

Vibrations of Finite Linear Chains of Molecules

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Abstract

Szigeti's (1961) method for obtaining the vibration frequencies of a finite chain (representing a long-chain molecule) from those of an associated infinite chain is analysed by a matrix partitioning technique. It is shown that this method has the advantage of reducing the dimensionality of the secular determinant. The approach is illustrated by an example.

Introduction

Recent experimental investigations of long-chain molecules, such as hydrocarbons, have regenerated interest in the vibrations of a linear chain of interacting units. Straightforward computations of the theoretical normal modes and frequencies of vibration of such a chain can be made by the usual matrix methods of small oscillation theory. However, when the range of interaction between the constituent groups is less than the length of the chain (as is the case for long-chain hydrocarbons), the computations can be simplified by adopting an alternative approach proposed by Szigeti (1961).^{*} This method involves calculating the normal modes and frequencies of a chain with the same intergroup interaction but assuming its length to be infinite, and then imposing the boundary conditions of the required finite chain to select out only those frequencies that are relevant. The object of the present paper is to examine Szigeti's method analytically, using a procedure based on matrix partitioning, in order to make his method more transparent than it appears to be in the present literature.

Theoretical Analysis

We begin by considering a finite chain of N units, each having one degree of freedom and capable of interacting with L neighbours on either side. The equation of vibratory motion for it can be written in the form

$$(\mathbf{M} - \mathbf{I}\omega^2)\Psi = 0, \quad (1)$$

where $\mathbf{M}$ is an $N \times N$ matrix. An infinite chain containing the same interacting units has a formally similar equation of motion:

$$(\mathbf{M}_1 - \mathbf{I}_1\omega_1^2)\Psi_1 = 0, \quad (2a)$$

^{*} Szigeti, B. (1961). *Proc. R. Soc. London A* **264**, 198-211.

We note that, for a given value of ω , there are in general $2L$ values of k . This follows from the fact that equation (4) is a polynomial equation of degree $2L$ in z , where

$$z = \exp(ik). \quad (5)$$

The roots of equation (4) for z are related to each other through ω and, in principle, each can be expressed in terms of any other by eliminating ω between them. Thus, the most general form for the eigenvector of the infinite chain is

$$\psi(n) = \sum_{j=1}^{2L} a_j z_j^n. \quad (6)$$

We now extract an equation for the relevant finite chain from equations (2a) and (2b) by rewriting them in the form

$$(\mathbf{M} - \mathbf{I}\omega^2)\psi_m + \{(\mathbf{M}' - \mathbf{M})\psi_m + \mathbf{M}_{im}\psi_i + \mathbf{M}_{mf}\psi_f\} = \mathbf{0}, \quad (7)$$

where ψ_i , ψ_m and ψ_f are appropriately partitioned vector components of the general eigenvector ψ chosen in the form (6). We now vary ψ by adjusting the parameters a_j and z_j (while preserving the relations between the different z_j through their dependence on ω) so that for some combination of these parameters we cause the second term in equation (7) to vanish, i.e.

$$(\mathbf{M}' - \mathbf{M})\psi_m + \mathbf{M}_{im}\psi_i + \mathbf{M}_{mf}\psi_f \equiv \mathbf{P}\psi = \mathbf{0}. \quad (8)$$

The set of parameters a_j and z_j that brings about this condition makes ψ_m an eigenvector of $\mathbf{M}$. The corresponding frequencies are then obtained from the z_j through equation (4) as

$$\omega^2 = \sum_{n=1}^L F_n (2 - z_j^n - z_j^{-n}). \quad (9)$$

Now the $N \times (N+2L)$ rectangular matrix $\mathbf{P}$ (defined in equation 8) has the partitioned form:

$$\mathbf{P} \equiv \begin{bmatrix} \mathbf{M}_{im} & \mathbf{M}' - \mathbf{M} & \mathbf{M}_{mf} \end{bmatrix}. \quad (10)$$

From the definitions of $\mathbf{M}_{im}$ and $\mathbf{M}_{mf}$, it is evident that the only nonvanishing elements of $\mathbf{P}$ constitute an $L \times 2L$ submatrix $\mathbf{P}_1$ located at the top left-hand corner and another $L \times 2L$ submatrix $\mathbf{P}_2$ located at the bottom right-hand corner, their centres being N columns apart. Thus we can rewrite equation (8) as

$$(\mathbf{P}\psi)^t \equiv \begin{bmatrix} (\mathbf{P}_1\psi_1)^t & \dots 0 \dots & (\mathbf{P}_2\psi_2)^t \end{bmatrix} = \mathbf{0}, \quad (11)$$

← L → ← $N-2L$ → ← L →

where the vectors have been transposed for convenience of layout. We have also used

$$(\psi_1)^t \equiv \begin{bmatrix} (\psi_i)^t & (\psi_{m,1})^t \end{bmatrix}, \quad (\psi_2)^t \equiv \begin{bmatrix} (\psi_{m,2})^t & (\psi_f)^t \end{bmatrix}, \quad (12)$$

where $\psi_{m,1}$ represents the first L elements of ψ_m , and $\psi_{m,2}$ represents the last L elements.

If we rewrite equation (11) in terms of the vector Z_j defined by

$$(Z_j)^t \equiv [z_j, z_j^2, \dots, z_j^n, \dots, z_j^{2L}] \quad (13)$$

we obtain

$$\sum_{j=1}^{2L} a_j \begin{bmatrix} \mathbf{P}_1 Z_j \\ z_j^N (\mathbf{P}_2 Z_j) \end{bmatrix} = \mathbf{0}. \quad (14)$$

Thus, effectively equation (14) is a set of $2L$ linear equations for a_j , the solvability condition being the vanishing of the $2L \times 2L$ determinant

$$\begin{vmatrix} \mathbf{P}_1 Z_1 & \mathbf{P}_1 Z_2 & \dots & \mathbf{P}_1 Z_{2L} \\ z_1^N (\mathbf{P}_2 Z_1) & z_2^N (\mathbf{P}_2 Z_2) & \dots & z_{2L}^N (\mathbf{P}_2 Z_{2L}) \end{vmatrix} = 0. \quad (15)$$

If, in this determinant, the z_j are replaced by their known functions of ω , equation (15) is converted into the secular equation for the finite chain. However, it may be computationally advantageous to vary the k_j in $z_j = \exp(ik_j)$ to find the roots of equation (15) since the roots z_j occur in pairs and the physical symmetry of the problem separates them into even and odd types. It is obvious that this method reduces the $N \times N$ secular determinant of the finite chain to a $2L \times 2L$ secular determinant, and is thus advantageous for

$$N > 2L. \quad (16)$$

The method outlined here is clearly suitable for studying torsional and other vibrations of long-chain hydrocarbons, for which Szigeti (1961) developed his method. In these chains, L seldom exceeds 4, and so a comparative study of the vibration spectra of chains of differing lengths becomes rather easy. The present method allows the construction of dynamical matrices involving parameterization of inertia parameters associated with torsional and other modes of such chains to be performed in exactly the same way as in Szigeti's work. An elementary illustration of the use of the present method is given in the Appendix.

We note that the oscillations of long-chain hydrocarbons are rather more complicated than those of a chain of point masses, and therefore the advantages of Szigeti's (1961) approach are in some cases probably much greater than would appear from the condition (16) alone. In this connection it is worth recalling Szigeti's paper. According to the paragraph which follows his equation (10), it is above all the fact that the CH_2 units cannot be treated as point masses which makes it extremely awkward to obtain analytical solutions by the traditional methods.

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Appendix

To illustrate the present method, let us consider a five-unit chain in which each unit interacts with two neighbours, so that

$$\omega^2(k) = 2F_1(1 - \cos k) + 2F_2(1 - \cos 2k). \quad (\text{A1})$$

For mathematical simplicity we choose $F_1 = 1$ and $F_2 = -\frac{1}{4}$. Thus, we have

$$\omega^2(k) = (1 - \cos k)^2 = \frac{1}{4}(1 - z)^4 z^{-2},$$

so that

$$z_{1,2} = (1 + \omega) \pm (\omega^2 + 2\omega)^{\frac{1}{2}}, \quad z_1 = 1/z_2, \quad (\text{A2a, b})$$

$$z_{3,4} = (1 - \omega) \pm (\omega^2 - 2\omega)^{\frac{1}{2}}, \quad z_3 = 1/z_4. \quad (\text{A2c, d})$$

$$\mathbf{M} = \begin{bmatrix} \frac{3}{4} & -1 & \frac{1}{4} & 0 & 0 \\ -1 & \frac{7}{4} & -1 & \frac{1}{4} & 0 \\ \frac{1}{4} & -1 & \frac{3}{2} & -1 & \frac{1}{4} \\ 0 & \frac{1}{4} & -1 & \frac{7}{4} & -1 \\ 0 & 0 & \frac{1}{4} & -1 & \frac{3}{4} \end{bmatrix}, \quad (\text{A3a})$$

$$(\mathbf{M}_{\text{im}})^t = \begin{bmatrix} \frac{1}{4} & 0 & 0 & 0 & 0 \\ -1 & \frac{1}{4} & 0 & 0 & 0 \end{bmatrix}, \quad (\mathbf{M}_{\text{mf}})^t = \begin{bmatrix} 0 & 0 & 0 & \frac{1}{4} & -1 \\ 0 & 0 & 0 & 0 & \frac{1}{4} \end{bmatrix}, \quad (\text{A3b, c})$$

$$\mathbf{M}' - \mathbf{M} = \begin{bmatrix} \frac{3}{4} & 0 & 0 & 0 & 0 \\ 0 & -\frac{1}{4} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{4} & 0 \\ 0 & 0 & 0 & 0 & \frac{3}{4} \end{bmatrix}. \quad (\text{A3d})$$

Thus we obtain

$$\begin{bmatrix} \mathbf{P}_1 \mathbf{Z}_j \\ z_j^N (\mathbf{P}_2 \mathbf{Z}_j) \end{bmatrix} = \frac{1}{4} \begin{bmatrix} z_j^3 (3 - z_j^{-1})(1 - z_j^{-1}) \\ z_j^4 (1 - z_j^2) \\ -z_j^6 (1 - z_j^2) \\ z_j^7 (3 - z_j)(1 - z_j) \end{bmatrix}. \quad (\text{A4})$$

The determinant in equation (15) can be expressed in terms of ω using the equations (A2) and, after some algebra, it can be shown that the even modes have frequencies which satisfy the equations

$$\omega^2 = 0, \quad 4\omega^4 - 17\omega^2 + 10 = 0,$$

or

$$\omega^2 = 0, \quad \omega^2 = \frac{17}{8} \pm \frac{1}{8}\sqrt{129}. \quad (\text{A5a, b})$$

The odd-mode frequencies arise out of

$$8\omega^4 - 18\omega^2 + 1 = 0,$$

or

$$\omega^2 = \frac{9}{8} \pm \frac{1}{8}\sqrt{73}. \quad (\text{A5c})$$

These frequencies can be checked by directly solving the secular equation for **M**.

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