5. Characteristic polynomial and spectrum for (**1**).



1

Edges	Rings
(1, 2) (1, 3)	(1, 2, 3)
(2, 3) (2, 6)	(2, 3, 4, 5, 6)
(3, 4)	(5, 6, 7, 8)
(4, 5)	(1, 2, 3, 4, 5, 6)
(5, 6) (5, 8)	(2, 3, 4, 5, 6, 7, 8)
(6, 7)	(1, 2, 3, 4, 5, 6, 7, 8)
(7, 8)	

Figure 6. Complete listing of edges and rings for (**1**).

S_7 Graphs	Contribution to a_7 (secular equation)
(1, 2, 3) (4, 5) + e = 2	$4\,(-1)^{7+3}\,(2)^1 = +8$
(1, 2, 3) (5, 6) + e = 1	
(1, 2, 3) (5, 8) + e = 1	
(2, 3, 4, 5, 6) + e = 1	$1\,(-1)^{7+2}\,(2)^1 = -2$
(2, 3, 4, 5, 6, 7, 8) = 1	$1\,(-1)^{7+1}\,(2)^1 = +2$
(1, 2, 3) (5, 6, 7, 8) = 1	$1\,(-1)^{7+2}\,(2)^2 = -4$

$$a_7 = 8 - 2 + 2 - 4 = +4$$

Figure 7. Rapid calculation of a_7 for the secular equation of (**1**).

bonds) and rings, (d) count graphs without drawing them and (e) apply the modified Sachs formula (equation 5) to obtain the secular equation. This approach is set up for **1** in Figure 6. Note that a list of rings includes all possible continuous circuits, not simply the three rings most chemists would recognize.

The graph-theoretical requirement that graph components be nonincident means that components collected into the same graph (Figure 6) may not have a common vertex, for example, (1, 2)(1, 3) would be an illegal s_4 graph for **1**.

The listing shown in Figure 6 can now be used in a manner analogous to an abacus. For example, to determine how many s_4 graphs contain the (1, 2) edge, put your pencil on (1, 2) (Figure 6) and count all of the edges that do not contain a 1 or a 2, you should find 6 such s_4 graphs. I require my students to write this out as shown in equation 6.

$$(1, 2) + e = 6 \tag{6}$$

If edges are listed, as shown in Figure 6, once all of the (1, 2) edge-containing graphs are counted, then one can proceed through the list finding all the s_4 graphs containing the (1, 3) edge and so on. All possible combinations of edges and rings with the appropriate number of vertices must be counted, so (5, 6, 7, 8) is also a valid s_4 graph. There are 29 two-edge s_4 graphs and one cyclic s_4 graph for **1**. Equation 7 shows how to calculate a_4 for the secular equation of **1** using the modified Sachs formula (see equation 5).

$$a_4 = 29(-1)^{4+2}\,(2)^0 + 1(-1)^{4+1}\,(2)^1 = +27 \tag{7}$$

It takes practice to avoid overlooking some cyclic graphs. Figure 7 shows how to obtain a_7 for **1**.

Now there is a manual graph-theoretical technique that will provide secular equations for small molecules in a far more rapid and much less error-prone manner. In my experience, undergraduates are willing to use this approach in preference to matrix diagonalization.

Secular Equations for Mobius Annulenes. These days, Hückel-level discussions about aromaticity often include both planar monocycles with parallel p orbitals (Hückel annulenes) and nonplanar monocycles in which each p orbital has been rotated by θ° relative to its contiguous neighbors (Mobius annulenes) [8]. The secular equation for a Hückel annulene may be obtained by enumerating Sachs graphs and using the modified Sachs formula (equation 5) while the characteristic polynomial may be obtained by enumerating Sachs graphs and using the original Sachs formula (equation 2).

For nonalternant annulenes, the secular equation for a given Hückel annulene has the same spectrum as that for the Mobius annulene, except that each root has been multiplied by –1. This relationship can be simply deduced from the Frost and Zimmerman circle mnemonics as they apply to nonalternant annulenes [9, 10]. Hence, the secular equation for a nonalternant Mobius annulene is the characteristic polynomial for the corresponding Hückel annulene. From the graph-theoretical standpoint, the sole difference between Sachs graphs for a Hückel annulene and the Sachs graphs for the corresponding Mobius annulene is that a Mobius cyclic Sachs graph is edge-weighted, that is, the a_n term for a nonalternant Hückel annulene must be multiplied by –1 to get a_n for the corresponding Mobius annulene (see reference 5a, Vol. 1, p 28). This generalization is subsumed by the general recognition that a nonalternant Mobius secular equation is the corresponding Hückel characteristic polynomial.

3 **4**

Figure 8. Compounds 3 and 4, nonalterant monocycles showing two nonbonding electrons in their Lewis structures.

For a given alternant annulene, the Mobius secular equation is identical to the Hückel characteristic polynomial with the exception of the *n*th term: a_n. For alternant annulenes, one can always draw two acyclic s_n graphs and one cyclic s_n graph. For 4N Hückel annulenes, the cyclic Sachs graphs, in conjunction with the Sachs formula, contribute +2 and the cyclic graph contributes –2 to a_n. Thus, all Hückel 4N annulenes have both secular equations and characteristic polynomials in which $a_n = 0$. The corresponding Mobius 4N annulenes have the same Sachs graphs, but now the cyclic Sachs graph is edge-weighted so that it also contributes +2 to a_n. Thus, all Mobius 4N annulenes have secular equations in which $a_n = +4$. A similar argument will show that all 4N + 2 Mobius annulenes must have secular equations in which $a_n = 0$. It is now a straightforward exercise to write a general relationship between the characteristic polynomial (${}^{H}P_{C}(x)$) for a given Hückel annulene and the secular equation (${}^{M}S(x)$) of the corresponding Mobius annulene (see equation 8).

$$ {}^{M}S(x) = {}^{H}P(x) + [2 + 2(-1)^{v}] \tag{8}$$

where *v* equals the number of vertices in the annulene

Given either the secular equation or the characteristic polynomial for a Hückel annulene, the relationship in equation 8 obviates the need to diagonalize matrices or count Sachs graphs in order to obtain quantitative data for the corresponding Mobius annulene. Note Heilbronner's suggestion [11] that eigenvalues for Mobius annulenes should have spectrum roots multiplied by cos θ (θ is the angle between adjacent p orbitals in a Mobius array). Thus, for Mobius cyclobutadiene, the secular equation is $x^4 - 4x^2 + 4$, the spectrum is –1.414, –1.414, 1.414, 1.414, θ = 45°, cos θ = 0.707, and the eigenvalues are $\alpha + \beta$, $\alpha + \beta$, $\alpha - \beta$, $\alpha - \beta$.

Why Bother With Manual Calculations? In spite of criticisms about Hückel-level eigenvalues and Hückel-level partial charges for nonalternant molecules like **2**, Hückel theory has produced some powerful chemical insights. Undoubtedly, the best known is the Hückel view of aromatic and antiaromatic structures like benzene and cyclobutadiene. The one major advantage Hückel theory has over higher levels of theory is that Hückel theory alone permits exact generalizations. For example, from the Pairing theorem (see reference 5b, p. 16), no carbon atoms will have net π-electron-derived charge in any alternant hydrocarbon. Initially, the best argument in favor of learning/teaching the graph-theoretical approach to obtaining the characteristic polynomial was that, in some cases, drawing/counting Sachs graphs was faster than manual matrix diagonalization. Even with the improved methodology described in this report, there are very few molecules for which one can obtain a secular equation or a characteristic polynomial faster by hand than one can with a computer (examples: ethylene and allyl).

Chemical graph theory offers computational power and insight that neither manual matrix diagonalization nor computer calculations can. Section 2 of the Results and Discussion sectopm provides a nice example. No matter how many specific structures are subjected to computer calculations, one can never be quite sure, on that basis, whether equation 8 would hold for the next Mobius annulene. Furthermore, it is not an obvious relationship for someone parked in front of a computer, but it is not hard to see for someone who knows some graph theory.

I conclude with a final example. Nonalternant monocycles, which must show two nonbonding electrons in their Lewis structures, are particularly interesting from the standpoint of polarity (Figure 8). Compounds **3** and **4** are a pair of representative structures.

Simple graph-theoretical arguments permitted the deduction that **3** (just one odd substituent on the ring) would be very polar, while **4** (more than one odd substituent on the ring) would be nonpolar at the Hückel level [12]. Higher-level calculations, both semiempirical and ab initio, fully support the very high polarity predicted by Hückel theory for the lowest-lying singlet state of **3** [12, 13]. It is difficult to see how someone with a Hückel program would recognize that computer calculations on **3** and **4** would be of interest, much less how they would prove that additional odd substituents must depolarize the structure.

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