

Chapt. 4: Vibrational Normal Modes: A Classical Mechanical Perspective

1 Illustration in a Prototypical Case

Consider the following collinear spring system:

$$\text{wall} - k_1 - m_1 - k_2 - m_2 - k_3 - \text{wall}$$

That is, there are two balls having masses m_1 and m_2 , respectively. They are connected to each other and to immobile walls via three springs, as shown in the figure. The position along the x-axis of each ball is measured by its displacement from the system's equilibrium configuration; these displacements are denoted as x_1, x_2 . The potential energy of the configuration (x_1, x_2) is given by:

$$V(x_1, x_2) = \frac{1}{2}k_1x_1^2 + \frac{1}{2}k_2(x_2 - x_1)^2 + \frac{1}{2}k_3x_2^2, \quad (1)$$

where $k_{1,2,3}$ are the spring constants that characterize the three springs. The function indicated above is a sum of three terms, one accounting for the extension/compression of each spring from its unstretched position. Now we can appeal to Newton's Second Law to get the equation of motion for each ball:

$$m\ddot{x}_1 = -\partial V/\partial x_1 = -k_1x_1 + k_2(x_2 - x_1) \quad (2)$$

$$m\ddot{x}_2 = -\partial V/\partial x_2 = -k_3x_2 + k_2(x_1 - x_2) \quad (3)$$

To simplify the introduction of the concept of normal modes, let us specialize to the case $m_1 = m_2 = m$ and $k_1 = k_3 = \kappa$. Eqs. (1) now take the form:

$$m \begin{pmatrix} \ddot{x}_1 \\ \ddot{x}_2 \end{pmatrix} = - \begin{bmatrix} \kappa + k_2 & -k_2 \\ -k_2 & \kappa + k_2 \end{bmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \quad (4)$$

To solve these equations, we make the ansatz that a solution of the form $(x_1(t), x_2(t)) = (v_1, v_2)\cos(\omega t)$ exists, with $\vec{v}^t = (v_1, v_2)$ being a constant vector and ω an angular frequency parameter to be determined. This ansatz, when substituted into Eq. 4, generates the eigenvalue/eigenvector equation:

$$\lambda \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = \begin{bmatrix} \kappa + k_2 & -k_2 \\ -k_2 & \kappa + k_2 \end{bmatrix} \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} \quad (5)$$

with $\lambda \equiv m\omega^2$. There are only a small number of nonzero vectors (in fact, 2, for the case of a 2×2 matrix considered in this example) for which this equality can be satisfied. Each such vector, called an ‘‘eigenvector’’, corresponds to a specific ‘‘eigenvalue’’, λ . The procedure for determining the eigenvalues and eigenvectors of an arbitrary $N \times N$ matrix is well-known from the theory of linear algebra (cf. Refs. below). The necessary manipulations are tedious but straightforward: in particular, they are easily carried out on digital computers. Mathcad has built-in routines that will find the eigenvalues/vectors of any matrix. We can exploit them to calculate normal modes of spring systems, e.g., molecules!

Although numerical methods are essential in the general case, for the simple example presented in Eq. 5, we can deduce the eigenvectors/values by inspection. The two eigenvectors are:

$$\vec{v}_1 = \begin{pmatrix} 1 \\ 1 \end{pmatrix} ; \vec{v}_2 = \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad (6)$$

It can easily be verified that \vec{v}_1 satisfies Eq. 5 if $\lambda_1 = \kappa$; analogously, \vec{v}_2 satisfies Eq. 5 if $\lambda_2 = \kappa + 2k_2$. Note that this implies vibrational frequencies $\omega_1 = \sqrt{\kappa/m}$ and $\omega_2 = \sqrt{(\kappa + 2k_2)/m}$ for the two normal modes of vibration.

Since \vec{v}_1 and \vec{v}_2 are orthogonal ($\vec{v}_1 \cdot \vec{v}_2 = 0$) the most general motion of this two coordinate system can be written as a superposition of the two normal modes, i.e.

$$\vec{x}(t) = [\alpha_1 \cos(\omega_1 t) + \beta_1 \sin(\omega_1 t)] \vec{v}_1 + [\alpha_2 \cos(\omega_2 t) + \beta_2 \sin(\omega_2 t)] \vec{v}_2 \quad (7)$$

Here $\alpha_{1,2}$ and $\beta_{1,2}$ are superposition coefficients which are uniquely determined by the initial position and velocities of the two coordinates, i.e. $\vec{x}(0)$ and $\dot{\vec{x}}(0)$. [For example, if $\vec{x}(0)^t = (1, 0)$ and $\dot{\vec{x}}(0) = \vec{0}$, then $\alpha_{1,2} = 1/2$ and $\beta_{1,2} = 0$.]

In the next section we generalize the arguments and examples presented here to an arbitrary system undergoing small vibrations.

2 General Theory of Normal Modes of Molecular Vibration

In general, a molecule is a 3D structure comprising N atoms. To begin, place the molecule in its equilibrium configuration (the overall orientation of the molecule is irrelevant).

Attach a space-fixed cartesian coordinate system to each atom – the displacements of each atom from will be measured as “ (x, y, z) ” with respect to its coordinate axes. Thus the total configuration space of displacements is $3N$ dimensional. Since the system is in equilibrium when all the displacements are zero, the restoring force along each cartesian coordinate of each atom will be linear. This is equivalent to the statement that the $3N$ dimensional potential energy function has a global minimum at this atomic configuration [1], which in turn implies that for small displacements the potential can be represented as a quadratic expansion about the equilibrium configuration. Hence, Newton’s Eqs. for small-amplitude displacements of the molecule about equilibrium take the form:

$$\mathbf{m}\ddot{\vec{x}}(t) = -\mathbf{V}''\vec{x}(t) \tag{8}$$

Here $\vec{x}(t)$ is the $3N$ dimensional vector of cartesian displacements of the atoms with respect to their equilibrium configurations. Moreover, \mathbf{m} is a diagonal matrix of atom masses (the same mass applies for all three cartesian coordinates of each atom!), and \mathbf{V}'' is the (symmetric) matrix of second derivatives of the potential about the equilibrium configuration; both matrices are $3N \times 3N$ dimensional. Next comes the crucial ansatz that solutions corresponding to simple harmonic motion exist, i.e. $\vec{x}(t) = \cos(\omega t)\vec{x}_0(t)$, where \vec{x}_0 is the initial displacement vector and ω and appropriate frequency (both to be determined). This converts the Newton’s Eqs. in Eq. 8 to an eigenvalue/vector problem:

$$\omega^2\mathbf{m}\vec{x}_0 = \mathbf{V}''\vec{x}_0 \tag{9}$$

Eq. 9 prescribes the essential eigenvalue/vector calculation. For computational convenience, it proves useful to massage it in the following way. Define $\vec{y}_0 = \mathbf{m}^{1/2}\vec{x}_0$. Here $\mathbf{m}^{1/2}$ is simply the square root of the mass matrix, i.e. a diagonal $3N \times 3N$ matrix with square roots of the appropriate masses along the diagonal. The coordinates \vec{y} defined in this way are called “mass weighted” coordinates for obvious reasons. With this substitution Eq. 9 becomes:

$$\lambda\vec{y}_0 = \mathbf{U}\vec{y}_0, \tag{10}$$

where $\lambda \equiv \omega^2$ and $\mathbf{U} \equiv \mathbf{m}^{-1/2}\mathbf{V}''\mathbf{m}^{-1/2}$. Note that \mathbf{U} is a (real) symmetric matrix, which guarantees that its $3N$ eigenvectors will be orthogonal. This is the principal reason for not working with Eq. 9, which entails diagonalization of a non-symmetric matrix ($\mathbf{m}^{-1}\mathbf{V}''$).

Two final comments are in order. The first concerns how \mathbf{V}'' , the matrix of cartesian second derivatives at equilibrium, is calculated. One way is to “write down” a potential energy function as a sum of all “local springs” holding the molecule together. This

includes bond stretches, bending motions, and hindered torsions. Each term will consist of a quadratic function (minimized at equilibrium) in the appropriate internal coordinate with an appropriate force constant. (The force constants can be calculated in principle from molecular electronic structure theory, or fit from measured optical spectra.) Then the desired cartesian second derivatives follow from a little geometry and judicious application of the chain rule.

Finally, we should note some important characteristics of the normal mode eigenvalues/vectors found from Eq. 10. For a nonlinear molecule, 6 of the eigenvalues λ will be 0. These correspond to 3 overall center of mass translations and 3 rotations. (The nature of the motions can be ascertained from the displacement eigenvector \vec{y}_0 .) The remaining $3N - 6$ eigenvalues will be positive, corresponding to real angular frequencies $\omega = \sqrt{\lambda}$. These are proper vibrational normal modes – the specific vibrational pattern that goes with a given vibrational frequency is prescribed by the corresponding displacement eigenvector. The same comments apply for a linear molecule, except that there are only 5 zero eigenvalues (3 center of mass translations and 2 overall rotations), leaving $3N - 5$ proper vibrations.

[1] In fact, one subtlety arises in treating the vibrations of an isolated molecule. There are six collective motions which generate zero restoring force (these are the “center of mass translations” and “overall rotations” discussed below). The simplest way not to disrupt the argument under development here is to artificially “attach” the molecule to walls by weak springs. Then *all* motions are restored to a unique equilibrium configuration. The force constants associated with the artificial constraining springs can be taken to zero at the end of the argument, which will produce the final results attained in this section.

References: Discussions of basic linear algebra and matrix manipulations can be found in: H.G. Campbell, *Matrices with Applications* (Meredith Corp., N.Y., 1968); T.M. Apostol *Calculus*, Vol. 2 (Xerox College Publishing, Waltham, Mass, 1969).