JOURNAL OF COMPUTATIONAL PHYSICS 93, 273–286 (1991)

Closed Form Solution for Localized Modes on a Polymer Chain with a Defect

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Received May 30, 1989; revised September 26, 1989

The problem of localized vibration modes on a polymer chain with a symmetry breaking defect is formulated as a finite sum of exponentially decaying waves on the polymer. Applying a set of similarity and unitary transformations and using the singular value decomposition technique, the size of the problem is reduced to relatively small dimensions as compared to the large size of the original set of equations for propagating modes on the chain. A modification of the polynomial eigenvalue problem converts the algebraic system to a simple eigenvalue problem which may be diagonalized to give eigenvectors of different decaying waves for an expansion set to describe general localized excitations. Application of proper boundary conditions at the site of broken symmetry leads to determination of the frequencies of the localized modes and corresponding eigenvector expansion. Possible applications of the algorithm to various defect problems on a polymer chain are discussed and some preliminary result on a particular defect are presented.

1. INTRODUCTION

An infinite polymer chain, with infinitely repeated monomers, possesses a translational symmetry. This translational symmetry makes the calculation of vibrational properties of the system easier. The chain can be viewed as a one-dimensional periodic lattice with a monomer as its unit cell. This leads to a set of equations of motion equal in number to the number of degrees of freedom N in a monomer. For a typical polymer this number itself may be quite large. This set of equations of motion has as its solutions harmonic propagating waves corresponding to the infinite extent of the chain. These ideas, along with the harmonic approximation, have long been used to calculate the vibrational phonon modes of DNA biopolymers [1], in which N is at least 123. Such a calculation leads to the vibrational spectrum of the system as a relation between the frequency ω of a mode and the wave-vector $\mathbf{k}$ (in case of a double helical DNA polymer the equivalent of $\mathbf{k}$ is the phase angle θ).

In real experimental situations the polymer chains are not infinite in length. The free ends of a finite chain are expected to affect the observable properties of the

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0021-9991/91 $3.00

system. Likewise a defect at some site on the polymer chain may also modify the physical properties of the system. In homopolymers like DNA or RNA a defect at some site is of much biological importance as it may play a significant role in the biological function of the system. For example, a defect in the base sequence or a missing base can give rise to completely different genetical information processing in these important biopolymers. Therefore, a study of the vibrational properties of such homopolyers or copolymers with some type of defects becomes important and deserves very careful theoretical developments.

For a polymer chain with a defect the translational symmetry is broken and one loses the simplifications arising from it. Symmetry breaking introduces new types of motion with relatively large amplitudes at the defect site, decaying to zero far from the defect. These localized excitations cannot be treated with the periodic boundary conditions used for the infinite chain. The simplest example of such a defect is a severed chain with a free end. Green's function-based algorithms have been developed for such a chain to calculate the localized end modes [2]. However, these algorithms involve integrations over the full spectrum of infinite chain modes. As a practical matter, the farther from the defect you study, the more finely spaced the mesh of calculated infinite chain modes must be, thus quickly setting a limit on applicability of the technique. Further, such Green's function-based methods may become very awkward to extend to other, more complex types of defects.

In a polymer chain with a defect, the interesting boundary conditions may be quite different from those for a pure infinite polymer. In addition to propagating waves of constant amplitude, a polymer chain supports exponentially growing or decaying solutions showing a rather richer variety of frequencies and propagation constants. One can, therefore, formulate the problem of localized excitations in terms of a number of exponentially decaying waves with finite amplitudes at the defect site, dying away to either side of the defect. It is expected that there will be only a modest number of such solutions, determined by the number of degrees of freedom linked to the neighbouring cells across the cell boundaries. This reduces the effective computational size of the localized excitation problem to a value relatively much smaller than N (the more complex possibilities for propagation constant introduce compensatory complications, however). This type of formulation can be applied to any set of boundary conditions at the defect, and the corresponding solutions for the localized excitations can then be found algebraically rather than through integration.

In this paper we present a closed form algorithm to calculate localized excitations on a polymer chain with any type of defect. We use the ideas pointed out above and construct general solutions as expansions in terms of a small basis set of exponentially decaying waves. The general formulation presented in Section 2 is independent of defect type. We present a general expansion for the excitations around the defect and develop how to extract the localized modes by applying appropriate boundary conditions. In Section 3 we present an application of this formalism to the semi-infinite polymer chain. We formulate the boundary conditions at the severed end of the chain and present closed form expressions which determine the

localized end modes on such a polymer. In the last section we present our calculations and results for a particular polymer and display the behavior of a local mode obtained through this calculation.

2. Formulation

Propagating harmonic oscillatory waves on an infinite polymer chain are described by

$$\mathbf{q}(m) = \mathbf{q}(0) \exp(i\theta m)\, e^{-i\omega t}, \tag{1}$$

where $\mathbf{q}$'s are N-dimensional vectors describing relative displacements of all the atoms in a monomer. $N = 3M$, where M is the number of atoms in one cell, m is an integer cell index, and θ is a reative phase angle. Equations of motion for the system can be written in matrix form as

$$[\mathbf{A} + \exp(i\theta)\mathbf{B} + \exp(-i\theta)\mathbf{B}^{\mathrm{T}} - \omega^2 \mathbf{I}]\mathbf{q} = \mathbf{0}, \tag{2}$$

where $\mathbf{A}$ is the $N \times N$ matrix, of rank N, of Hooke's law force constants within a unit cell. It is assumed that dynamical connections are of no greater range than one monomer spacing although generalization of this restraint is possible. $\mathbf{B}$ is a matrix of force constants for the connections between—say—cell 0 and cell 1. $\mathbf{B}^{\mathrm{T}}$ is the transpose of $\mathbf{B}$ and represents connections across cells 0 and -1. $\mathbf{B}$ and $\mathbf{B}^{\mathrm{T}}$ are both very sparse singular matrices, each of rank $n \ll N$, ω is the mode frequency, and $\mathbf{I}$ is the identity matrix. This problem can be solved, to obtain mode frequencies and the corresponding eigenvector as functions of θ, by direct diagonalization of the total force constant matrix [1].

The waves of Eq. (1) assume a certain boundary condition at $m = \pm\infty$, namely periodicity, appropriate to the translational symmetry situation. Other solutions exist, however, satisfying different boundary conditions. Waves with finite amplitude at $m = 0$, vanishing as $m \to +\infty$ can also be constructed. A corresponding wave to Eq. (1) is then

$$\mathbf{q}(m) = \mathbf{q}(0) \exp\{i(\theta + i\Delta)m\}, \tag{3}$$

which decays to the right for positive values of Δ.

For a polymer chain with a defect the translational symmetry breaking at the site will lead to the existence of exponentially decaying waves along the chain on either side. In this case the normal mode eigenvectors can be expressed as a sum of solutions like Eq. (3),

$$\mathbf{Q}(m) = \sum_{\lambda} b_{\lambda} \mathbf{q}_{\lambda}(0) \exp\{i(\theta_{\lambda} + i\Delta_{\lambda})m\}, \tag{4}$$

where the Δ_{λ} describe the decay of the constituent waves. The most general possible

dynamical solution consists of vectors like (1) and (3) together, in which case the terms in (4) represent end corrections to the bulk, infinite chain modes. When solutions of the algebraic problem exist containing only terms as in (4), we have a purely local mode. The algebraic problem describing the individual component wave is now written

$$\left[\{\mathbf{A}-\omega^2\mathbf{I}\}+z\mathbf{B}+\frac{1}{z}\mathbf{B}^{\mathrm{T}}\right]\mathbf{q}=\mathbf{0}, \tag{5}$$

where

$$z=\exp(i\theta-\Delta) \tag{6}$$

is a complex number describing the decaying waves. For each fixed frequency ω there exists a set of allowed z values z_λ and corresponding eigenvectors $\mathbf{q}_\lambda$. At this level the size of the problem is $N\times N$ and the solution cannot be obtained by a reltively simple diagonalization.

As the matrices $\mathbf{B}$ and $\mathbf{B}^{\mathrm{T}}$ describe relatively few connections across cell boundaries, they are very sparse. Further, $\mathbf{B}$ and $\mathbf{B}^{\mathrm{T}}$ span complementary subspaces in the N-dimensional space spanned by the complete system, since they represent connections on the opposite sides of the central unit cell. This fact can be used to reduce the effective dimensionality of the problem to a more manageable value. In order to achieve this we need to write these matrices in upper block forms by a set of similarity transformations. To the set of Eqs. (5) we first apply an orthogonal similarity transformation $\mathbf{S}$, moving to a new representation in which $\mathbf{B}+\mathbf{B}^{\mathrm{T}}$ is diagonal,

$$\mathbf{S}^{\dagger}\left[\{\mathbf{A}-\omega^2\mathbf{I}\}+z\mathbf{B}+\frac{1}{z}\mathbf{B}^{\mathrm{T}}\right]\mathbf{S}\cdot\mathbf{S}^{\dagger}\mathbf{q}=\mathbf{0}, \tag{7}$$

to obtain

$$\left[\{\mathbf{A}'-\omega^2\mathbf{I}\}+z\mathbf{B}'+\frac{1}{z}\mathbf{B}'^{\mathrm{T}}\right]\mathbf{q}'=\mathbf{0}. \tag{8}$$

As a practical, computational matter, we next apply a permutation transformation $\mathbf{P}_1$ which rearranges the coordinate axes in such a way that $\mathbf{B}'$ and $\mathbf{B}'^{\mathrm{T}}$ have all their non-zero elements confined as much as possible to an upper left-hand corner block matrix of small dimension $2n\times 2n$, giving

$$\left[\mathbf{A}_0+z\mathbf{B}_0+\frac{1}{z}\mathbf{B}_0^{\mathrm{T}}\right]\mathbf{q}_0=\mathbf{0}, \tag{9}$$

where

$$\mathbf{A}_0=\mathbf{P}_1\mathbf{A}'\mathbf{P}_1^{\mathrm{T}}-\omega^2\mathbf{I}, \tag{10}$$

$$\mathbf{B}_0=\mathbf{P}_1\mathbf{B}'\mathbf{P}_1^{\mathrm{T}}, \tag{11}$$

and

$$\mathbf{q}_0 = \mathbf{P}_1 \mathbf{q}'. \tag{12}$$

Matrices $\mathbf{B}_0$ and $\mathbf{B}_0^{\mathrm{T}}$ now have maximum dimensionality $2n$ corresponding to an upper left block matrix of non-zero elements.

In Eq. (9) the matrices $\mathbf{B}_0$ and $\mathbf{B}_0^{\mathrm{T}}$ have their lower $N-2n$ rows of elements zero and the matrix $\mathbf{A}_0$ does not depend on z. Therefore, for any value of z, a vector $\mathbf{q}_0$ must be orthogonal to all of the lower $N-2n$ rows of the matrix $\mathbf{A}_0$. We proceed by generating the space of all such vectors. To generate this type of vector we now construct a singular, auxiliary matrix $\mathbf{A}_s$ whose topmost $2n$ rows have all zero elements and whose lower $N-2n$ rows are those of the matrix $\mathbf{A}_0$. The needed vectors $\mathbf{q}_0$ span the null space of the matrix $\mathbf{A}_s$, that is,

$$\mathbf{A}_s \cdot \mathbf{q}_0 = \mathbf{0}. \tag{13}$$

The vectors in the null space of a singular matrix can be generated by using the *singular value decomposition* (VSD) technique [3]. The SVD applied to the matrix $\mathbf{A}_s$ leads to a $2n$-dimensional subspace, spanned by $2n$ N-dimensional vectors each of which is individually orthogonal to all of the lower $N-2n$ rows of $\mathbf{A}_s$ and therefore also to the corresponding rows of $\mathbf{A}_0$. Let us denote these N-dimensional vectors by $\mathbf{v}_i$ ($i=1, 2, ..., 2n$). A vector $\mathbf{q}_0$ satisfying Eq. (9) can thus be formed as a linear combination of $\mathbf{v}_i$'s writing

$$\mathbf{q}_0 = \sum_{i=1}^{2n} a_i \mathbf{v}_i. \tag{14}$$

Thus substituting Eq. (14) in Eq. (9) one obtains

$$\sum_{i=1}^{2n} \left[\mathbf{A}_0 + z\mathbf{B}_0 + \frac{1}{z}\mathbf{B}_0^{\mathrm{T}} \right] \mathbf{v}_i a_i = \mathbf{0}. \tag{15}$$

Since lower $N-2n$ rows of $\mathbf{B}_0$ and $\mathbf{B}_0^{\mathrm{T}}$ are zero and the corresponding rows of $\mathbf{A}_0$ are orthogonal to all $\mathbf{v}_i$'s, we can project the matrices $\mathbf{B}_0$, $\mathbf{B}_0^{\mathrm{T}}$, and $\mathbf{A}_0$ on to the subspace of $2n$ vectors $\mathbf{v}_i$'s. Thus Eq. (15) takes the form, in this reduced subspace,

$$\left[\mathbf{A}_1 + z\mathbf{B}_1 + \frac{1}{z}\mathbf{B}_2 \right] \mathbf{a} = \mathbf{0}, \tag{16}$$

where $\mathbf{a}$ is 2n-dimensional vector formed with a_i's as its elements and

$$(\mathbf{A}_1)_{ij} = \sum_{k=1}^{N} (\mathbf{A}_0)_{ik} (\mathbf{v}_j)_k, \tag{17}$$

$$(\mathbf{B}_1)_{ij} = \sum_{k=1}^{N} (\mathbf{B}_0)_{ik} (\mathbf{v}_j)_k, \tag{18}$$

and

$$(\mathbf{B}_2)_{ij} = \sum_{k=1}^{N} (\mathbf{B}_0^T)_{ik} (\mathbf{v}_j)_k \tag{19}$$

for $i, j = 1, 2, ..., 2n$. $(\mathbf{v}_j)_k$ is the k th element of $\mathbf{v}_j$. One can see that the original $N \times N$ problem as given by Eq. (5) has been reduced to a relatively smaller problem of size $2n \times 2n$.

As mentioned earlier, the matrices $\mathbf{B}$ and $\mathbf{B}^T$ span complementary spaces, and in Eq. (8) we transformed the system to a basis where $\mathbf{B} + \mathbf{B}^T$ is diagonal. Therefore matrices $\mathbf{B}_1$ and $\mathbf{B}_2$ are singular in the complementary subspaces. In fact $\mathbf{B}_1$ and $\mathbf{B}_2$ span n-dimensional complementary subspaces and each is singular in the subspace spanned by the other. If $\mathbf{B}_1$ and $\mathbf{B}_2$ were non-singular, one could solve Eq. (16) by direct application of the "polynomial eigenvalue" technique [4], but some preparation is first necessary. In order to sove Eq. (16) we first write it as

$$[z^2\mathbf{B}_1 + z\mathbf{A}_1 + \mathbf{B}_2]\mathbf{a} = \mathbf{0}. \tag{20}$$

In order to reduce this to a simple eigenvalue problem we first need to write the matrix $\mathbf{B}_1$ in an upper (or lower) block diagonal form. Consider the eigenvalues and eigenvectors of $\mathbf{B}_1$. The transformation $\mathbf{U}^{-1}\mathbf{B}_1\mathbf{U}$ diagonalizes $\mathbf{B}_1$. Thus we write Eq. (20) as

$$\mathbf{U}^{-1}[z^2\mathbf{B}_1 + z\mathbf{A}_1 + \mathbf{B}_2]\mathbf{U} \cdot \mathbf{U}^{-1}\mathbf{a} = \mathbf{0} \tag{21}$$

or

$$[z^2\mathbf{B}_1' + z\mathbf{A}_1' + \mathbf{B}_2']\mathbf{a}' = \mathbf{0}, \tag{22}$$

where

$$\mathbf{B}_1' = \mathbf{U}^{-1}\mathbf{B}_1\mathbf{U}, \tag{23}$$

$\mathbf{B}_1'$ is a diagonal matrix and has only n non-zero diagonal elements; correspondingly,

$$\mathbf{A}_1' = \mathbf{U}^{-1}\mathbf{A}_1\mathbf{U}, \tag{24}$$

$$\mathbf{B}_2' = \mathbf{U}^{-1}\mathbf{B}_2\mathbf{U}, \tag{25}$$

and

$$\mathbf{a}' = \mathbf{U}^{-1}\mathbf{a}. \tag{26}$$

We now apply a permutation transformation $\mathbf{P}_2$ which rearranges the coordinate axes in such a way that all the non-zero (diagonal) elements of $\mathbf{B}_1'$ are confined to a lower right-hand $n \times n$ block. This leads to

$$[z^2\mathbf{B}_3 + z\mathbf{A}_2 + \mathbf{B}_4]\mathbf{b} = \mathbf{0}, \tag{27}$$

with

$$\mathbf{A}_2 = \mathbf{P}_2 \mathbf{A}_1' \mathbf{P}_2^{\dagger}, \tag{28}$$

$$\mathbf{B}_4 = \mathbf{P}_2 \mathbf{B}_2' \mathbf{P}_2^{\dagger}, \tag{29}$$

$$\mathbf{b} = \mathbf{P}_2 \mathbf{a}', \tag{30}$$

and

$$\mathbf{B}_3 = \mathbf{P}_2 \mathbf{B}_1' \mathbf{P}_2^{\dagger}. \tag{31}$$

$\mathbf{B}_3$ now has the block diagonal form

$$\mathbf{B}_3 = \begin{bmatrix} \mathbf{0}_n & \mathbf{0}_n \\ 0_n & \mathbf{B}_d \end{bmatrix}, \tag{32}$$

where $\mathbf{B}_d$ is an $n \times n$ diagonal non-singular matrix with the nonzero eigenvalues of $\mathbf{B}_3$ as its elements. $\mathbf{0}_n$ is the nth-order zero matrix. Now using a transformation for singular polynomial eigenvalue systems [5] one can rewrite Eq. (27) as the eigenvalue problem

$$[z\mathbf{C} + \mathbf{D}]\mathbf{c} = \mathbf{0}, \tag{33}$$

where $\mathbf{C}$ and $\mathbf{D}$ are $3n \times 3n$ matrices defined as

$$\mathbf{C} = \begin{bmatrix} & & \mathbf{0}_n \\ & \mathbf{A}_2 & \\ & & \mathbf{I}_n \\ \mathbf{0}_n & \mathbf{B}_d & \mathbf{0}_n \end{bmatrix} \tag{34}$$

and

$$\mathbf{D} = \begin{bmatrix} & & \mathbf{0}_n \\ & \mathbf{B}_4 & \\ & & \mathbf{0}_n \\ \mathbf{0}_n & \mathbf{0}_n & -\mathbf{I}_n \end{bmatrix}, \tag{35}$$

where $\mathbf{I}_n$ is the $n \times n$ identity matrix.

$\mathbf{c}$ is a $3n$-dimensional vector defined as

$$\mathbf{c} = \mathbf{D}_1 \mathbf{b}, \tag{36}$$

where $\mathbf{D}_1$ is a $3n \times 2n$ matrix defined by

$$\mathbf{D}_1 = \left[\begin{array}{c|c} \multicolumn{2}{c}{\mathbf{I}_{2n}} \\ \hline \mathbf{0}_n & z\mathbf{B}_d \end{array}\right] \tag{37}$$

and $\mathbf{I}_{2n}$ is the $2n \times 2n$ identity matrix.

Equation (33) can now be solved first by inverting $\mathbf{C}$ and then diagonalizing $\mathbf{DC}^{-1}$. The matrix $\mathbf{C}$ can be singular only if a $2n \times 2n$ matrix $\mathbf{C}'$, whose first n rows are exactly the same as the corresponding rows of $\mathbf{A}_2$ and whose lower n rows are equal to the corresponding rows of $\mathbf{B}_3$, is also singular [5]. Diagonalizing $\mathbf{DC}^{-1}$ by the standard method finally gives the permitted z values and the corresponding vectors, $\mathbf{c}$. Since the matrix $\mathbf{B}_4$ is singular, the matrix $\mathbf{D}$ is also singular and has n zero eigenvalues. As a result of this, the number of acceptable non-zero solutions for z values is exactly equal to $2n$, the effective dimensionality of the matrix $\mathbf{B}_0$ in Eq. (9). These $2n$ solutions separate into two groups of n solutions each. One set describes waves decaying exponentially to the right of the defect site and the other set waves decaying to the left of the defect site. Let us label these solutions by z_λ^+ and z_λ^- with vectors $\mathbf{c}_\lambda^+$ and $\mathbf{c}_\lambda^-$, respectively, as acceptable solutions of Eq. (33). Let $\theta_\lambda^\pm$ and $\Delta_\lambda^\pm$ represent the values of θ and Δ corresponding to $z_\lambda^\pm$ in accordance with the defining equation (6).

Once we have the set of vectors $\mathbf{c}_\lambda^\pm$ as solutions of Eq. (33) for the values $z_\lambda^\pm$, applying all the transformations in the reverse order, one can obtain the set of vectors $\mathbf{a}_\lambda^\pm$ which are solutions of Eq. (16) for the corresponding z values. These transformations can be written as

$$\mathbf{a}_\lambda^\pm = \mathbf{U}\mathbf{P}_2^\dagger \mathbf{G}_\lambda^\pm \mathbf{c}_\lambda^\pm, \tag{38}$$

where $\mathbf{G}_\lambda^\pm$ is a $2n \times 3n$ matrix defined as

$$\mathbf{G}_\lambda^\pm = \mathbf{F}_\lambda^\pm (\mathbf{D}_\lambda^\pm)^\dagger, \tag{39}$$

with

$$\mathbf{F}_\lambda^\pm = [(\mathbf{D}_\lambda^\pm)^\dagger \mathbf{D}_\lambda^\pm]^{-1}, \tag{40}$$

$\mathbf{D}_\lambda^\pm$ being the same as matrix $\mathbf{D}_1$ with z replaced with $z_\lambda^\pm$.

Using the definition, Eq. (14) one then obtains the vectors $\mathbf{q}_{0\lambda}^{\pm}$ for solutions of Eq. (9) as

$$\mathbf{q}_{0\lambda}^{\pm} = \sum_{j=1}^{2n} (\mathbf{a}_{\lambda}^{\pm})_j \mathbf{v}_j. \tag{41}$$

Finally one obtains for the solution of the original problem Eq. (5) the vectors $\mathbf{q}_{\lambda}^{\pm}$ as

$$\mathbf{q}_{\lambda}^{\pm} = \mathbf{S}\mathbf{P}_1^{\mathrm{T}} \mathbf{q}_{0\lambda}^{\pm}. \tag{42}$$

The vector $\mathbf{q}_{\lambda}^{+}$ represents an exponentially decaying wave of frequency ω and complex phase factor $(\theta_{\lambda}^{+} - i\Delta_{\lambda}^{+})$. A general solution of Eq. (5) for a decaying mode of frequency ω can be formed as a linear combination of all the $2n$ solutions obtained for the $z_{\lambda}^{\pm}$ values. Thus the general (localized) solution $\mathbf{Q}(m, \omega)$ at frequency ω, if one exists, can be written as

$$\mathbf{Q}(m, \omega) = \sum_{\lambda=1}^{n} [b_{\lambda}^{+} \mathbf{q}_{\lambda}^{+} \exp\{m(i\theta_{\lambda}^{+} - \Delta_{\lambda}^{+})\} + b_{\lambda}^{-} \mathbf{q}_{\lambda}^{-} \exp\{m(i\theta_{\lambda}^{-} + \Delta_{\lambda}^{-})\}], \tag{43}$$

where $b_{\lambda}^{\pm}$ are numerical coefficients chosen to fit the apprprpiate boundary condition at the defect site. The solution given by Eq. (43) is a general solution for decaying waves with frequency ω. However, all the solutions for any frequency are not allowed to propogate along the chain. Application of the appropriate boundary conditions, balancing all the symmetry breaking forces at the defect site, determines the frequency and corresponding solution for the localized mode around the defect site. In the next section we discuss a simple application of the algorithm develop in this section.

3. Semi-infinite Polymer Chain

As an example of the application of the algorithm, we discuss the calculation of localized end modes on a semi-infinite polymer chain. This system has been studied before [2] and provides a valuable comparison for our results. Consider an infinite chain divided in two semi-infinite halves by cutting all the connections across the cell boundary between cells 0 and -1. We seek localized end modes on the right half of the chain beginning at cell 0. As the left half of the chain is totally disconnected, any forces coming from the severed part of the chain must be zero. This defines the appropriate boundary conditions at the cut end in terms of the normal interactions. Further, as only the right half of the chain exists, only the basis functions z_{λ}^{+} and $\mathbf{q}_{\lambda}^{+}$ for the waves decaying to the right will be of interest. In this case a general solution for a local mode with frequency ω on the half chain can be written

$$\mathbf{Q}^{+}(m, \omega) = \sum_{\lambda=1}^{n} b_{\lambda}^{+} \mathbf{q}_{\lambda}^{+} (z_{\lambda}^{+})^m \tag{44}$$

$$= \sum_{\lambda=1}^{n} b_{\lambda}^{+} \mathbf{q}_{\lambda}^{+} \exp\{m(i\theta_{\lambda}^{+} - \Delta_{\lambda}^{+})\}. \tag{45}$$

Substituting this solution in the original $N \times N$ equations of motion and then equating all the forces from the missing left half of the chain at the 0th cell to zero, one gets the boundary condition

$$\sum_{\lambda=1}^{n} \mathbf{B}^{\mathrm{T}} \mathbf{q}_{\lambda}^{+} \exp\{-(i\theta_{\lambda}^{+} - \Delta_{\lambda}^{+})\} b_{\lambda}^{+} = 0. \tag{46}$$

If there is any frequency for which this boundary condition can be satisfied with any $b_{\lambda}^{+} \neq 0$ that frequency is a normal mode frequency for a localized excitation, an end mode. The corresponding algebraic system is

$$\mathbf{B}_{c}^{+} \mathbf{b}^{+} = \mathbf{0}, \tag{47}$$

where $\mathbf{B}_{c}^{+}$ is the $n \times n$ matrix defined by

$$(\mathbf{B}_{c}^{+})_{\lambda'\lambda} = \sum_{i=1}^{N} \sum_{j=1}^{N} (\mathbf{q}_{\lambda'}^{+})_{i}^{*} (\mathbf{B}^{\mathrm{T}})_{ij} (\mathbf{q}_{\lambda}^{+})_{j} \exp\{-(i\theta_{\lambda}^{+} - \Delta_{\lambda}^{+})\}. \tag{48}$$

The vector $\mathbf{b}^{+}$ comprises the coefficients b_{λ}^{+}. The existence of a solution is signalled by the vanishing of $\det |\mathbf{B}_{c}^{+}|$ or any of its eigenvalues. This finally leads to the complete solution for the eigenvector (Eq. (44)) of the localized end mode.

It should be noted that the localized mode problem in this formalism has been reduced to $n \times n$ size as compared to the large size $N \times N$ of the original set of equations of motion. Further, this method gives the complete eigenvectors of the localized modes directly and allows computation of behavior arbitrarily deep into the chain. Our earlier investigations [2] into this problem could yield this information in principle, but only at the computational cost of more and more finely spaced infinite chain solutions. This method also lends itself to investigations of other sorts of defects. Once the basis functions $\mathbf{q}_{\lambda}^{\pm}$ are obtained, different boundary solutions can be readily expanded, and closed form expressions written down. Unfortunately, a scan on ω is still required.

4. Calculation and Results

We have made numerical calculations, based on the method described in the last two sections, for possible localized end modes on a semi-infinite Poly(dA)-Poly(dT) B-form DNA polymer. In this case $N = 123$ and n turns out to be 14. An interesting frequency range runs from 70.00 to 73.55 cm^{-1}, a band gap in the normal mode spectrum of the infinite, perfect Poly(dA)-Poly(dT) polymer with the force constant model used in the present calculation. In the range of frequencies scanned, most of the eigenvalues of the boundary condition matrix $\mathbf{B}_{c}^{+}$ as well as its determinant are real. In Fig. 1 we have plotted the quantity

$$h(\omega) = \mathrm{Sign}[v(i)] \times \log[1 + |v(i)| \times 10^{8}] \tag{49}$$

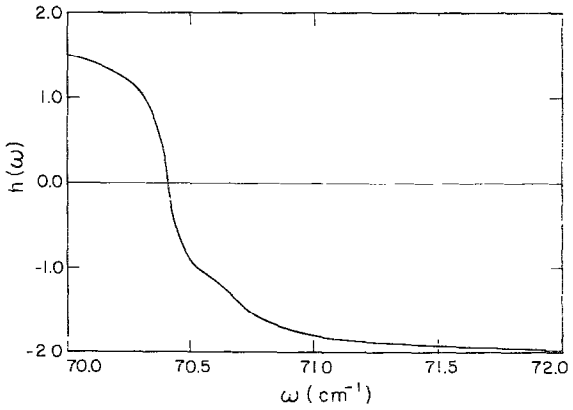

FIG. 1. Variation of the real-part of one of the eigenvalues $v(i)$ of the matrix $\mathbf{B}_c^+$, shown as the quantity $h(\omega) = \text{Sign}[v(i)] * \log[1 + |v(i)| \times 10^8]$ plotted as a function of frequency ω.

as a function of frequency ω; $v(i)$ is the eigenvalue (real) of the matrix $\mathbf{B}_c^+$ which changes sign within the frequency range stated above. None of the other eigenvalues of this matrix pass through zero in this range of frequencies. Figure 2 displays the quantity

$$\text{Sign}(D) \log\{1 + |D|\} \tag{50}$$

as a function of frequency ω, where D is the determinant (real) of the matrix $\mathbf{B}_c^+$. From these two figures one can see that the plotted quantities vanish at the frequency 70.41 cm^{-1}, indicating that the boundary condition Eq. (47) is satisfied for this frequency. Thus we have found a local mode frequency. In Table I we list the values of $A_\lambda^+, \theta_\lambda^+$, and the corresponding coefficients b_λ^+, which satisfy the boundary condition Eq. (47) for this frequency.

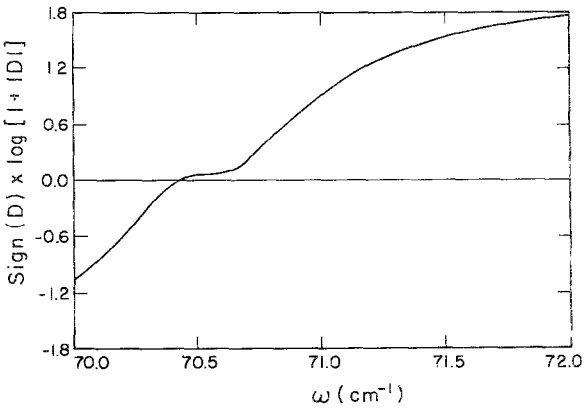

FIG. 2. Variation of the determinant D (real) of the matrix $\mathbf{B}_c^+$, shown as the quantity $\text{Sign}(D) * \log[1 + |D|]$ as a function of frequency ω.

TABLE I

Values of Δ_λ^+, θ_λ^+, and b_λ^+ which satisfy the boundary conditions for the local mode at 70.41 cm^{-1}

λ	Δ_λ^+	θ_λ^+	$\mathrm{Re}(b_\lambda^+)$	$\mathrm{Im}(b_\lambda^+)$
1	−15.816439	−0.048032	0.013309	0.066880
2	−15.180337	0.007213	−0.009246	−0.053948
3	−7.011092	−0.000052	−0.009248	−0.077890
4	−4.715403	0.000006	−0.027370	−0.199343
5	−4.518871	0.210324	−0.137135	0.045323
6	−4.518871	−0.210324	0.144305	0.008052
7	−3.540579	1.167920	−0.057425	0.585608
8	−3.540579	−1.167920	0.208143	0.549201
9	−2.672197	0.000000	−0.025715	−0.194507
10	−1.412505	0.542678	0.015540	−0.204332
11	−1.412505	−0.542678	−0.068583	−0.193134
12	−0.847147	0.000000	0.038675	0.289859
13	−0.685792	−0.962110	0.047807	−0.010317
14	−0.685792	0.962110	−0.048806	0.002576

Once the coefficients b_λ^+ are known one can construct the vectors $\mathbf{Q}(m)$, from Eq. (45), for various cells. We chose a typical coordinate i and calculated the ratio

$$a_i(m) = \frac{(\mathbf{Q}^+(m))_i}{(\mathbf{Q}^+(0))_i} \tag{51}$$

which measures the displacement of the coordinate i in cell m relative to the same coordinate in cell 0. For the mode at 70.41 cm^{-1} this ratio turns out to be essentially real and decays rapidly with increasing cell number. To display this behavior we have plotted in Fig. 3 the quantity

$$\mathrm{amp}(m) = \mathrm{Sign}(\mathrm{Re}[a_i(m)]) \times \log\{1 + |a_i(m)| \times 10^6\}. \tag{52}$$

We find the behavior of amp(m) as expected for a localized mode. It oscillates, with decreasing amplitude, for the first few cells and then dies out. The amplitude of $a_i(m)$ decays to about 1% of its value at the cut within five cells. Thus it is clear that this is a well-defined local mode confined within a few cells of the free end. The eigenvector $\mathbf{Q}^+(0)$ at the cut end for this local mode has a strong component along the eigenvector of the nearest band edge at 70.02 cm^{-1}.

This example shows a single local mode in this band gap. Similar scans of other ranges of frequency ω show other local modes. To find out all possible local modes the whole range of frequencies covered by the spectrum of the infinite perfect polymer should be scanned.

This completes our exposition of an algorithm for calculating the localized modes on a polymer chain with a defect. We have formulated the problem in terms of

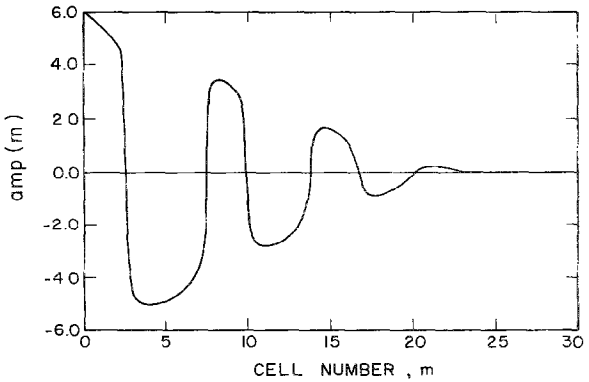

FIG. 3. Variation of the quantity amp(m) with the cell number m.

exponentially decaying waves along the chain. By applying the singular value decomposition technique, we have reduced the effective size of the problem to a relatively small value. Using a set of similarity transformations and a transformation for polynomial eigenvalue systems, the system of equations is reduced to a simple eigenvalue equation which gives closed form solutions for the exponentially decaying waves on the chain. Application of appropriate boundary conditions, balancing the resultant symmetry breaking forces at the defect site, leads to the determination of the local mode eigenfrequencies and the corresponding eigenvectors. An important feature of the method is that it gives the complete eigenvectors of the localized modes, leading to a complete physical picture of the motions characteristic of the local mode. This feature and the closed form solution in reduced space make this method potentially more useful as compared to other existing methods based on perturbative expansion or Green's function based algorithms.

5. DISCUSSION

In summary, we have developed a method to solve the $N \times N$ quadratic eigenvalue problem of the form

$$[z^2\mathbf{B} + z\mathbf{A} + \mathbf{B}^T]\mathbf{q} = 0, \tag{53}$$

where $\mathbf{B}$ and $\mathbf{B}^T$ are very sparse singular matrices. By using a series of similarity transformations and using the polynomial eigenvalue technique [5] we have been able to reduce the size of the problem from $N \times N$ to $n \times n$, where n is the rank of $\mathbf{B}$ or $\mathbf{B}^T$. We have obtained experience running the code based on this method for a model DNA polymer, where $N = 123$. On essentially equivalent systems, VAX 750, ISI, and Mac II machines, the code runs satisfactorily and leads to

physical solutions for the localized end modes for a semi-infinite DNA polymer. Hence this algorithm represents a practical solution to a thorny numerical problem and is not merely an exercise in computer theory. For DNA, the size of the problem is reduced to 14×14 compared to the original 123×123.

As mentioned earlier the method described in this paper can be successfully coded and applied to various types of defects on homopolymers and copolymers with localized defects, where a finite set of local mode solutions will appear as solutions. Another possible application of the method may be in surface physics, for example, for obtaining the localized surface modes in a three-dimensional semi-infinite solid, where a band of frequencies would appear as a final solution of the problem. We have not developed this application.

ACKNOWLEDGMENT

This work was performed under the Office of Navel Research (ONR) Contract No. N00014-87-K-0162 funded by the SDIO.

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