Topological characterization of normal modes in chains and rings

David D. Keeports

Department of Physical Sciences, Mills College, Oakland, California 94613, USA

A method for predicting molecular stretching frequencies and normal coordinates for chain and ring pseudomolecules from topological considerations is presented. From previously published hydrocarbon force fields, complete GF product matrices for stretching are calculated for the chain and ring species. It is seen that with little loss of computational accuracy, these GF products can be approximated as $GF = \alpha E + \beta A$, where A is a topological adjacency matrix. Consequently, semi-quantitative calculation of the stretching spectra of the pseudomolecules considered requires only a specification of bond connectivities.

Key words: Graph theory—molecular topology—normal mode analysis—Hückel theory

1. Introduction

The construction of π system molecular orbitals reduces to a graph theoretical problem at the Hückel level of approximation [1, 2]. According to the Hückel method, electron interactions are neglected, and the secular equation

$$|H_{ij} - S_{ij}E| = 0 \tag{1}$$

is simplified by the substitutions

$$H_{ij} = \alpha \text{ if } i = j$$

$$H_{ij} = \beta \text{ if } i \text{ and } j \text{ refer to adjacent atoms} \tag{2}$$

$$H_{ij} = 0 \text{ otherwise}$$

$$S_{ij} = 1 \text{ if } i = j$$

$$S_{ij} = 0 \text{ if } i \neq j. \tag{3}$$

According to the above simplifications eigenvalues and eigenvectors are found for a Hückel matrix H given by

$$H = \alpha E + \beta A \tag{4}$$

where E is an identity matrix and A is the topological adjacency matrix defined by

$A_{ij} = 1$ if i and j refer to adjacent atoms

$A_{ij} = 0$ otherwise. $\tag{5}$

If α is taken as the origin of the eigenvalue scale, then the treatment of a molecule's electron π system reduces to the diagonalization of the molecule's atomic adjacency matrix. Thus, according to Hückel theory, a molecule's π system is characterized by the atomic connectivities within the molecule. It is the purpose of this paper to show that for the simple cases of chain and ring pseudomolecules, vibrational normal modes are likewise topologically characterized.

2. Method

The standard Wilson GF-matrix method [3] for the determination of vibrational frequencies and normal coordinates requires the calculation of the eigenvalues and eigenvectors of the GF product matrix expressed in terms of suitable internal coordinates. In the equation

$$GFL = L\Lambda, \tag{6}$$

Λ is a diagonal matrix whose diagonal entries are

$$\lambda_i = 4\pi^2 \nu_i^2, \tag{7}$$

where ν_i is the frequency of the ith normal mode, and L is the matrix which transforms normal coordinates Q into internal coordinates R:

$$LQ = R. \tag{8}$$

A nontrivial solution to Eq. 6 exists only if

$$|GF - \lambda E| = 0 \tag{9}$$

where E is an identity matrix. Solution of Eq. 9 leads to the determination of λ_i values. Relationships among entries of the ith column of L are found by substitution of λ_i into the equation

$$(GF - \lambda_i E)[c_i] = [0] \tag{10}$$

where $[0]$ is a column matrix of zeros and $[c_i]$ is a column matrix of initially undetermined constant coefficients.

According to Eq. 8, the coefficients which express the normal coordinates as linear combinations of the internal coordinates are given by the rows of L^{-1}.

$$Q = L^{-1}R. \tag{11}$$

Estimates of dipole derivatives and thus of infrared intensities can be made from calculated normal coordinates. While the desired L^{-1} matrix can be determined from L by the adjoint method or by elementary row operations, computational effort by the adjoint method or by elementary row operations, computational effort is saved if L^{-1} is calculated directly by substituting the λ_i values from Eq. 9 into the equation

$$[c_i](GF - \lambda_i E) = [0] \tag{12}$$

where here $[0]$ and $[c_i]$ are row matrices. Eq. 12 leads to relationships among the entries in the ith row of L^{-1}. Alternately, in special cases where GF is symmetric, L will be an orthogonal matrix whose inverse is simply its transpose. It is important to stress that while G and F are both symmetric matrices, the product GF is in general not symmetric.

Topological treatment of normal mode analysis requires the simplification of the GF matrix for the species under consideration to the form of the H matrix in Eq. 4 with bond adjacency rather than atomic adjacency considered. The validity of such a simplification can be evaluated by examination of the numbers occurring in the GF matrix for the species. For this purpose, the Schachtschneider vibrational programs [4] have been modified to output the GF matrix before its diagonalization.

Two classes of pseudomolecules, including one-dimensional chains of from three to seven atoms and rings of from three to six atoms, were considered. Carbon masses and bond distances of 1.50 Å were used in all cases. Only bond stretching force constants and stretch/stretch interaction constants between adjacent bonds were included in the calculations. Based upon published force constants for propane and cyclopropane [5], force constant values of 4.3 and 0.11 m dyn Å^{-1} for linear cases and 4.8 and −0.13 m dyn Å for ring cases were chosen.

3. Results

For all pseudomolecules under consideration, the individual G matrices and F matrices are of the form of the H matrix of Eq. 4, i.e. each is the sum of a diagonal matrix and a constant times an adjacency matrix. Most importantly for the purposes of the present study, all GF products are indeed of the form of H in Eq. 4 to a very good approximation.

The complete GF product matrices for both the chains and rings considered here are in fact symmetric. In the case of the linear pseudomolecules, only four distinct nonzero numbers appear in the GF product. In each matrix for the linear cases, the first and last elements along the main diagonal are 0.708, while other diagonal elements are 0.698. Elements removed one column from the main diagonal are −0.340, and elements removed two columns from the main diagonal are −0.009. All other elements are zero. These numbers suggest that if GF is called H, then exactly those simplifications given by Eq. 2 above (with i and j now referring to bonds) are appropriate with $\alpha = 0.70$ and $\beta = -0.34$.

In the case of the ring pseudomolecules, only three distinct nonzero numbers appear in each of the complete GF matrices. Again, exactly those simplifications given by Eq. 2. can be made. Elements along the main diagonal range from 0.789 for the three-membered ring to 0.811 for the six-membered ring. Thus, a substitution of $\alpha = 0.80$ along main diagonals is appropriate for all ring cases considered here. The small magnitudes of H_{ij} values (-0.022 to 0.005) when i and j refer to atoms with one intervening atom suggest that these elements be set to zero. When i and j refer to adjacent atoms, all H_{ij} elements have a common value for a given ring. Thus, these elements can be replaced by a parameter β. Unlike the linear pseudomolecule cases, however, different β values are required for each of the ring cases. Appropriate β values are 0.17, -0.02, -0.15, and -0.22, respectively, for rings of three, four, five, and six atoms.

From the simplifications of Eq. 2, the vibrational secular equations for the linear pseudomolecules are identical in form to the Hückel secular equations for the ethylene, allyl, butadiene, pentadienyl, and hexatriene π systems, while the vibrational secular equations for the ring pseudomolecules are identical in form to the Hückel secular equations for the cyclopropenyl, cyclobutadiene, cyclopentadienyl, and benzene π systems. The reader is referred to standard textbook discussions [6, 7] of the solutions of the above Hückel secular equations.

Table 1. Eigenvalues and frequencies for linear pseudomolecules

No. of atoms	Eigenvalues		Frequencies, cm^{-1}	
	approx.	exact	approx.	exact
2	0.70	0.7167	1090	1103
3	1.04	1.0475	1330	1334
	0.36	0.3675	780	790
4	1.18	1.1792	1420	1415
	0.70	0.7167	1090	1103
	0.22	0.2175	610	608
5	1.25	1.2428	1460	1453
	0.91	0.9233	1240	1252
	0.49	0.5030	910	924
	0.15	0.1425	500	492
6	1.29	1.2781	1480	1473
	1.04	1.0475	1330	1334
	0.70	0.7167	1090	1103
	0.36	0.3675	780	790
	0.11	0.1003	430	413
7	1.31	1.2996	1490	1486
	1.12	1.1264	1380	1383
	0.85	0.8662	1200	1213
	0.55	0.5635	970	978
	0.28	0.2784	690	688
	0.088	0.0742	390	355

Table 2. Eigenvalues and frequencies for ring pseudomolecules

No. of atoms	Eigenvalues		Frequencies, cm^{-1}	
	approx.	exact	approx.	exact
3	1.14	1.1350	1390	1388
	0.63	0.6163	1030	1023
	0.63	0.6163	1030	1023
4	0.84	0.8433	1190	1197
	0.80	0.8000	1170	1166
	0.80	0.8000	1170	1166
	0.76	0.7567	1140	1134
5	1.04	1.0438	1330	1331
	1.04	1.0438	1330	1331
	0.71	0.7115	1100	1099
	0.71	0.7115	1100	1099
	0.50	0.5228	920	942
6	1.24	1.2650	1450	1466
	1.02	1.0271	1320	1321
	1.02	1.0271	1320	1321
	0.58	0.5838	990	996
	0.58	0.5838	990	996
	0.36	0.3783	780	802

4. Discussion

Table 1 compares exact eigenvalues and frequencies determined by the Schachtschneider programs for the linear pseudomolecules to those calculated from simplified secular equations. A similar comparison for the ring pseudomolecules is presented in Table 2. Excellent agreement is seen to exist between exact and approximate solutions in both cases. Thus, the **GF** products for these species can be simplified to the form

$$\mathbf{GF} = \alpha \mathbf{E} + \beta \mathbf{A} \tag{13}$$

with little loss of computational accuracy. Consequently, the **GF** matrix reduces to a function of the adjacency matrix of the species.

In summary, for the simple chain and ring pseudomolecules considered here, stretching normal modes in terms of an eigenvalue scale origin α and an adjacency weight parameter β are determined by specification of bond connectivities without reference to a particular force field. Thus, semi-quantitative vibrational spectra for the stretches of these species can be derived from purely topological considerations.

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