

## 17.11: A General Vibrating System

For convenience, I'll refer to a collection of masses connected by springs as a "molecule", and the individual masses as "atoms". In a molecule with  $N$  atoms, the number of degrees of vibrational freedom (the number of normal modes of vibration)  $n = 3N - 6$  for nonlinear molecules, or  $n = 3N - 5$  for linear molecules. Three equations are needed to express zero translational motion, and three (or two) are needed to express zero rotational motion.

While reading this Section, it might be worthwhile for the reader to follow at the same time the treatment given to the OCS molecule in Section 17.6. Bear in mind, however, that in that section we did not consider the possibility of the molecule bending. Indeed we treated the molecule as if it were constrained inside a drinking straw, and it remained linear at all times. That being the case only  $N$  coordinates (rather than  $3N$ ) suffice to describe the state of the molecule. Only one equation is needed to express zero translational motion, and none are needed to express zero rotational motion. Thus there are  $N - 1$  internal coordinates, and hence  $N - 1$  normal vibrational modes. In the case of OCS,  $N = 3$ , so there are two normal vibrational modes.

A molecule with  $n$  degrees of vibrational freedom can be described at some instant of time by  $n$  internal coordinates  $q_i$ . A typical such coordinate may be related to the external coordinates of two atoms, for example, by some expression of the form  $q = x_2 - x_1 - a$ , as we saw in our example of the molecule OCS. Its potential energy can be written in the form

$$\begin{aligned} 2V = & \kappa_{11}q_1^2 + \kappa_{12}q_1q_2 + \dots + \kappa_{1n}q_1q_n \\ & + \kappa_{21}q_2q_1 + \kappa_{22}q_2^2 + \dots + \kappa_{2n}q_2q_n \\ & + \dots \\ & + \kappa_{n1}q_nq_1 + \kappa_{n2}q_nq_2 + \dots + \kappa_{nn}q_nq_n. \end{aligned} \quad (17.11.1)$$

Unless the  $q$  are the judiciously chosen "normal coordinates" (see our example of the transverse vibrations of three masses on an elastic string), there will in general be cross terms, such as  $q_1q_2$ . If both  $qs$  of a term are linear displacements, the corresponding  $\kappa$  is a force constant (dimensions  $MT^{-2}$ ). If both  $qs$  are angles,  $\kappa$  is a torsion constant (dimensions  $ML^2T^{-2}$ ). If one is a linear displacement and the other is an angular displacement,  $\kappa$  will be a coefficient of dimensions  $MLT^{-2}$ .

The matrix is symmetric, so that Equation 17.11.1 could also be written

$$\begin{aligned} 2V = & \kappa_{11}q_1^2 + \kappa_{12}q_1q_2 + \dots + 2\kappa_{1n}q_1q_n \\ & + \kappa_{22}q_2^2 + \dots + 2\kappa_{2n}q_2q_n \\ & + \dots \\ & + \kappa_{nn}q_nq_n. \end{aligned} \quad (17.11.2)$$

In matrix notation, the Equation (i.e. Equations 17.11.1 or 17.11.2) could be written:

$$2V = \tilde{\mathbf{q}}\kappa\mathbf{q}. \quad (17.11.3)$$

or in vector/tensor notation,

$$2V = \mathbf{q} \cdot \kappa \mathbf{q}. \quad (17.11.4)$$

The kinetic energy can be written in terms of the time rates of change of the external coordinates  $x_i$ :

$$2T = m_1\dot{x}_1^2 + m_2\dot{x}_2^2 + \dots + m_{3N}\dot{x}_{3N}^2. \quad (17.11.5)$$

To make use of the Lagrangian equations of motion, we need to express  $V$  and  $T$  in terms of the same coordinates, and it is usually advantageous if these be the  $n$  internal coordinates rather than the  $3N$  external coordinates – so that we have to deal with only  $n$  rather than  $3N$  lagrangian equations. (Recall that  $n = 3N - 6$  or  $5$ .) The relations between the external and internal coordinates are given as a set of equations that express a choice of coordinates such that there is no pure translation and no pure rotation of the molecule. These equations are of the form

$$\mathbf{q} = \mathbf{A}\mathbf{x}. \quad (17.11.6)$$

Here  $\mathbf{q}$  is an  $n \times 1$  column matrix,  $\mathbf{x}$  a  $3N \times 1$  column matrix, and  $\mathbf{A}$  is a matrix with  $n$  rows and  $3N$  columns, and it may need a little trouble to set up. We could then use this to express  $V$  in terms of the external coordinates, so we would then have both  $V$  and

$T$  in terms of the external coordinates. We could then apply Lagrange's equation to each of the  $3N$  external coordinates and arrive at  $3N$  simultaneous differential equations of motion.

A better approach is usually to set up the equations connecting  $\dot{q}$  and  $\dot{x}$ :

$$\dot{\mathbf{q}} = \mathbf{B}\dot{\mathbf{x}}. \quad (17.11.7)$$

(These correspond to Equations 17.6.3 and 17.6.4 in our example of the linear triatomic molecule in Section 17.6.) We then want to invert Equation 17.11.7 in order to express  $\dot{x}$  in terms of  $\dot{q}$ . But we can't do this, because  $\mathbf{B}$  is not a square matrix.  $\dot{x}$  has  $3N$  elements while  $\dot{q}$  has only  $n$ . We have to add an additional six (or five for linear molecules) equations to express zero pure translational and zero pure rotational motion. This adds a further 6 or 5 rows to  $\mathbf{B}$ , so that  $\mathbf{B}$  is now square (this corresponds to Equation 17.6.6), and we can then invert Equation 17.11.7

$$\dot{\mathbf{x}} = \mathbf{B}^{-1}\dot{\mathbf{q}} \quad (17.11.8)$$

(This corresponds to Equation 17.6.7.)

By this means we can express the kinetic energy in terms of the time rates of change of only the  $n$  internal coordinates:

$$\begin{aligned} 2T = & \mu_{11}\dot{q}_1^2 + \mu_{12}\dot{q}_1\dot{q}_2 + \dots + \mu_{1n}\dot{q}_1\dot{q}_n \\ & + \mu_{21}\dot{q}_2\dot{q}_1 + \mu_{22}\dot{q}_2^2 + \dots + \mu_{2n}\dot{q}_2\dot{q}_n \\ & + \dots \\ & + \mu_{n1}\dot{q}_n\dot{q}_1 + \mu_{n2}\dot{q}_n\dot{q}_2 + \dots + \mu_{nn}\dot{q}_n^2 \end{aligned} \quad (17.11.9)$$

Since the matrix is symmetric, the equation could also be written in a form analogous to Equation 17.11.2. The equation can also be written in matrix notation as

$$2T = \dot{\mathbf{q}}\mu\dot{\mathbf{q}}. \quad (17.11.10)$$

or in vector/tensor notation,

$$2T = \dot{\mathbf{q}} \cdot \mu \dot{\mathbf{q}}. \quad (17.11.11)$$

Here the  $\mu_{ij}$  are functions of the masses. If both  $q$ s in a particular term have the dimensions of a length, the corresponding  $\mu$  and  $\kappa$  will have dimensions of mass and force constant. If both  $q$ s are angles, the corresponding  $\mu$  and  $\kappa$  will have dimensions of rotational inertia and torsion constant. If one  $q$  is a length and the other is an angle, the corresponding  $\mu$  and  $\kappa$  will have dimensions ML and MLT<sup>-2</sup>.

Apply Lagrange's equation successively to  $q_1, \dots, q_n$  to obtain  $n$  equations of the form

$$\mu_{11}\ddot{q}_1 + \dots + \mu_{1n}\ddot{q}_n + \kappa_{11}q_1 + \dots + \kappa_{1n}q_n = 0. \quad (17.11.12)$$

That is to say

$$\mu\ddot{\mathbf{q}} = -\kappa\mathbf{q}. \quad (17.11.13)$$

Seek simple harmonic solutions of the form  $\ddot{q} = -\omega^2 q$

and we obtain  $n$  equations of the form

$$(\kappa_{11} - \mu_{11}\omega^2)q_1 + \dots + (\kappa_{1n} - \mu_{1n}\omega^2)q_n = 0. \quad (17.11.14)$$

The frequencies of the normal modes can be obtained by equating the determinant of the coefficients to zero, and hence the displacement ratios can be determined.

If  $N$  is large, this could be a formidable task. The work can be very much reduced by making use of symmetry relations of the molecule, in which case the determinant of the coefficients may be factored into a number of much smaller subdeterminants. Further, if the configuration of the molecule could be expressed in terms of *normal coordinates* (combinations of the internal coordinates) such that the potential energy contained no cross terms, the equations of motion for each normal coordinate would be in the form  $\ddot{q} = -\omega^2 q$ .

This page titled 17.11: A General Vibrating System is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Jeremy Tatum via source content that was edited to the style and standards of the LibreTexts platform.