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Generation of the eigenvectors of the topological matrix from graph theory

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The technique of describing the characteristic polynomial of a graph is here extended to construction of the eigenvectors. Recurrence relations and path tracing are combined to generate eigenvector coefficients as polynomial functions of the eigenvalues. The polynomials are expressed as linear functions of Chebyshev polynomials in order to simplify the computational effort. Particular applications to the Hückel MO theory, including heteroatom effects, are shown.

Key words: Characteristic polynomial—eigenvector construction—graph theory

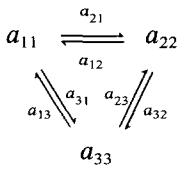
1. Introduction

The characteristic polynomial of the general $n \times n$ matrix A, defined as $(-1)^n \det(A - xI)$, where I is the identity matrix, may be written [1]

$$(-1)^n \begin{vmatrix} a_{11}-x & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22}-x & \cdots & a_{2n} \\ \vdots & \vdots & & \vdots \\ a_{n1} & a_{n2} & \cdots & a_{nn}-x \end{vmatrix}$$

In this convention the leading term of the polynomial always has a positive sign. The matrix A may be represented by a directed multigraph including edge and

vertex weights as follows



where a_{ii} is a vertex weight and a_{ij} is the edge weight of the edge directed from vertex j to vertex i. Thus row i of the matrix contains the weights for edges directed *to* vertex i, while column j contains the weights for edges directed *from* vertex j. In the simple Hückel case, where $a_{ii}=0$ and $a_{ij}=a_{ji}=0$ or 1, the characteristic polynomial can be assembled by the technique of Heilbronner [2] using the Chebyshev polynomials [3] and their recurrence relations. Practical application of the method is limited to sparse matrices.

Once the eigenvalues are obtained, the numerical values of the corresponding eigenvectors of A may be determined from the cofactors of a row of the characteristic matrix [4]. Certain problems which occasionally arise with this procedure, and methods for dealing with them, will be discussed later. It will first be shown that the cofactors of any element of the characteristic matrix can be expressed analytically by as simple a procedure as used to develop the characteristic polynomial. Thus, the eigenvector coefficients and any functions derived from them can be expressed analytically as well. The procedure will be demonstrated for the Hückel MO problem, and the inclusion of heteroatoms will be shown to be a straightforward extension of the technique. Since the normalized eigenvectors correspond to the atomic orbital coefficients in each molecular orbital, they contain all the information required for calculable molecular properties. It is then possible to express other quantities of interest, particularly bond orders, in closed form as well.

2. Theory

To simplify the notation we will first refer to the diagonal elements of the characteristic matrix, $a_{ii}-x$, by just a_{ii}. Then we may write

$$\det(A-xI)=\varepsilon_{i_1 i_2 \ldots i_n}\{a_{1i_1}a_{2i_2}\ldots a_{ni_n}\}$$

where $i_1, i_2, \ldots, i_n$ take on all permutations of the values $1, 2, \ldots, n$, and $\varepsilon_{i_1 i_2 \ldots i_n}$ is the permutation tensor, ± 1 for even or odd permutations of the column numbers with the row numbers in natural order [5]. Expanding in terms of the cofactors of elements of a row

$$\det(A-xI)=\sum_{\beta} a_{\alpha\beta}[(-1)^{\alpha+\beta}\varepsilon_{i_1 i_2 \ldots i_{n-1}}\{a_{1i_1}a_{2i_2}\ldots a_{ni_{n-1}}\}]$$

where the set of row numbers $1, 2, \ldots, n$ does not include α, and the column numbers $i_1, i_2, \ldots, i_{n-1}$ take on all permutations of the values $1, 2, \ldots, n$ not including β. In terms of the graph, since $a_{\alpha\beta}$ is the weight of the edge directed from vertex β to vertex α, the cofactor in square brackets contains no other edges

directed either from vertex β or to vertex α. Separating the cofactor of the diagonal element from those of the remainder of the row

$$\det(A-xI) = a_{\alpha\alpha}[\varepsilon_{i_1 i_2 \ldots i_{n-1}}\{a_{1i_1}a_{2i_2}\ldots a_{ni_{n-1}}\}] + \sum_{\beta\neq\alpha} a_{\alpha\beta}[(-1)^{\alpha+\beta}\varepsilon_{i_1 i_2 \ldots i_{n-1}}\{a_{1i_1}a_{2i_2}\ldots a_{ni_{n-1}}\}]$$

where $\operatorname{cof}(a_{\alpha\alpha})$ now contains identical sets of row and column numbers not including α.

For $\beta \neq \alpha$ we may expand $\operatorname{cof}(a_{\alpha\beta})$ by successively extracting terms from the determinant to leave smaller determinants which have identical sets of row and column numbers. This may be written

$$\begin{aligned}\det(A-xI) = a_{\alpha\alpha}[&\varepsilon_{i_1 i_2 \ldots i_{n-1}}\{a_{1i_1}a_{2i_2}\ldots a_{ni_{n-1}}\}] \\ &+ \sum_{\beta\neq\alpha} a_{\alpha\beta}[-a_{\beta\alpha}\varepsilon_{i_1 i_2 \ldots i_{n-2}}\{a_{1i_2}a_{2i_2}\ldots a_{ni_{n-2}}\} \\ &+ \sum_{\lambda\neq\alpha,\beta} a_{\beta\lambda}a_{\lambda\alpha}\varepsilon_{i_1 i_2 \ldots i_{n-3}}\{a_{1i_1}a_{2i_2}\ldots a_{ni_{n-3}}\} \\ &\quad\vdots \\ &+ (-1)^{n-1} \sum_{\substack{\lambda,\mu,\ldots,\xi\neq\alpha,\beta \\ \lambda\neq\mu,\ldots,\xi}} a_{\beta\lambda}a_{\lambda\mu}\ldots a_{\xi\alpha} \\ &\quad\vdots \qquad].\end{aligned}$$

The cofactor of $a_{\alpha\beta}$ is then a linear combination of determinants which are successively reduced in size. The coefficients of each determinant are strictly products of off-diagonal elements of the matrix A which form a sequential set of row (and column) numbers between β and α. The sign of each term has been determined by the alternating nature of the permutations required to bring the row and column numbers of the coefficients into identical order. Interchanges of even or odd numbers of column indices are odd or even permutations, respectively.

We may now write the determinants in the same format as that of the characteristic polynomial by factoring appropriate powers of -1 to match the sizes of the determinants. Thus we obtain

$$\begin{aligned}\det(A-xI) = (-1)^{n-1}a_{\alpha\alpha}[&(-1)^{n-1}\varepsilon_{i_1 i_2 \ldots i_{n-1}}\{a_{1i_1}a_{2i_2}\ldots a_{ni_{n-1}}\}] \\ &+ (-1)^{n-1}\sum_{\beta\neq\alpha} a_{\alpha\beta}[a_{\beta\alpha}(-1)^{n-2}\varepsilon_{i_1 i_2 \ldots i_{n-2}}\{a_{1i_1}a_{2i_2}\ldots a_{ni_{n-2}}\} \\ &+ \sum_{\lambda\neq\alpha,\beta} a_{\beta\lambda}a_{\lambda\alpha}(-1)^{n-3}\varepsilon_{i_1 i_2 \ldots i_{n-3}}\{a_{1i_1}a_{2i_2}\ldots a_{ni_{n-3}}\} \\ &\quad\vdots \\ &+ \sum_{\substack{\lambda,\mu,\ldots,\xi\neq\alpha,\beta \\ \lambda\neq\mu,\ldots,\xi}} a_{\beta\lambda}a_{\lambda\mu}\ldots a_{\xi\alpha} \\ &\quad\vdots \qquad].\end{aligned}$$

The cofactor of the diagonal term, $a_{\alpha\alpha}$, is within a multiplicative sign factor equal to the characteristic polynomial produced from $A - xI$ by eliminating row α and column α. The equivalent graph is the subgraph which results from eliminating vertex α and all edges incident with it from the original graph. The cofactor of $a_{\alpha\beta}$ is, within the same multiplicative sign factor, equal to a linear combination of terms each containing the product of edge weights directed from α to β multiplied by the characteristic polynomial produced from $A - xI$ by eliminating rows and columns labelled by α, β and any intervening indices. The equivalent graph is the subgraph which results from eliminating all edges directed from vertex β and to vertex α. Each term in the expansion is then equivalent to tracing a path from vertex α to vertex β, taking the product of the edge weights traversed, and multiplying the product by the characteristic polynomial of the subgraph obtained by eliminating all vertices and incident edges along the traced path.

3. Hückel MO

To demonstrate the procedure we begin with the adjacency matrix. All vertex weights are zero and all the nonzero edge weights are identically one. The characteristic polynomial in the variable x will be given by linear combinations of the Chebyshev polynomial (designated $S_n(x)$ in [3]) which is defined as

$$L_n \equiv L_n(x) = \sum_{m=0}^{[n/2]} (-1)^m x^{n-2m} \binom{n-m}{m} = x^n - (n-1)x^{n-2} + \cdots$$

where L_n obeys the recurrence relation

$$L_n = xL_{n-1} - L_{n-2}.$$

We will also make use of the product and derivative expansions

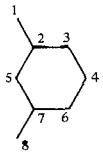
$$L_n L_{n+i} = \sum_{m=0}^{n} L_{2n+i-2m} = L_{2n+i} + L_{2n+i-2} + \cdots + L_i$$

and

$$\frac{dL_n}{dx} = \sum_{m=0}^{[n/2-1]} (n-2m) L_{n-1-2m} = nL_{n-1} + (n-2)L_{n-3} + \cdots.$$

The polynomial L_n is well known as the characteristic polynomial of the adjacency matrix for a linear chain of carbon atoms [1, 6]. Its recurrence relation demonstrates how the polynomial for a linear chain of n atoms is simply formed by addition of a single atom onto the end of a chain which is one bond length shorter. Noting that $L_1 = x$, we see that L_n is equal to the product of the polynomials of the two combining sections minus that of the residual fragment left after the two newly linking atoms are eliminated. More generally, Heilbronner has demonstrated an extension of the method to the piecewise connection of any two sections and to the closure of rings [2]. We will make use of this factorization method, and the reader is referred to Streitwieser for further details [6].

We will now consider the Huckel MO treatment of *m*-xylene where the numbers



1-8 are used for vertex identification and are not weights. The characteristic polynomial can be quickly derived using the factorization method [2, 6] to be

$$L_1^2[L_6 - 3L_4 + 3L_2 - 5] = 0$$

or,

$$x^2[x^6 - 8x^4 + 18x^2 - 12] = 0.$$

The roots are found to be

$$x = 0, 0, \pm(3+\sqrt{3})^{1/2}, \pm(3-\sqrt{3})^{1/2}, \pm\sqrt{2}.$$

To select a vertex about which to evaluate the eigenvectors we wish, if possible, to avoid selecting one which has a corresponding zero eigenvector coefficient for any of the eigenvalues, since in the case of a symmetric matrix all the cofactors will turn out to be identically zero. This problem may be unavoidable at times and more than one vertex would have to be used to generate the complete eigenvector matrix. In most cases the problem is avoided by selecting the vertex of lowest degree which is not coincident with a symmetry axis of the graph. For this reason vertex 1 has been selected for the calculation.

Eigenvector coefficient C_1, which is given by the characteristic polynomial of $\mathrm{cof}(a_{11})$, is first found by eliminating vertex 1 from the graph and evaluating the polynomial of the resulting subgraph:

$$C_1 = L_7 - L_5 - L_3 - 2L_1.$$

Then, C_2 is determined from a path of length one from vertex 1 to vertex 2 and the polynomial of the subgraph resulting from elimination of the two vertices:

$$C_2 = L_6 - L_2.$$

There are two self-avoiding paths from vertex 1 to each of the remaining vertices 3-8. The paths from vertex 1 to vertex 3 are (1-2-3) and (1-2-5-7-6-4-3), lengths 2 and 6, respectively. Then C_3 is simply a linear combination of the two subgraph polynomials L_5-L_1 and L_1:

$$C_3 = L_5.$$

Two paths may be traversed from vertex 1 to vertex 4, with resulting subgraph polynomials L_4-1 and L_2+1:

$$C_4 = L_4 + L_2.$$

Finally,

$$C_5 = L_5 + L_1$$
$$C_6 = 2L_3 + L_1$$
$$C_7 = L_4 + 2L_2 + 1$$
$$C_8 = L_3 + L_1.$$

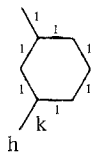
The eigenvector coefficients for the nondegenerate eigenvalues may now be simply obtained by substitution. The coefficients will all be identically zero for the degenerate eigenvalues, however, as expected. These eigenvalues are thus roots of the eigenvector polynomials and, since the coefficients are only known to within a multiplicative constant, the degenerate roots could be factored from each of the coefficients. A less tedious procedure is to use l'Hospital's rule and take $n-1$ derivatives of the coefficients for an n-tuple degeneracy, using the derivative expansion given earlier, and completing the degenerate eigenvector set through symmetry. The doubly degenerate eigenvectors are then given by

$$C = \begin{bmatrix} 7L_6 - 3L_2 - 3 \\ 6L_5 + 4L_3 \\ 5L_4 + 3L_2 + 1 \\ 4L_3 + 4L_1 \\ 5L_4 + 3L_2 + 2 \\ 6L_2 + 3 \\ 4L_3 + 6L_1 \\ 3L_2 + 2 \end{bmatrix}$$

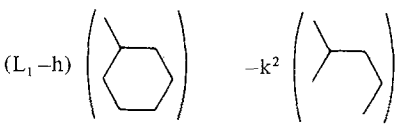
Since m-xylene contains a mirror symmetry plane the eigenvectors are in fact either symmetric or antisymmetric with respect to that plane. Heilbronner, McClelland, King, and Herndon and Ellzey [7] have shown the use of a graphical method for reducing a graph with symmetry elements to simpler subgraphs whose characteristic polynomials yield the roots corresponding to states of a particular irreducible representation. Each subgraph polynomial is a factor of the parent graph polynomial and is of lower, order, not only simplifying the calculations but also breaking the symmetry based degeneracies. The eigenvector method may then be applied to the subgraphs to simply determine the eigenvectors belonging to each representation.

4. Heteroatoms

Consider now the same structure with atom 8 being a heteroatom. The graph is given by



where h is the vertex weight and k is the edge weight for atom 8. Or equivalently, $a_{78} = a_{76} = k$ and $a_{88} = h$. The characteristic polynomial may be factorized symbolically as



where the structures are to be replaced by their characteristic polynomials. The characteristic equation then becomes

$$L_1(L_1-h)(L_6-2L_4+L_2-3)-k^2L_1^2(L_4-2L_2+2)=0.$$

For $h=0$ and $k=1$ this equation reverts to the expression found earlier for the topological matrix. Note that in general the degeneracy has been broken by the appearance of $h \neq 0$ and but a single zero root occurs.

The inequivalence of atoms 1 and 8 poses an interesting question concerning the vertex to be used for the eigenvector calculation. While atom 8 would appear to be an ideal selection in terms of computational ease, we see that the eigenvectors would be identical to the set previously calculated with the exception that seven of the eight coefficients would now be multiplied by k. Since these vector were already shown to vanish for the zero root, and since the degeneracy no longer exists, we immediately see that the eigenvector coefficient for atom 8 must vanish for the zero root. Using vertex 1 again for the calculation we obtain

$$C=\begin{bmatrix}(L_1-h)(L_6-L_4-2)-k^2L_5\\(L_1-h)L_5-k^2(L_4+L_2)\\(L_1-h)(L_4+1)-k^2(L_3+L_1)\\(L_1-h)(L_4+1)-k^2L_3\\(L_1-h)(L_3+L_1)-k^2(L_2+1)\\2(L_1-h)L_2-k^2L_1\\(L_1-h)(L_3+L_1)\\k(L_3+L_1)\end{bmatrix}$$

Indeed, $C_2=C_5=C_7=C_8=0$ for $L_1=x=0$.

5. Conclusions

It has been demonstrated from expansion of the characteristic matrix that the cofactors of any elements, and hence the eigenvectors, can be simply extracted from a graph. The eigenvector coefficients are expressed as polynomials, and root substitution yields their numerical values. The method is quite general and is amenable to any type of acyclic or cyclic system within the bounds of reasonable numbers of path tracings. However, path counting is unnecessary. The extension to heteroatom systems has been shown and the implications for simplifying the usual computational effort are significant.

It is apparent also that applications to other problems with sparse matrices may be beneficial in terms of providing analytical expressions where numerical solutions are the normal course. This would be particularly useful where the solutions contain functions of the eigenvector matrix, such as its inverse. An object of a future report will be the demonstration of the method's applicability to problems in consecutive, reversible first-order reactions.

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