

# Chapter 4 Small Oscillations

## 4-1 Introduction

The systems of interacting particles we studied in the previous chapter in connection with the motion of rigid bodies were many-body systems of a rather special type because of the assumed nature of the interactions between particles (they were such as to render the system *rigid*). Here, we discuss another many-body problem of a rather special type: small oscillations of the constituent particles of the system about a stable equilibrium configuration. Such systems are realized, by for example, relaxing the condition of complete rigidity imposed in Chap. 3, but considering only small displacements away from equilibrium of the particles forming a rigid body. Notice that there is no guarantee that displacing particles in a many-body system away from their equilibrium positions in this manner always leads to oscillatory motion. For that to happen, the equilibrium configuration must be a *stable* one. This in turn is dictated by the nature of the potential energy function of the system in the neighborhood of the equilibrium configuration.

## 4-2 A simple example: Coupled pendulums.

To begin the study of small oscillations we look at a typical problem and try to guess a solution. Afterwards, we can proceed with the formal theory that leads to the solution in an organized and rigorous fashion. The rather innocent looking problem we discuss first is that of two simple pendulums each of length  $l$ , coupled to each other by a weightless spring, see Fig. 4.1(a).

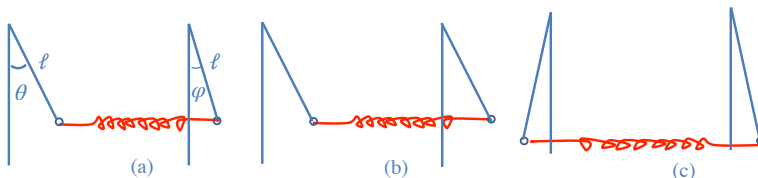


Figure 4.1: Coupled pendulums.

In terms of the angular displacements  $\theta$  and  $\phi$  the Lagrange function is readily found to be

$$L = \frac{1}{2}ml^2\dot{\theta}^2 - mgl(1 - \cos\theta) + \frac{1}{2}ml^2\dot{\phi}^2 - mgl(1 - \cos\phi) - \frac{1}{2}m\kappa l^2(\theta - \phi)^2,$$

if  $m$  is the mass of either bob, and  $\kappa$  is the spring constant. The last term in this expression provides a coupling between the free motion of each pendulum separately. Call  $x_1, x_2$  the horizontal displacements of each bob from the equilibrium positions. Then, for *small* displacements ( $l\theta, l\phi \ll 1$ )

$$x_1 \simeq l\theta, \quad x_2 \simeq l\phi,$$

and the Lagrange function becomes

$$L \simeq \frac{1}{2}m\dot{x}_1^2 + \frac{1}{2}m\dot{x}_2^2 - \frac{1}{2}m\omega_0^2 x_1^2 - \frac{1}{2}m\omega_0^2 x_2^2 - \frac{1}{2}m\kappa(x_1 - x_2)^2,$$

where  $\omega_0 = \sqrt{g/l}$  is the angular frequency of either pendulum oscillating freely. The equations of motion for  $x_1$  and  $x_2$  are

$$\frac{\partial L}{\partial x_k} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}_k}\right) = 0, \quad k = 1, 2,$$

or

$$\begin{aligned} \ddot{x}_1 + \omega_0^2 x_1 &= -\kappa(x_1 - x_2) \\ \ddot{x}_2 + \omega_0^2 x_2 &= -\kappa(x_2 - x_1). \end{aligned}$$

These equations are not independent because of the *foreign* coordinate  $x_1$  or  $x_2$  on the right hand sides of these equations respectively. If it were not for such *coupling terms* each pendulum would oscillate with its own frequency  $\omega_0$ . We try a solution of the form

$$x_1 = u_1 e^{i\Omega t}, \quad x_2 = u_2 e^{i\Omega t},$$

(we later can take real or imaginary parts, see remarks below (2.9)), where  $\Omega$  is an unknown but common frequency and  $u_1, u_2$  arbitrary amplitudes. This solution is compatible with the equations of motion if

$$\begin{aligned} (\omega_0^2 + \kappa - \Omega^2)u_1 - \kappa u_2 &= 0 \\ -\kappa u_1 + (\omega_0^2 + \kappa - \Omega^2)u_2 &= 0 \end{aligned}$$

or

$$\begin{bmatrix} \omega_0^2 + \kappa - \Omega^2 & -\kappa \\ -\kappa & \omega_0^2 + \kappa - \Omega^2 \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} = 0.$$

Thus, we obtain a pair of *homogeneous* algebraic equations for the amplitudes  $u_1$  and  $u_2$ . These are non-zero only if the determinant of their coefficients vanishes, that is

$$\begin{vmatrix} \omega_0^2 + \kappa - \Omega^2 & -\kappa \\ -\kappa & \omega_0^2 + \kappa - \Omega^2 \end{vmatrix} = (\omega_0^2 + \kappa - \Omega^2)^2 - \kappa^2 = 0,$$

which provides for a determination of the unknown  $\Omega$ . This is an algebraic equation of the second degree in  $\Omega^2$ . Hence, there are *two* possible frequencies

$$\Omega_1 = \omega_0, \quad \text{and} \quad \Omega_2 = \sqrt{\omega_0^2 + 2\kappa} \simeq \omega_0 + \frac{\kappa}{\omega_0},$$

the last approximation holding if the coupling is weak,  $\kappa/\omega_0^2 \ll 1$ , at which  $x_1$  and  $x_2$  can vibrate. The two values of  $\Omega$  we have just found are called *eigenfrequencies* of the coupled system. The amplitudes of  $x_1$  and  $x_2$  in an *eigenvibration*, or *normal mode*, are found by returning to the homogeneous equations for  $u_1$  and  $u_2$  and substituting in the two values of  $\Omega$ . Thus, for  $\Omega = \Omega_1$  we find

$$\begin{bmatrix} \kappa & -\kappa \\ -\kappa & \kappa \end{bmatrix} \begin{bmatrix} u_1^{(1)} \\ u_2^{(1)} \end{bmatrix} = 0, \quad \text{or} \quad u_1^{(1)} = u_2^{(1)}$$

and for  $\Omega = \Omega_2$

$$\begin{bmatrix} -\kappa & -\kappa \\ -\kappa & -\kappa \end{bmatrix} \begin{bmatrix} u_1^{(2)} \\ u_2^{(2)} \end{bmatrix} = 0, \quad \text{or} \quad u_1^{(2)} = -u_2^{(2)},$$

now adding superscripts 1 and 2 to the  $u$ 's to distinguish between the two normal modes. Thus, only the *ratios* of  $u_1$  to  $u_2$  are determined. The motion of the system in the normal mode  $\Omega_1 = \omega_0$  thus has ( $\alpha_1$  is the phase of the arbitrary complex amplitude  $A_1$ )

$$x_1 = x_2 = \text{Re}(A_1 e^{i\Omega_1 t}) = |A_1| \cos(\Omega_1 t + \alpha_1)$$

or the pendulums oscillating in phase without ever stretching the spring, while the mode  $\Omega_2 = \sqrt{\omega_0^2 + 2\kappa}$  has the pendulums oscillating out of phase,

$$x_1 = -x_2 = \text{Re}(A_2 e^{i\Omega_2 t}) = |A_2| \cos(\Omega_2 t + \alpha_2),$$

with  $A_2 = |A_2| \exp i\alpha_2$  as before. The two normal modes are shown in Fig. 4.1(b) and (c).

The solutions we have just found are clearly very special. They are called the *eigensolutions*, or *eigenvibrations*, of the system. In terms of them, we can write the general solutions as the superpositions

$$x_1 = |A_1| \cos(\Omega_1 t + \alpha_1) + |A_2| \cos(\Omega_2 t + \alpha_2)$$

for  $x_1$ , and

$$x_2 = |A_1| \cos(\Omega_1 t + \alpha_1) - |A_2| \cos(\Omega_2 t + \alpha_2)$$

for  $x_2$ . For instance, if the left hand pendulum is pulled aside a (small) distance  $a$  and released, the initial conditions  $x_1 = a$ ,  $x_2 = 0$ ,  $\dot{x}_1 = \dot{x}_2 = 0$  are met by the choice of constants

$$|A_1| = |A_2| = \frac{1}{2}a, \quad \alpha_1 = \alpha_2 = 0.$$

The subsequent motion of each pendulum is then described by

$$\begin{aligned}x_1 &= \frac{1}{2}a[\cos \Omega_1 t + \cos \Omega_2 t] = a \cos\left(\frac{\Omega_2 - \Omega_1}{2}t\right) \cos\left(\frac{\Omega_1 + \Omega_2}{2}t\right) \\x_2 &= \frac{1}{2}a[\cos \Omega_1 t - \cos \Omega_2 t] = a \sin\left(\frac{\Omega_2 - \Omega_1}{2}t\right) \sin\left(\frac{\Omega_1 + \Omega_2}{2}t\right).\end{aligned}$$

In the latter form these expressions show the familiar phenomenon of *beats*. This is most easily appreciated in the weak coupling limit when

$$\frac{1}{2}(\Omega_2 - \Omega_1) \simeq \frac{\kappa}{2\omega_0}, \quad \frac{1}{2}(\Omega_2 + \Omega_1) \simeq \omega_0.$$

Then

$$x_1 \simeq a \cos\left(\frac{\kappa t}{2\omega_0}\right) \cos \omega_0 t, \quad x_2 \simeq a \sin\left(\frac{\kappa t}{2\omega_0}\right) \sin \omega_0 t$$

showing that each pendulum oscillates with its natural frequency  $\omega_0$  but with an amplitude that varies slowly with time like  $a \cos(\kappa t/2\omega_0)$  or  $a \sin(\kappa t/2\omega_0)$ . Thus, the amplitude of the right hand pendulum increases at the expense of the amplitude of the left hand pendulum and vice versa, each alternately coming to rest and reaching a maximum oscillation amplitude.

This example teaches us one very important fact. If we call

$$\operatorname{Re}(A_1 e^{i\Omega_1 t}) = \zeta_1 \quad \text{and} \quad \operatorname{Re}(A_2 e^{i\Omega_2 t}) = \zeta_2,$$

and note that

$$\zeta_1 = \frac{x_1 + x_2}{2}, \quad \zeta_2 = \frac{x_1 - x_2}{2},$$

then the equations of motion for  $x_1$  and  $x_2$  can be rewritten as

$$\frac{1}{2}(\ddot{x}_1 + \ddot{x}_2) + \frac{1}{2}\omega_0^2(x_1 + x_2) = 0, \quad \text{or} \quad \ddot{\zeta}_1 + \omega_0^2\zeta_1 = 0,$$

and

$$\frac{1}{2}(\ddot{x}_1 - \ddot{x}_2) + \frac{1}{2}(\omega_0^2 + 2\kappa)(x_1 - x_2) = 0, \quad \text{or} \quad \ddot{\zeta}_2 + (\omega_0^2 + 2\kappa)\zeta_2 = 0,$$

that is, the equations of motion *uncouple* in the coordinate  $\zeta$ . Correspondingly the Lagrange function is reduced to a sum of squares,

$$L = \frac{1}{2}m(\dot{\zeta}_1^2 + \dot{\zeta}_2^2) - \frac{1}{2}m\omega_0^2\zeta_1^2 - \frac{1}{2}m(\omega_0^2 + 2\kappa)\zeta_2^2$$

when expressed in such coordinates, called the *normal coordinates* of the problem. It is our intention in the following to seek such coordinates in general for the solution of small oscillation problems. The eigenfrequencies will again appear as a byproduct of this procedure.

### 4-3 Statement of the Problem

Let us examine the motion of a many-body system consisting of  $N$  interacting particles. The Lagrange function is given by (2.105), that is

$$L = \sum_k \frac{1}{2} m_k \dot{x}_k^2 - V(x_1, x_2, \dots), \quad (4.1)$$

where the sum on  $k$  runs from 1 to  $3N$  as there are  $3N$  degrees of freedom. The potential  $V$  is due to the mutual interaction between particles only. We exclude for the time being the presence of an external field.

We are interested in the motion described by (4.1) in the neighbourhood of an *equilibrium configuration*  $(x_1^0, x_2^0, \dots)$  in which all particles are permanently at rest. This means that

$$\left( \frac{\partial V}{\partial x_k} \right)_{x_k=x_k^0} = 0 \quad (4.2)$$

at equilibrium, for all  $k$ . The set of  $3N$  equations (4.2) define the equilibrium coordinates  $x_k = x_k^0$  of the system. Since we are interested in small displacements of the system about the  $x_k^0$ , we treat each displacement  $x_k - x_k^0$  as small and expand  $L$  about its equilibrium value  $L_0 = -V(x_1^0, x_2^0, \dots)$ . Then,

$$L = L_0 + \sum_k \frac{1}{2} m_k \dot{x}_k^2 - \sum_{kl} \frac{1}{2} V_{kl} (x_k - x_k^0)(x_l - x_l^0) - \dots \quad (4.3)$$

The constants  $V_{kl}$  are given by

$$V_{kl} = \frac{\partial^2 V}{\partial x_k^0 \partial x_l^0} \quad (4.4)$$

and are symmetrical in the indices  $k$  and  $l$ ,  $V_{kl} = V_{lk}$ .

The further development of the theory of small oscillations now proceeds on the assumption that higher order terms in (4.3) may be neglected. Measuring each  $x_k$  from its equilibrium value and dropping the constant  $L_0$  our approximation to the full Lagrange function reads

$$L = \sum_k \frac{1}{2} m_k \dot{x}_k^2 - \sum_{kl} \frac{1}{2} V_{kl} x_k x_l. \quad (4.5)$$

Clearly this Lagrangian describes a system with restoring forces between particles proportional to particle displacements away from equilibrium. One then speaks of a system of coupled linear oscillators.

The difficulty with (4.5) lies with the coupling between the different  $x_k$ . We therefore try to decouple these coordinates by introducing new coordinates  $\zeta_i$  such that  $L$  assumes the form

$$L = \sum_{i=1}^{3N} \left( \frac{1}{2} \dot{\zeta}_i^2 - \frac{1}{2} \Omega_i^2 \zeta_i^2 \right), \quad (4.6)$$

i.e. turns into a sum of  $3N$  independent oscillators each having its own frequency  $\Omega_i$  when expressed in the coordinates  $\zeta$ . This form of  $L$  is often called its *normal form*.

#### 4-4 Normal Modes of a System of Coupled Oscillators

The transformation leading to the normal form of  $L$  is usually accomplished in two steps: (i) introduction of *mass weighted* coordinates  $x'_k = \sqrt{m_k}x_k$  instead of the  $x_k$ . Then,  $L$  assumes the form

$$L = \sum_k \frac{1}{2} \dot{x}'_k{}^2 - \sum_{kl} \frac{1}{2} W_{kl} x'_k x'_l, \quad (4.7)$$

where  $W_{kl} = V_{kl}/\sqrt{m_k m_l}$ . This is just a scale transformation. (ii) introduction of the  $\zeta_i$  by means of a linear orthogonal transformation (a rotation)

$$x'_k = \sum_i U_{ki} \zeta_i \quad (4.8)$$

with constant coefficients  $U_{ki}$ . The velocities  $\dot{x}'_k$  then transform in the same way,

$$\dot{x}'_k = \sum_i U_{ki} \dot{\zeta}_i \quad (4.9)$$

since the coefficients  $U_{ki}$  are independent of time. The orthogonality of the transformation (4.8) is expressed, as in Chap. 3, by the conditions

$$\sum_i U_{ik} U_{il} = \sum_i U_{ki} U_{li} = \delta_{kl} \quad (4.10)$$

or

$$U^T U = U U^T = I \quad (4.11)$$

in matrix notation, where  $U$  is the array

$$U = \begin{pmatrix} U_{11} & U_{12} & \dots \\ U_{21} & U_{22} & \dots \\ \cdot & \cdot & \\ \cdot & \cdot & \\ \cdot & \cdot & \cdot \end{pmatrix}.$$

As before  $U^T$  denotes the transpose<sup>52</sup> of the matrix  $U$ , and  $I$  the unit matrix. In terms of the new coordinates,  $L$  reads

$$L = \sum_{ijk} \frac{1}{2} \dot{\zeta}_i U_{ki} U_{kj} \dot{\zeta}_j - \sum_{ijkl} \frac{1}{2} \zeta_i U_{ki} W_{kl} U_{lj} \zeta_j,$$

or

$$L = \frac{1}{2} \dot{\zeta}^T (U^T U) \dot{\zeta} - \frac{1}{2} \zeta^T (U^T W U) \zeta, \quad (4.12)$$

<sup>52</sup> The matrix obtained by interchanging the rows and columns of  $U$ . The reader unfamiliar with elementary matrix operations is advised to consult A.C. Aitken, *Determinants and Matrices*, Seventh Edition, Oliver and Boyd, Edinburgh and London, 1951.

using the more compact notation of matrix multiplication. Here,  $\zeta^T$  and  $\zeta$  stand for the row and column vectors

$$\zeta^T = (\zeta_1, \zeta_2, \dots); \quad \zeta = \begin{pmatrix} \zeta_1 \\ \zeta_2 \\ \cdot \\ \cdot \\ \cdot \end{pmatrix} = \{\zeta_1, \zeta_2, \dots\}.$$

In what follows we will often abbreviate the column vector by writing it as a row vector in curly brackets as shown above. Finally the matrix  $W$  stands for the symmetrical array

$$W = \begin{pmatrix} W_{11} & W_{12} & \dots \\ W_{12} & W_{22} & \dots \\ \cdot & \cdot & \\ \cdot & \cdot & \\ \cdot & \cdot & \cdot \end{pmatrix}.$$

Since  $U$  has been taken as an orthogonal matrix the kinetic energy term in (4.12) already has the desired form. To obtain a diagonal form for the potential energy term shown in (4.6), we also require that

$$U^T W U = (\Omega_i^2 \delta_{ij}) = \begin{pmatrix} \Omega_1^2 & 0 & \dots \\ 0 & \Omega_2^2 & \dots \\ \cdot & \cdot & \\ \cdot & \cdot & \\ \cdot & \cdot & \cdot \end{pmatrix}, \quad (4.13)$$

i.e. the matrix  $W$  is brought into a diagonal form by the orthogonal transformation  $U$ . It is known from matrix theory that such transformation matrices can always be found if, as here, the matrix to be diagonalized is real and symmetric.

Once  $L$  is in the form (4.6) one easily calculates that the equation of motion

$$\ddot{\zeta}_i + \Omega_i^2 \zeta_i = 0 \quad (4.14)$$

holds for each  $\zeta_i$ . Hence

$$\zeta_i(t) = \text{Re}(C_i \exp i\Omega_i t) = |C_i| \cos(\Omega_i t + \delta_i), \quad (4.15)$$

where  $C_i = |C_i| \exp \delta_i$  is a complex integration constant. Knowing the  $\zeta_i$  as a function of time, and the matrix  $U$ , one can determine the  $x'_k$  (and hence the  $x_k$ ) as a function of time from (4.8).

As in the example of the coupled pendulums, the frequencies  $\Omega_i$  of each  $\zeta_i$  are known as the *eigenfrequencies* of the system, the  $\zeta_i$  as its *normal coordinates*. Thus, (4.8) simply says that the actual displacements  $x_k$  are given as a *linear superposition* of the normal modes of the system.

How to find the  $\Omega_i$  and the  $\zeta_i$ ? Equation (4.13) provides the answer to the first part of this query. We must diagonalize  $W$ . In the process one also obtains the matrix  $U$  and hence the  $\zeta_i$ , as we now show.

To this end consider the operation of  $W$  on an arbitrary column vector  $\mathbf{u}$ . This is given by

$$W\mathbf{u} = \mathbf{v}, \quad (4.16)$$

with the interpretation:  $W$  operates on  $\mathbf{u}$  and produces a new column vector  $\mathbf{v}$ . We saw in Chap. 3 (3.27), that such an operation corresponds to a rotation of the vector  $\mathbf{u}$  into a new vector  $\mathbf{v}$  if the transformation is length preserving. This latter property is not necessarily true for an arbitrary matrix  $W$ , and  $\mathbf{v}$  can differ from  $\mathbf{u}$  in magnitude and direction. However, there exists a certain class of vectors, called *eigenvectors*<sup>53</sup> on which operation by  $W$  produces a change in magnitude only. Let  $\mathbf{u}$  be such a vector. Then

$$W\mathbf{u} = \lambda\mathbf{u}, \quad (4.17)$$

where the factor  $\lambda$  gives the change in length;  $\lambda$  is called the *eigenvalue* of  $W$  belonging to the eigenvector  $\mathbf{u}$ . Clearly,  $\mathbf{u}$  and  $\lambda$  are special vectors and numbers associated with the matrix  $W$ . Equation (4.17) represents an *eigenvalue problem* for these quantities. We determine them as follows. Write (4.17) in component form,

$$\sum_l W_{kl}u_l = \lambda u_k. \quad (4.18)$$

This form shows explicitly that the eigenvector components  $u_k$  satisfy  $3N$  *homogeneous* equations with constant coefficients since  $W$  has dimensions  $3N \times 3N$ . Therefore, a non-trivial solution ( $u_k \neq 0$  for at least one value of  $\lambda$ ) exists only if the determinant of these coefficients vanishes<sup>54</sup>

$$\text{Det}(W - \lambda I) = \begin{vmatrix} W_{11} - \lambda & W_{12} & \dots \\ W_{12} & W_{22} - \lambda & \dots \\ \cdot & \cdot & \\ \cdot & \cdot & \\ \cdot & \cdot & \cdot \end{vmatrix} = 0. \quad (4.19)$$

The determinantal condition is obviously equivalent to a  $3N^{\text{th}}$  order polynomial in  $\lambda$  whose  $3N$  roots (not necessarily all different or all real<sup>55</sup>) determine the allowed values of  $\lambda$  in (4.17). The relation (4.19) is called the *secular determinant*<sup>56</sup> for the eigenvalues of  $W$ . Let us assume that these roots are all distinct for the moment. (Prob. 4-2 presents an opportunity for worrying about the case where the roots are not all distinct - the so-called degenerate case). Call these values  $\lambda_i, i = 1, 2, \dots, 3N$ . Then, substituting these values of  $\lambda$  back into (4.18) provides us with the *ratios*  $u_1 : u_2 : \dots$  of the components of the eigenvector  $\mathbf{u}$ .

<sup>53</sup> See for example H. Margenau and G.M. Murphy, *The Mathematics of Physics and Chemistry*, O. van Nostrand and Company, Inc., New York 1947, p. 304.

<sup>54</sup> H. Margnau and G.M. Murphy, *ibid.*

<sup>55</sup> The roots are all real if, as supposed here,  $W$  is real and symmetric, see Prob. 4-1.

<sup>56</sup> The name originated in the perturbation methods of celestial mechanics.

There are thus  $3N$  distinct eigenvectors (one for each  $\lambda_1$ ) which we label as  $\mathbf{u}^{(i)}$  as in the example of Sec. 4-2, equation (4.17) should thus read

$$W\mathbf{u}^{(i)} = \lambda_i \mathbf{u}^{(i)}, \quad i = 1, 2, \dots, 3N, \quad (4.20)$$

that is, this equation is satisfied by a *whole set* of eigenvectors  $\mathbf{u}^{(i)}$  belonging to distinct eigenvalues  $\lambda_i$ .

Now construct the product  $WU$  where the matrix  $U$  has the  $3N$  eigenvectors  $\mathbf{u}^{(i)}$  as columns,  $U_{ki} = u_k^{(i)}$ :

$$U = \begin{pmatrix} u_1^{(1)} & u_1^{(2)} & \dots \\ u_2^{(1)} & u_2^{(2)} & \dots \\ \cdot & \cdot & \\ \cdot & \cdot & \\ \cdot & \cdot & \cdot \end{pmatrix}. \quad (4.21)$$

Then, using (4.20) repeatedly, there results

$$\begin{aligned} WU &= \begin{pmatrix} W_{11} & W_{12} & \dots \\ W_{12} & W_{22} & \dots \\ \cdot & \cdot & \\ \cdot & \cdot & \\ \cdot & \cdot & \cdot \end{pmatrix} \begin{pmatrix} u_1^{(1)} & u_1^{(2)} & \dots \\ u_2^{(1)} & u_2^{(2)} & \dots \\ \cdot & \cdot & \\ \cdot & \cdot & \\ \cdot & \cdot & \cdot \end{pmatrix} = \begin{pmatrix} \lambda_1 u_1^{(1)} & \lambda_2 u_1^{(2)} & \dots \\ \lambda_1 u_2^{(1)} & \lambda_2 u_2^{(2)} & \dots \\ \cdot & \cdot & \\ \cdot & \cdot & \\ \cdot & \cdot & \cdot \end{pmatrix} \\ &= \begin{pmatrix} u_1^{(1)} & u_1^{(2)} & \dots \\ u_2^{(1)} & u_2^{(2)} & \dots \\ \cdot & \cdot & \\ \cdot & \cdot & \\ \cdot & \cdot & \cdot \end{pmatrix} \begin{pmatrix} \lambda_1 & 0 & \dots \\ 0 & \lambda_2 & \dots \\ \cdot & \cdot & \\ \cdot & \cdot & \\ \cdot & \cdot & \cdot \end{pmatrix} = U\Lambda, \end{aligned} \quad (4.22)$$

where  $\Lambda$  is the diagonal matrix

$$\Lambda = \begin{pmatrix} \lambda_1 & 0 & \dots \\ 0 & \lambda_2 & \dots \\ \cdot & \cdot & \\ \cdot & \cdot & \\ \cdot & \cdot & \cdot \end{pmatrix}.$$

Hence

$$U^{-1}WU = \Lambda, \quad \text{a diagonal matrix} \quad (4.23)$$

provided that  $U$  is non-singular, i.e.  $\det U \neq 0$ , so that the inverse  $U^{-1}$  can be found. Thus, as a byproduct of the eigenvalue problem for a square matrix  $W$  we have shown how to construct a matrix  $U$  that diagonalizes  $W$  according to the transformation (4.23). The diagonal elements of the transformed matrix are then just the eigenvalues of  $W$ .

The *reduction to diagonal form* of  $W$  given in (4.23) is unique except for the order (your choice!) in which the eigenvalues  $\lambda_i$  appear along the diagonal. Operations like  $U^{-1}WU$  on  $W$  (whether or not they produce a diagonal matrix) are called *similarity transformations*.

Equation (4.23) almost solves our problem for a single square matrix. Except that the operation in (4.13) is of the form  $U^T W U$ , not  $U^{-1}WU$ . However, if  $W$  is a symmetric matrix, (its elements are symmetric about the principal diagonal), then the transpose  $W^T$  equals  $W$ . In this case  $U^{-1} = U^T$ , as we now show. Multiply (4.20) on the left with  $\mathbf{u}^{(j)T}$ , the transpose of the eigenvector with eigenvalue  $\lambda_j$ ,

$$\mathbf{u}^{(j)T} W \mathbf{u}^{(i)} = \lambda_i \mathbf{u}^{(j)T} \mathbf{u}^{(i)}. \quad (4.24)$$

Interchanging  $i$  and  $j$  gives another relation

$$\mathbf{u}^{(i)T} W \mathbf{u}^{(j)} = \lambda_j \mathbf{u}^{(i)T} \mathbf{u}^{(j)}. \quad (4.25)$$

On the other hand the transpose of (4.24) is directly

$$\mathbf{u}^{(i)T} W^T \mathbf{u}^{(j)} = \lambda_i \mathbf{u}^{(i)T} \mathbf{u}^{(j)}. \quad (4.26)$$

If  $W$  is symmetric as supposed,  $W = W^T$ , and the left hand sides of (4.25) and (4.26) become identical. Therefore, it follows that

$$(\lambda_i - \lambda_j) \mathbf{u}^{(i)T} \mathbf{u}^{(j)} = 0. \quad (4.27)$$

If there is no degeneracy, (i.e.  $\lambda_i = \lambda_j$  only if  $i = j$ ) then this relation implies that

$$\mathbf{u}^{(i)T} \mathbf{u}^{(j)} = \sum_{k=1}^{3N} u_k^{(i)} u_k^{(j)} = 0, \quad \text{if } \lambda_i \neq \lambda_j. \quad (4.28)$$

This equation expresses the *orthogonality* of two eigenvectors belonging to two different eigenvalues, i.e. they are perpendicular to each other in a multidimensional sense.

The matrix product of  $U$  in (4.21) and its transpose  $U^T$  therefore has the value

$$U^T U = \begin{pmatrix} u_1^{(1)} & u_2^{(1)} & \dots \\ u_1^{(2)} & u_2^{(2)} & \dots \\ \cdot & \cdot & \dots \\ \cdot & \cdot & \dots \\ \cdot & \cdot & \dots \end{pmatrix} \begin{pmatrix} u_1^{(1)} & u_1^{(2)} & \dots \\ u_2^{(1)} & u_2^{(2)} & \dots \\ \cdot & \cdot & \dots \\ \cdot & \cdot & \dots \\ \cdot & \cdot & \dots \end{pmatrix} = \begin{pmatrix} \mathbf{u}^{(1)T} \mathbf{u}^{(1)} & 0 & \dots \\ 0 & \mathbf{u}^{(2)T} \mathbf{u}^{(2)} & \dots \\ \cdot & \cdot & \dots \\ \cdot & \cdot & \dots \\ \cdot & \cdot & \dots \end{pmatrix}$$

using the result (4.28) repeatedly. The value of  $\mathbf{u}^{(i)T} \mathbf{u}^{(i)}$  for each  $i$  is left undetermined by (4.28). This is in accord with our previous information that only the ratios  $u_1^{(i)} : u_2^{(i)} : \dots$  of the components of each eigenvector are determined by the eigenvalue equation. Therefore  $\mathbf{u}^{(i)T} \mathbf{u}^{(i)} = \sum_k u_k^{(i)2}$

is an *arbitrary constant* (its length) for each eigenvector that is not predetermined. If we *normalize* our eigenvectors so that each one has the *same* length then  $U^T U$  becomes proportional to the unit matrix. Obviously, we can then go the whole way and choose this common length to be unity. The eigenvectors are then said to be normalized to unity; they are orthogonal by (4.28) in any event. Such a set of eigenvectors is termed *orthonormal*, and is free of arbitrary constants. Hence, if

$$\mathbf{u}^{(i)T} \mathbf{u}^{(j)} = \delta_{ij}, \quad (4.29)$$

the transformation matrix  $U$  built out of such eigenvectors is orthogonal,  $UU^T = U^T U = I$ , or

$$U^{-1} = U^T, \quad (4.30)$$

so that (4.11) can be met. Thus, (4.23) reads

$$U^T W U = \Lambda \quad (4.31)$$

in this case. This transformation of  $W$  is called an *orthogonal transformation*. Hence: real, symmetric matrices may always be diagonalized by an orthogonal transformation.

The importance of symmetry in determining the transformation matrix  $U$  is illustrated by comparing the diagonalization of

$$W = \begin{pmatrix} 1 & 6 \\ 6 & 1 \end{pmatrix} \quad \text{and} \quad W' = \begin{pmatrix} 1 & 9 \\ 4 & 1 \end{pmatrix}.$$

Both have the same characteristic equation for their eigenvalues, viz.

$$\lambda^2 - 2\lambda - 35 = 0, \quad \text{or } \lambda = 7 \text{ and } -5$$

and hence the same diagonal form

$$\begin{pmatrix} 7 & 0 \\ 0 & -5 \end{pmatrix}.$$

The two unnormalized eigenvectors for  $W$  are

$$\mathbf{u}^{(1)} = \begin{pmatrix} 1 \\ 1 \end{pmatrix} \text{ for } \lambda = 7, \quad \mathbf{u}^{(2)} = \begin{pmatrix} 1 \\ -1 \end{pmatrix} \text{ for } \lambda = -5, \quad (i)$$

and for  $W'$

$$\mathbf{u}^{(1)'} = \begin{pmatrix} 3 \\ 2 \end{pmatrix} \text{ for } \lambda = 7, \quad \mathbf{u}^{(2)'} = \begin{pmatrix} 3 \\ -2 \end{pmatrix} \text{ for } \lambda = -5, \quad (ii)$$

respectively. Notice that  $\mathbf{u}^{(1)}$  and  $\mathbf{u}^{(2)}$  are orthogonal,

$$\mathbf{u}^{(1)T} \mathbf{u}^{(2)} = (1 \ 1) \begin{pmatrix} 1 \\ -1 \end{pmatrix} = 0$$

but that

$$\mathbf{u}^{(1)T} \mathbf{u}^{(2)'} = (3 \ 2) \begin{pmatrix} 3 \\ -2 \end{pmatrix} = 5 \neq 0.$$

The eigenvectors of  $W'$  are *not* orthogonal to each other.

The eigenvectors of  $W$  and  $W'$  in (i) and (ii) can still have arbitrary length. We noted the advantage of normalizing them in the case of orthogonal eigenvectors. Doing so for the set (i) we obtain the transformation matrix

$$U = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix}, \quad U^T = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix} = U^{-1},$$

so that

$$\begin{aligned} U^{-1} W U &= U^T W U = \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} 1 & 6 \\ 6 & 1 \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \\ &= \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} 7 & -5 \\ 7 & 5 \end{pmatrix} = \begin{pmatrix} 7 & 0 \\ 0 & -5 \end{pmatrix}, \end{aligned}$$

as expected. Since the eigenvectors of  $W'$  set (ii) are not orthogonal there is really no point in normalizing them. We construct the transformation matrix  $U'$  directly from (ii) as

$$U' = \begin{pmatrix} 3 & 3 \\ 2 & -2 \end{pmatrix}; \quad U'^{(-1)} = \frac{1}{12} \begin{pmatrix} 2 & 3 \\ 2 & -3 \end{pmatrix},$$

so that

$$\begin{aligned} U'^{-1} W' U' &= \frac{1}{12} \begin{pmatrix} 2 & 3 \\ 2 & -3 \end{pmatrix} \begin{pmatrix} 1 & 9 \\ 4 & 1 \end{pmatrix} \begin{pmatrix} 3 & 3 \\ 2 & -2 \end{pmatrix} \\ &= \frac{1}{12} \begin{pmatrix} 2 & 3 \\ 2 & -3 \end{pmatrix} \begin{pmatrix} 21 & -15 \\ 14 & 10 \end{pmatrix} = \begin{pmatrix} 7 & 0 \\ 0 & -5 \end{pmatrix}. \end{aligned}$$

We also take this opportunity to point out that interchanging the columns of  $U$  or  $U'$  merely reorders the appearance of the roots 7 and  $-5$  to give

$$\begin{pmatrix} -5 & 0 \\ 0 & 7 \end{pmatrix} \quad \text{instead of} \quad \begin{pmatrix} 7 & 0 \\ 0 & -5 \end{pmatrix}$$

for the diagonal form of  $W$  or  $W'$ . (Can the rows of  $U$  or  $U'$  also be interchanged?)

We see that a knowledge of the eigenvalues and eigenvectors of the matrix  $W$  solves the problem of bringing the Lagrangian (4.12) into normal form (4.6), with eigenfrequencies  $\Omega_i$

$$\Omega_i = \sqrt{\lambda_i}, \quad i = 1, 2, \dots, 3N, \quad (4.32)$$

where  $\lambda_i$  are the roots of the secular determinant, (4.19).

The normal coordinates themselves are given by (4.15) as a function of time. Introducing these solutions into (4.8) one finds

$$x'_k = \sqrt{m_k} x_k = \sum_{i=1}^{3N} u_k^{(i)} C_i \cos(\sqrt{\lambda_i} t + \delta_i) \quad (4.33)$$

in terms of the eigenvectors  $\mathbf{u}^{(i)}$  of  $W$ , for the mass scaled  $x'_k$  and actual  $x_k$  displacements of the system. Here,  $u_k^{(i)}$  is the  $k^{\text{th}}$  component of the  $i^{\text{th}}$  eigenvector of the matrix  $U$  as constructed in (4.21). In words: each coordinate  $x_k$  is a linear superposition of normal coordinates with relative amplitudes determined by the eigenvector components  $u_k^{(i)}$ . Thus, each  $x_k$  does *not* oscillate with a definite frequency. Rather their time-dependence depends in a complicated way on how many normal coordinates have been excited and with what amplitudes and phases.

Often only a single normal mode is excited. Then *all* the  $x_k$  oscillate with the common frequency  $\sqrt{\lambda_i}$  of *this* normal mode, viz.

$$\sqrt{m_k} x_k(t) = u_k^{(i)} C_i \cos(\sqrt{\lambda_i} t + \delta_i) \quad (4.34)$$

if only  $\zeta_i$  is excited. The system is then said to be vibrating in its  $i^{\text{th}}$  *normal mode*. Notice that in any normal mode vibration all particles pass through their equilibrium positions simultaneously.

## 4-5 Applications I

### Free oscillations

Consider the longitudinal oscillations of a system of two particles, each mass  $m$ , joined to a center particle of mass  $M$  by identical springs (a mechanical model for a linear  $XY_2$  molecule, e.g.  $CO_2$ ). The system is shown in Fig. 4.2.

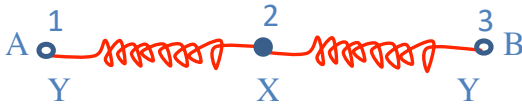


Figure 4.2: A linear  $XY_2$  molecule.

Suppose that the spring constant for each spring is  $\kappa$ . The restoring forces for displacements of the particles along  $AB$  is taken to be proportional to the extensions in the springs. Hence, particles 1, 2 and 3 are subjected to forces

$$F_1 = -\kappa(x_2 - x_1), \quad F_2 = \kappa(x_1 - 2x_2 + x_3), \quad F_3 = -\kappa(x_3 - x_2),$$

where  $x_1, x_2$  and  $x_3$  are the displacements away from equilibrium of these particles. These forces are derivable from the potential function

$$V = \frac{1}{2} \frac{\kappa}{m} (x_1'^2 + 2x_2'^2 + x_3'^2 - 2x_1'x_2' - 2x_2'x_3'),$$

using the scaled coordinates  $x_1' = \sqrt{m}x_1$ , etc. of the problem. Thus, the  $W$  matrix reads

$$W = \begin{pmatrix} \frac{\kappa}{m} & -\frac{\kappa}{\sqrt{mM}} & 0 \\ -\frac{\kappa}{\sqrt{mM}} & \frac{2\kappa}{M} & -\frac{\kappa}{\sqrt{mM}} \\ 0 & -\frac{\kappa}{\sqrt{mM}} & \frac{\kappa}{m} \end{pmatrix}$$

for this potential. Its eigenvalue problem

$$W\mathbf{u} = \lambda\mathbf{u}$$

leads to the secular determinant

$$\begin{vmatrix} \frac{\kappa}{m} - \lambda & -\frac{\kappa}{\sqrt{mM}} & 0 \\ -\frac{\kappa}{\sqrt{mM}} & \frac{2\kappa}{M} - \lambda & -\frac{\kappa}{\sqrt{mM}} \\ 0 & -\frac{\kappa}{\sqrt{mM}} & \frac{\kappa}{m} - \lambda \end{vmatrix} = 0,$$

or

$$-\lambda\left(\frac{\kappa}{m} - \lambda\right)\left(\frac{\kappa}{m} + \frac{2\kappa}{M} - \lambda\right) = 0.$$

The roots are thus  $\lambda_1 = 0$ ;  $\lambda_2 = \kappa/m$ ,  $\lambda_3 = \kappa/m + 2\kappa/M$ . The associated normalized eigenvectors are obtained from the eigenvalue equation in the manner shown by the following calculations.

For  $\lambda_1 = 0$ ,

$$\begin{pmatrix} \frac{\kappa}{m} & -\frac{\kappa}{\sqrt{mM}} & 0 \\ -\frac{\kappa}{\sqrt{mM}} & \frac{2\kappa}{M} & -\frac{\kappa}{\sqrt{mM}} \\ 0 & -\frac{\kappa}{\sqrt{mM}} & \frac{\kappa}{m} \end{pmatrix} \begin{pmatrix} \sqrt{m} \\ \sqrt{M} \\ \sqrt{m} \end{pmatrix} = 0, \quad \text{or } \mathbf{u}^{(1)} = \frac{1}{(2m + M)^{\frac{1}{2}}} \begin{pmatrix} \sqrt{m} \\ \sqrt{M} \\ \sqrt{m} \end{pmatrix}.$$

For  $\lambda_2 = \kappa/m$ ,

$$\begin{pmatrix} 0 & -\frac{\kappa}{\sqrt{mM}} & 0 \\ -\frac{\kappa}{\sqrt{mM}} & \frac{2\kappa}{M} - \frac{\kappa}{m} & -\frac{\kappa}{\sqrt{mM}} \\ 0 & -\frac{\kappa}{\sqrt{mM}} & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} = 0, \quad \text{or } \mathbf{u}^{(2)} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix},$$

and for  $\lambda_3 = \kappa/m + 2\kappa/M$

$$\begin{pmatrix} -\frac{2\kappa}{M} & -\frac{\kappa}{\sqrt{mM}} & 0 \\ -\frac{\kappa}{\sqrt{mM}} & -\frac{\kappa}{m} & -\frac{\kappa}{\sqrt{mM}} \\ 0 & -\frac{\kappa}{\sqrt{mM}} & -\frac{2\kappa}{M} \end{pmatrix} \begin{pmatrix} \sqrt{M} \\ -2\sqrt{m} \\ \sqrt{M} \end{pmatrix} = 0, \quad \text{or } \mathbf{u}^{(3)} = \frac{1}{(2M + 4m)^{\frac{1}{2}}} \begin{pmatrix} \sqrt{M} \\ -2\sqrt{m} \\ \sqrt{M} \end{pmatrix}.$$

The eigenfrequencies of the system are thus

$$\Omega_1 = 0, \quad \Omega_2 = \sqrt{\kappa/m}, \quad \Omega_3 = \sqrt{\frac{\kappa}{m} + 2\frac{\kappa}{M}}.$$

The normal modes can be read off from the eigenvectors according to (4.34):

$$(1) \quad \Omega_1 = 0, \quad \sqrt{m}x_1 \sim \sqrt{m}\zeta_1, \quad \sqrt{M}x_2 \sim \sqrt{M}\zeta_1, \quad \sqrt{m}x_3 \sim \sqrt{m}\zeta_1,$$

or

$$x_1 = x_2 = x_3.$$

Therefore, all three particles suffer the same displacement. This mode corresponds to the displacement of the center-of-mass of the system as a whole without a change in the interparticle equilibrium distances. This cannot be a *vibrational* mode since the springs are not called into play. Indeed the equation of motion for  $\zeta_1$  confirms this:

$$\ddot{\zeta}_1 = 0, \quad \dot{\zeta}_1 = a, \quad \zeta_1 = a + bt$$

( $a$  and  $b$  are constants). Therefore the center-of-mass moves with a constant velocity as it should.

$$(2) \quad \Omega_2 = \sqrt{\frac{\kappa}{m}}, \quad \sqrt{m}x_1 \sim \zeta_2, \quad \sqrt{M}x_2 \sim 0, \quad \sqrt{m}x_3 \sim -\zeta_2,$$

or

$$x_1 = -x_3, \quad x_2 = 0.$$

The outer particles move out of phase with equal displacements and the center particle is undisplaced.

$$(3) \quad \Omega_3 = \sqrt{\frac{\kappa}{m} + 2\frac{\kappa}{M}}, \quad \sqrt{m}x_1 \sim \sqrt{M}\zeta_3; \quad \sqrt{M}x_2 \sim -2\sqrt{m}\zeta_3, \quad \sqrt{m}x_3 \sim \sqrt{M}\zeta_3,$$

or

$$x_1 = x_3, \quad x_2 = -2\frac{m}{M}x_1.$$

The outer particles move in phase with equal displacements while the center particle moves the fraction  $2m/M$  of  $x_1$  in the opposite direction, thus keeping the center-of-mass at rest. Notice that as  $M/m \rightarrow \infty$  this mode describes two particles attached to an infinitely heavy center particle and vibrating in phase with frequency  $\sqrt{\kappa/m}$  as one expects physically. The three normal modes are illustrated in Fig. 4.3.

Actually, we could have decided from the beginning that a linear  $XY_2$  molecule has one zero frequency and two non-zero frequencies for longitudinal vibrations. We have just seen that the zero frequency motion pattern corresponds to the motion of the center-of-mass only. But (4.6) showed that there are as many frequencies  $\Omega_i$  as there are degrees of freedom. Therefore one degree of freedom for  $XY_2$  must correspond to a translation of the center-of-mass and this must be described by a normal coordinate of zero frequency since this normal coordinate *cannot* appear in  $L$  (otherwise it would spoil the momentum conservation). The remaining two degrees of freedom then possess normal coordinates

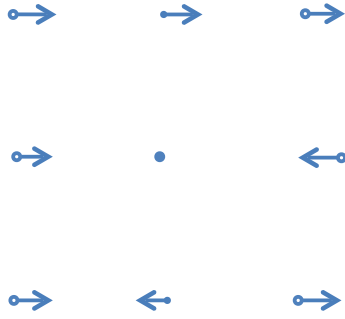


Figure 4.3: Normal modes of a linear  $XY_2$  molecule.

with non-zero frequencies. In general then, an interacting system of  $N$  particles possesses  $3N - 6$  non-zero eigenfrequencies and 6 zero eigenfrequencies corresponding to three coordinates describing the translation of the center-of-mass of the system in three dimensions and three coordinates describing the rotation of the system as a whole about its center-of-mass. None of these motions require the interparticle spacing to change but are possible motions, and hence must belong to zero eigenfrequencies of the system. The normal coordinates describing such motions must therefore reside completely in the kinetic energy of the system. The expression for  $L$  in (4.6) is thus more correctly written as  $L_{int} + L_0$ , where

$$L_{int} = \sum_{i=1}^{3N-6} \frac{1}{2} \dot{\zeta}_i^2 - \sum_{i=1}^{3N-6} \frac{1}{2} \Omega_i^2 \zeta_i^2, \tag{4.35}$$

describes the intrinsic vibration of the system,  $L_0$  its translational and rotational energy.

### 4-6 Applications II

#### Forced oscillations

Let us briefly consider the situation where an external field  $V_{ext}(x_1, x_2, \dots, t)$  is admitted to the problem. The Lagrange function (4.1) then becomes

$$L = \sum_k \frac{1}{2} m_k \dot{x}_k^2 - V(x_1, x_2, \dots) - V_{ext}(x_1, x_2, \dots, t).$$

Expanding this entire expression about the equilibrium configuration of the system again leads to

$$L \simeq T - V + \sum_k F_k^{(e)}(x_k - x_k^0),$$

where  $T - V$  is the free oscillation Lagrangian of (4.5) and

$$F_k^{(e)} = -\left(\frac{dV_{ext}}{dx_k}\right)_{x_k=x_k^0}$$

the external force component on the motion described by coordinate  $x_k$  at equilibrium. Transforming to normal coordinates we find immediately that

$$L = \sum_i \left( \frac{1}{2} \dot{\zeta}_i^2 - \frac{1}{2} \omega_i^2 \zeta_i^2 \right) + \sum_i f_i^{(e)} \zeta_i,$$

where

$$f_i^{(e)} = \sum_k F_k^{(e)} \frac{U_{ki}}{\sqrt{m_k}}$$

is identified by the following equation of motion as the external force component on the  $i^{\text{th}}$  normal coordinate:

$$\ddot{\zeta}_i + \omega_i^2 \zeta_i = f_i^{(e)}.$$

Thus, the normal coordinates obey the equation of motion of a *driven oscillator* if external forces are present. To illustrate the effect of the  $f_i^{(e)}$  suppose that they are periodic, with a common frequency  $\omega$ . Then,

$$f_i^{(e)} = f_i^{(e)}(0) e^{-i\omega t},$$

where the  $f_i^{(e)}(0)$  are constants. (Again the real or imaginary part of this expression may be used by those unwilling to accept the advantages of the complex notation!) With this force component acting,  $\zeta_i$  has the special solution that oscillates with the frequency of the applied field:

$$\zeta_i^{(s)} = \frac{f_i^{(e)}(0) e^{-i\omega t}}{\omega_i^2 - \omega^2}.$$

Notice that the  $i^{\text{th}}$  normal mode can only be excited in this fashion if  $F_k^{(e)}$  has a component "along" it, i.e.  $f_i^{(e)} \neq 0$ . The complete solution of the motion is obtained by adding to  $\zeta_i^{(s)}$  any solution of the homogeneous equation (4.14) that results by setting all  $f_i$  equal to zero. If, as is usually the case, the homogeneous equation contains a damping term this part of the solution dies out in time and only  $\zeta_i^{(s)}$  remains. For this reason  $\zeta_i^{(s)}$  is called the *steady-state* solution (hence the superscript) in the presence of an external driving force.

Thus the steady-state solution tells us how the system responds to an external field. In fact this "response" is very useful in studying the eigenfrequencies of a system. Suppose for simplicity we have a linear array of  $N$  particles subjected to a common force  $F_k^{(e)} \exp(-i\omega t) = F_0 \exp(-i\omega t)$  for all  $k$  (such as an electric field acting on a system of identically charged particles) and we determine its response to this field by measuring the *average* displacement of the system,

$$\langle x \rangle = \frac{1}{N} \sum_k x_k = \frac{1}{N} \sum_k \frac{U_{ki}}{\sqrt{m_k}} \zeta_i^{(s)}.$$

Filling in the value of  $\zeta_i^{(s)}$  we find

$$\langle x \rangle = F_0 e^{-i\omega t} \sum_i \frac{a_i^2}{\omega_i^2 - \omega^2},$$

where  $a_i = (1/\sqrt{N}) \sum_k U_{ki} / \sqrt{m_k}$ . The ratio  $\langle x \rangle / F_0$  of the maximum amplitude induced in  $\langle x \rangle$  by a force strength  $F_0$  is called a *response function*  $\chi(\omega)$ , or

$$\chi(\omega) = \sum_i \frac{a_i^2}{\omega_i^2 - \omega^2}.$$

We notice that  $\chi(\omega)$  refers to properties of the *free* system only; it is independent of the exciting force. The important feature about  $\chi(\omega)$  is that it has *poles* as a function of the applied frequency at the eigenfrequencies of the system under study (unless the corresponding  $a_i$  is zero of course). The measurement of  $\chi(\omega)$  is thus one experimental way of probing the eigenfrequencies of an oscillatory system.

### 4-7 Applications III

#### *Vibrations of non-linear molecules*

Consider the "vibrating triangle" molecule  $X_3$  as pictured in Fig. 4.4, consisting of three identical atoms situated at the vertices of an equilateral triangle. Label each vertex as 1,2 or 3 and set up parallel  $x_p - y_p$  coordinate axes as shown where  $p = 1, 2, 3$ . The displacements of the atom in position  $p$  (note: the *position* not the atom is labelled) are then  $(x_p, y_p)$  or  $\mathbf{x}_p$  for short.

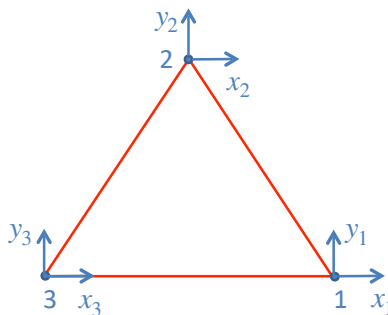


Figure 4.4: The molecule  $X_3$ .

Assuming that the potential energy of the system depends quadratically on the extensions  $\delta l_{pq}$  of the sides of the triangle (linear restoring forces), one has

$$V = \frac{1}{2} \kappa [(\delta l_{12})^2 + (\delta l_{23})^2 + (\delta l_{31})^2]$$

with

$$\begin{aligned}\delta l_{12} &= \frac{1}{2}(x_1 - x_2) - \frac{\sqrt{3}}{2}(y_1 - y_2) \\ \delta l_{23} &= \frac{1}{2}(x_2 - x_3) + \frac{\sqrt{3}}{2}(y_2 - y_3) \\ \delta l_{31} &= x_1 - x_3.\end{aligned}\quad (4.36)$$

$\kappa$  is the coupling constant. We can now substitute these expressions into the potential energy  $V$ , but the calculation requires courage. Instead, let us introduce new coordinates  $Q_i$  via the transformation

$$\{x_1, y_1, x_2, y_2, x_3, y_3\} = U\{Q_{A1}, Q_{A2}, Q_{E1}, Q_{E2}, Q'_{E1}, Q'_{E2}\}, \quad (4.37)$$

where

$$U = \frac{1}{2\sqrt{3}} \begin{pmatrix} \sqrt{3} & 1 & 2 & 0 & 2 & 0 \\ -1 & \sqrt{3} & 0 & -2 & 0 & 2 \\ 0 & -2 & -1 & -\sqrt{3} & 2 & 0 \\ 2 & 0 & -\sqrt{3} & 1 & 0 & 2 \\ -\sqrt{3} & 1 & -1 & \sqrt{3} & 2 & 0 \\ -1 & -\sqrt{3} & \sqrt{3} & 1 & 0 & 2 \end{pmatrix}, \quad (4.38)$$

which is readily demonstrated to be orthogonal,  $U^{-1} = U^T$ . Performing the transformation to the  $Q$ , we find that the Lagrange function for the  $X_3$  molecule reads

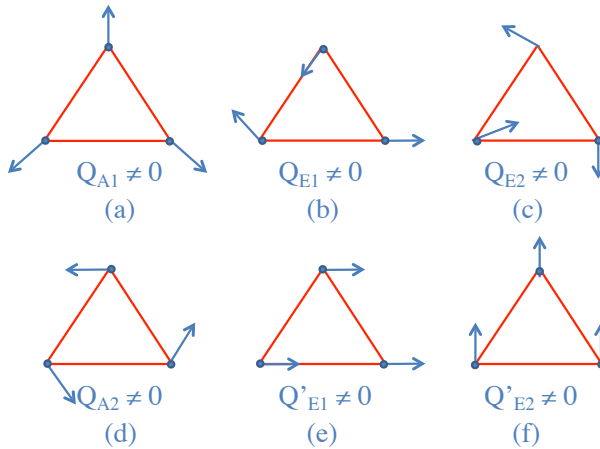
$$L = \frac{1}{2}m\{\dot{Q}_{A1}^2 + \dot{Q}_{A2}^2 + \dot{Q}_{E1}^2 + \dot{Q}_{E2}^2 + \dot{Q}'_{E1}{}^2 + \dot{Q}'_{E2}{}^2\} - \frac{1}{2}\left(\frac{3\kappa}{2}\right)\{2Q_{A1}^2 + Q_{E1}^2 + Q_{E2}^2\} \quad (4.39)$$

if  $m$  is the mass of any atom. Thus,  $L$  is already in normal form. Only  $Q_{A1}$ ,  $Q_{E1}$  and  $Q_{E2}$  appear in the potential energy. They must therefore be normal coordinates for vibrations. The frequencies are seen to be

$$\begin{aligned}\Omega_1 &= \sqrt{\frac{3\kappa}{m}} \quad \text{for } Q_{A1} \\ \Omega_2 = \Omega_3 &= \sqrt{\frac{3\kappa}{2m}} \quad \text{for } Q_{E1} \text{ and } Q_{E2}.\end{aligned}\quad (4.40)$$

Notice that the coordinates  $Q_{E1}$  and  $Q_{E2}$  vibrate with the same frequency, i.e. they are *degenerate*. The normal mode patterns are shown in Fig. 4.5(a), (b), and (c) as deduced from (4.3). The arrows indicate the amount and direction of displacement of each atom. The remaining coordinates  $Q_{A1}$ ,  $Q'_{E1}$ , and  $Q'_{E2}$  have zero frequency and thus correspond to translations and rotations of the molecular framework as a whole. This expectation is borne out in Fig. 4.5(d), (e) and (f).

Thus, the problem is solved. We have given the solution in the above form, depending as it does on the pivotal transformation matrix  $U$  of

Figure 4.5: Normal modes of an  $X_3$  molecule.

(4.38), in order to encourage the ambitious reader to tackle the next section with some sense of purpose. The point is: coordinates like the  $Q_i$  (even the curious subscripts used in the above problem has good reason) can often be determined from the *symmetry* that the molecule possesses in its undisturbed state. For instance, the  $X_3$  molecule is unaffected by (a) rotating it through  $\pm 120 (= \pm 2\pi/3)$  about an axis perpendicular to the molecular plane and passing through the center-of-mass, or (b) reflecting the structure in plane mirrors bisecting the three vertices of the triangle. The full set of such operations the symmetry of a molecule allows forms a *group*, the so-called *symmetry group* of the molecule. To benefit from this fact requires some of the machinery of a branch of mathematics called *group theory*. We consider some salient points of this subject in the following sections.

#### 4-8 Point Groups and their Representations

It is *not* our intention in this short synopsis of the theory of point groups to give anything like a complete discussion of this important subject, but rather to provide a sufficient background for the more ambitious reader to appreciate the elegance of this powerful tool in the analysis of molecular vibrations. Most of the important theorems will simply be stated without proof. A rigorous discussion of all such theorems may, for example, be found in E.P. Wigner, *Group Theory* (Academic Press, 1959, translated from the German by J.J. Griffin).

A few definitions are in order: (i) A collection of objects  $A, B, C, \dots$  called *elements* form a *group* if the following four conditions are obeyed by every element of the group:

1) a law of combination called the *product*, is prescribed such that the product of any two elements produces a third element that also falls in

the group. We write the combination of  $A$  and  $B$  as  $AB = C$  and call  $AB$  the product of  $A$  and  $B$ . Note carefully that ordinary multiplication is not implied (or excluded) by this definition of product.

- 2) the set of elements includes a unit element  $E$  such that  $EA = AE = A$  holds for every element  $A$  of the group.
- 3) every element  $A$  of the group has an inverse element  $A = A^{-1}$ , also in the group, such that  $XA = AX = E$ .
- 4) the associative law holds for group multiplication:  $A(BC) = (AB)C = ABC$ .

Notice that the group multiplication need not (but can be) commutative, i.e.

$$AB \neq BA \tag{4.41}$$

in general. If an equality sign holds in (4.41) for every pair of elements of the group, it is called an *abelian* group.

The number of elements  $g$  in a group is called its *order*. It is possible to have groups with a finite or an infinite number of elements.

Exercise. Examine (i) the set of positive integers  $1, 2, \dots, \infty$  and (ii) the set of elements  $E = 1, B = -1, C = i, D = -i$  for group properties, choosing ordinary multiplication for the group multiplication in both instances.

The group multiplication among the elements of a group is best displayed by means of a group multiplication table like that shown in Table 4.1.

The table is constructed (and used) by reading off the intersection of the row and column identified by the two elements whose product is sought, e.g.

$$BC = D$$

from the intersection of row  $B$  and column  $C$ . Notice that each element appears once and only once in each row or column. This is a general group property (see Prob. 4-3).

Table 4.1: A group multiplication table for example (ii) of the text.

	E	B	C	D
E	E	B	C	D
B	B	E	D	C
C	C	D	B	E
D	D	C	E	B

*The concept of conjugate elements and class*

Two elements  $A$  and  $B$  are said to be *conjugate* if they are connected by a relation

$$A = C^{-1}BC,$$

where  $C$  is some element of the group. Collecting all conjugate elements together, we form a *class* of the group. We state without proof that the elements of a group can be segregated into various classes by pre- and postmultiplying each element with every element of the group such that no element appears in more than one class (see Prob. 4-4). Taking, for example, the group whose multiplication table is displayed in Table 4-1,

one finds each element is in a class by itself since the group is abelian (Prob. 4-5.) The *number* of classes a group possesses will be important in our applications later on.

(iii) Group representations. A very useful concept in group theory is that of a *representation* of the elements of a group by means of a group of square matrices that have the same *matrix multiplication table* as the multiplication table of the group they represent.

Thus, if  $\Gamma(A)$  and  $\Gamma(B)$  are matrices that are to represent the elements  $A$  and  $B$  of a group and  $AB = C$ , where  $C$  is another element in the group, then

$$\Gamma(A)\Gamma(B) = \Gamma(C) \quad (4.42)$$

must hold, where  $\Gamma(C)$  is a matrix representing the element  $C$ . The law of combination in (4.42) is ordinary matrix multiplication.

The use of matrices to represent non-abelian groups is of course essential in order to mirror the non-commutative nature of the former. We make three further remarks about the matrices  $\Gamma(A), \Gamma(B), \dots$ . First, it is entirely possible for one matrix to represent more than one element of the group. Secondly the matrices  $\Gamma(A), \Gamma(B), \dots$  are by no means unique. For if they form a representation then so do

$$U^{-1}\Gamma(A)U, \quad U^{-1}\Gamma(B)U, \quad \dots \quad (4.43)$$

where  $U$  is any square, invertible matrix. The matrices in (4.43) (call them  $\Gamma(A), \Gamma(B), \dots$ ) form an *equivalent* representation. Equivalent representations are not counted as different representations of a group. The third point concerns the dimension of the matrices  $\Gamma$ . If  $\Gamma'(A)$  and  $\Gamma''(A)$  are representations of a group element  $A$  (equivalent or not) then so is

$$\Gamma(A) = \begin{pmatrix} \Gamma'(A) & 0 \\ 0 & \Gamma''(A) \end{pmatrix}, \quad (4.44)$$

as follows immediately from the rules of matrix multiplication. A representation like (4.44) that breaks down into matrices of smaller dimension is termed *reducible*. A similar property may hold for the constituent matrices in  $\Gamma(A)$ . The matrix  $\Gamma(A)$  is reducible by construction. But a *similarity transformation* on  $\Gamma(A)$  would generally destroy its "block" form by scrambling its rows and columns without, however, upsetting its reducibility. The property of being reducible is then by no means obvious and has to be tested for by group theoretic procedures that we indicate presently.

The dimension of the matrices providing a representation of a group is called the *dimension of the representation*. Clearly all the matrices forming a particular representation of a group must share this dimension. We denote the *collection* of such matrices by the single symbol  $\Gamma$ , and refer to this collection as the representation  $\Gamma$ .

Let us return to the property of reducibility. Given a representation  $\Gamma$  we say this representation is *reducible* if *all* these matrices can be brought into a block diagonal form of (4.44):

$$\Gamma(R) = \begin{pmatrix} D^{(1)}(R) & & & \\ & D^{(2)}(R) & & \\ & & D^{(3)}(R) & \\ & & & \dots \end{pmatrix}, \quad (4.45)$$

with the *same* similarity transformation for every element  $R$  in the group. If this cannot be done, the representation is *irreducible*. Irreducible representations will play a special role in our further considerations.

The submatrices  $D^{(\mu)}(R)$  along the diagonal of  $\Gamma(A)$  in (4.45) are all group representations of smaller dimension than  $\Gamma(A)$ . If they are in turn reducible a further similarity transformation is carried out reducing the matrix  $\Gamma(A)$  still further. If no further such transformations are possible the representation  $\Gamma$  is said to be fully reduced. Suppose this is the case in (4.45). Then, the  $D^{(\mu)}(A), D^{(\mu)}(B), \dots$  are termed the *irreducible* representations of the group.

From now on we reserve the symbol  $D^{(\mu)}(R)$ , with the superscript  $\mu$  for the  $\mu^{\text{th}}$  irreducible representation of the element  $R$ , where  $R$  stands for an arbitrary element of the group, and refer to the collection of such matrices as the representation  $\Gamma^{(\mu)}$  of the group. The index  $\mu$  thus distinguishes between different irreducible representations of the group. But what does "different" mean when applied to a representation? The set of matrices  $\Gamma^{(\mu)}$  are clearly determined only up to a similarity transformation so that equivalent representations cannot be considered different. The remaining possibilities are (i) that the dimensions of the various representations  $\Gamma^{(\mu)}$  differ, or (ii) if the dimensions are the same, that such representations are *inequivalent*. Thus, for two representations  $\Gamma^{(1)}, \Gamma^{(2)}$  to differ they must either differ in dimension, or be inequivalent if they have the same dimension.

In the process of reducing  $\Gamma$  it is entirely possible that the same irreducible representation appears *more than once* in the reduced form; nor need all the possible irreducible representations of the group be present. To emphasize these points the reduction process is usually displayed by writing  $\Gamma(R)$  as

$$\Gamma(R) = a_1 D^{(1)}(R) \oplus a_2 D^{(2)}(R) \oplus \dots = \sum_{\mu} a_{\mu} D^{(\mu)}(R) \quad (4.46)$$

for each group element  $R$  separately, or collectively as

$$\Gamma = \sum_{\mu} a_{\mu} \Gamma^{(\mu)},$$

where  $a_{\mu}$  is an integer giving the number of times the representation  $\Gamma^{(\mu)}$  appears in the reduction of  $\Gamma$ . Neither of these equalities should be

interpreted as sums in an arithmetic sense. They are simply a symbolic notation for how the representation of  $\Gamma$  is composed of other representations.

Next follow, without complete proofs, some theorems for the irreducible representations of *finite* groups:

Theorem I: a representation with square matrices having non-zero determinants is always equivalent to a representation with unitary matrices<sup>57</sup>.

<sup>57</sup> A unitary matrix  $U$  has its inverse equal to its hermitian conjugate of the complex conjugate  $U^*$  of  $U$ .

Theorem II: (the Great Orthogonality Theorem): the set of inequivalent, unitary, irreducible matrices  $D^{(\mu)}(R)$  of dimension  $n_\mu$  that represent a group of order  $g$ , satisfy the relation

$$\sum_R D^{(\mu)*}(R)_{\alpha\beta} D^{(\nu)}(R)_{\gamma\delta} = \frac{g}{n_\mu} \delta_{\mu\nu} \delta_{\alpha\gamma} \delta_{\beta\delta}, \tag{4.47}$$

where the sum is over all the elements of the group. Here  $D^{(\mu)}(R)_{\alpha\beta}$  is the  $\alpha\beta^{\text{th}}$  element of the matrix  $D^{(\mu)}(R)$ , and the asterisk (\*) denotes complex conjugation.

The matrix elements  $D^{(\mu)}(R)_{\alpha\beta}$ , for fixed  $\mu, \alpha\beta$  can be viewed as the  $g$  components of a "vector"

$$\{D^{(\mu)}(A)_{\alpha\beta}, D^{(\mu)}(B)_{\alpha\beta}, \dots\}$$

in the space of the group elements, as  $R$  runs through all the elements of the group. Then, (4.47) says that these vectors form an orthogonal set. Since the triad  $\mu, \alpha\beta$  distinguishes the different vectors, there are  $n_\mu^2$  of them per representation (i.e. for given  $\mu$ ) or

$$\sum_{\mu=1}^p n_\mu^2$$

in all, if the group possesses  $p$  distinct irreducible representations. But we cannot have more orthogonal vectors than the dimension of the space they span. Hence,

$$\sum_{\mu} n_\mu^2 \leq g.$$

Additional arguments have to be invoked (see, for example, E.P. Wigner, *ibid.*, p.115) to show that the equality sign holds, leading to Theorem III,

$$n_1^2 + n_2^2 + \dots + n_p^2 = g \tag{4.48}$$

as a fundamental relation between the *order* of a group and the *dimensions* of its various irreducible representations. This remarkable theorem often allows one to determine these dimensions (i.e. the numbers  $n_\mu$ ) uniquely if the number  $p$  of different irreducible representations is known. However, this latter number can be found as follows: The procedure makes use of the concept of the *character*  $\chi(R)$  of the representation

of a group element  $R$ . This is simply defined as the trace of the matrix that represents  $R$ :

$$\chi(R) = \sum_{\alpha} \Gamma(R)_{\alpha\alpha},$$

the sum extending over all diagonal elements of the matrix  $\Gamma(R)$ . If the representation is an irreducible one, we indicate this by appending  $\mu$  to  $\chi(R)$  thus:  $\chi^{(\mu)}(R) = \sum D^{(\mu)}(R)_{\alpha\alpha}$ .

Since the trace of any square matrix is unaffected by a similarity transformation of that matrix, it is clear that group elements in the same *class* have the same character.

Now, we get a theorem about the character of a group by specializing Theorem II as follows: set  $\alpha = \beta, \gamma = \delta$  and sum on  $\alpha$  and  $\gamma$ . Then,

$$\sum_{\alpha, \gamma} \sum_R D^{(\mu)*}(R)_{\alpha\alpha} D^{(\nu)}(R)_{\gamma\gamma} = \frac{g}{n_{\nu}} \delta_{\mu\nu} \sum_{\alpha, \gamma} \delta_{\alpha\gamma},$$

or

$$\sum_R \chi^{(\mu)*}(R) \chi^{(\nu)}(R) = g \delta_{\mu\nu}, \quad (4.49)$$

since  $\sum_{\alpha, \gamma} \delta_{\alpha\gamma} = \sum_{\alpha} 1 = n_{\mu}$ . Thus, the characters  $\chi^{(\mu)}(R)$  for various  $\mu$  are also "orthogonal vectors" in group-element space. However, these vectors are not all different since we saw above that elements in the same class have the same character. If, however, we sum over all *classes* in (4.49) ( $C_k$  is any element of the  $k^{\text{th}}$  class containing  $N_k$  elements), then

$$\sum_{k=1} N_k \chi^{(\mu)*}(C_k) \chi^{(\nu)}(C_k) = g \delta_{\mu\nu}. \quad (4.50)$$

Thus, the characters  $\chi^{(\mu)}$  also form an orthogonal set of vectors in *class-space*. There must be  $p$  such vectors (one for each irreducible representation) so that

$$p \leq \text{number of classes}$$

The equality sign is found to hold again, and so Theorem IV: the number of distinct irreducible representations

$$p = \text{number of classes in the group.} \quad (4.51)$$

No less remarkable than (4.48), this relation determines the number of irreducible representations of a group as the number of classes it contains. Armed with (4.48) and (4.51) it is usually possible to determine the dimensions  $n_{\mu}$  of these irreducible representations uniquely<sup>58</sup>.

We have just seen how the number of irreducible representations of a group and their dimensions may be found. A related question is *how many times* a given irreducible representation  $\Gamma^{(\mu)}$  appears in the reduction of an arbitrary reducible representation  $\Gamma$  or the group, i.e. the determination of the integers  $a_{\mu}$  in (4.46). The  $a_{\mu}$  can be found once the

<sup>58</sup> This statement is true for all the groups of interest in molecular vibration problems.

characters of the representation  $\Gamma$  are known. We see from (4.45) that the character of a typical element  $R$  is given by

$$\chi(R) = \sum_{\mu=1}^p a_{\mu} \chi^{(\mu)}(R)$$

( $p$  is as before the number of different irreducible representations) in terms of the characters  $\chi^{(\mu)}(R)$  of the irreducible representations. Multiply this equation on the left with a particular  $\chi^{(\mu)*}(R)$  and sum over all elements  $R$  of the group. Then,

$$g a_{\mu} = \sum_R \chi^{(\mu)*}(R) \chi(R)$$

on using the orthogonality of the  $\chi^{(\mu)}$ . Since the characters of all elements in a class are the same we can sum over classes instead and obtain

$$a_{\mu} = \frac{1}{g} \sum_{k=1}^p \chi^{(\mu)*}(C_k) \chi(C_k) N_k, \quad (4.52)$$

using the same notation as in (4.50).

	$N_1 C_1$	$N_2 C_2$	$N_3 C_3$
$\Gamma^{(1)}$	$\chi^{(1)}(C_1)$	$\chi^{(1)}(C_2)$	$\chi^{(1)}(C_3)$
$\Gamma^{(2)}$	$\chi^{(2)}(C_1)$	$\chi^{(2)}(C_2)$	$\chi^{(2)}(C_3)$
$\Gamma^{(3)}$	$\chi^{(3)}(C_1)$	$\chi^{(3)}(C_2)$	$\chi^{(3)}(C_3)$
...	...	...	...

Table 4.2: A character table.

(iv) The character table. From the foregoing it is clear that the characters  $\chi^{(\mu)}(R)$  play an important role in characterizing a group representation (hence their name!). Furthermore, the  $\chi^{(\mu)}(R)$  are insensitive to similarity transformations that produce equivalent representations, so that this non-uniqueness is not present in the characters. The characters of the various irreducible representations  $\Gamma^{(\mu)}$  of a group are usually displayed in the form of a *character table* like that shown in Table ??.

The left hand column lists the different irreducible representations, the top row a typical element of each class, preceded by the number of elements  $N_k$  in that class. The characters  $\chi^{(\mu)}(C_k)$  are then distinguished according to representation ( $\mu$ ) and class ( $k$ ) within that representation.

#### 4-9 Symmetry Operations

In this Section we examine more closely the concept *symmetry operation* that was mentioned at the end of Sec. 4-7. Consider an arbitrary polyatomic molecule in its equilibrium state. Let us be interested in the displacement<sup>59</sup> of this structure as a whole about a fixed point  $O$  in

<sup>59</sup> The word "displacement" is used here in a purely geometrical sense of moving the molecule as a rigid structure about its center-of-mass.

space (usually the center-of-mass), the atoms remaining in their equilibrium positions. The orientation in space of the molecular framework is fixed by fixing the positions of any three non-collinear atoms. The only geometrical displacements that are possible are therefore rotations of this structure about an axis passing through the fixed point and reflections of this structure in a plane containing the fixed point. Let us consider these two operations in more detail.

(i) Rotations. Denote the operation of rotating the molecular framework through an angle  $\alpha$  about a direction  $\mathbf{e}_3$  (usually the  $z$  direction) by  $C(\alpha)$ . The effect of  $C(\alpha)$  on a point  $P$  attached to the framework is shown in Fig. 4.6.

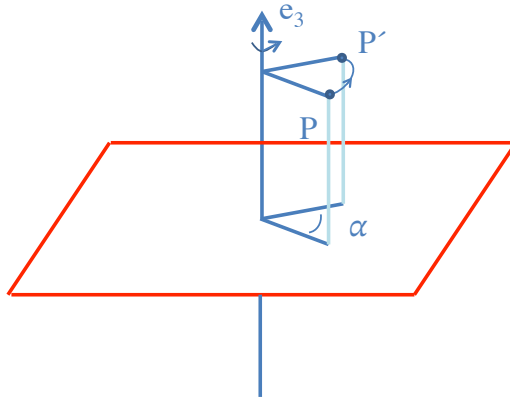


Figure 4.6: A rotation about  $\mathbf{e}_3$  through an angle  $\alpha$ .

The combination (product) of two rotations about the same axis is again a rotation by the sum of the angles. Furthermore, such operations commute:

$$C(\alpha)C(\beta) = C(\beta)C(\alpha) = C(\alpha + \beta). \quad (4.53)$$

A particular case of this relation arises if  $\beta = -\alpha$ . Then,

$$C(-\alpha)C(\alpha) = C(\alpha)C(-\alpha) = C(0) = E,$$

where  $E$  is the identity operation (the process of doing nothing). Thus,  $C(-\alpha)$  is the *inverse* of the operation  $C(\alpha)$ ,

$$C^{-1}(\alpha) = C(-\alpha), \quad (4.54)$$

a result that is geometrically obvious.

Often the rotation angle of interest is a rational fraction of  $2\pi$ ,  $\alpha = 2\pi/n$ ,  $n = 1, 2, \dots$ . Then it is more convenient to write

$$C\left(\frac{2\pi}{n}\right) = C_n, \quad (4.55)$$

and specify  $n$  instead of  $\alpha$ . We notice that performing the operation  $C_n$   $n$

times is equivalent to the identity operation:

$$\underbrace{C_n C_n \dots}_{n \text{ factors}} = C_n^n = C\left(n \frac{2\pi}{n}\right) = C(2\pi) = E,$$

that is, the operations (including the identity!)

$$C_n, C_n^2, \dots, C_n^{n-1}, C_n^n = E \quad (4.56)$$

are simply repeated in the set of operations

$$C_n^{n+1}, \dots, C_n^{2n-1}, C_n^{2n}.$$

In addition each operation in (4.56) has an inverse, and the triple product of any three operations obeys the associative law. Hence, the set of operations  $C_n, C_n^2, \dots, C_n^{n-1}, C_n^n = E$  forms a *group* of order  $n$  in the sense of Sec. 4-6. This group of rotation elements about a common axis is usually denoted by  $C_n$ . It is an abelian group.

(ii) Reflections. Consider next the geometrical operation of a reflection of the molecular framework in a plane passing through  $O$ . Denote the plane and the operation of reflection in it by the symbol  $\sigma$ . The effect of  $\sigma$  on a point  $P$  is shown in Fig. 4.7. This figure shows two planes that are of particular interest: (a) a "vertical" plane  $\sigma_v$  passing through  $O$  that contains the rotation axis  $e_3$ ; (b) the "horizontal" plane  $\sigma_h$  that also passes through  $O$  and is perpendicular to  $\sigma_v$ .

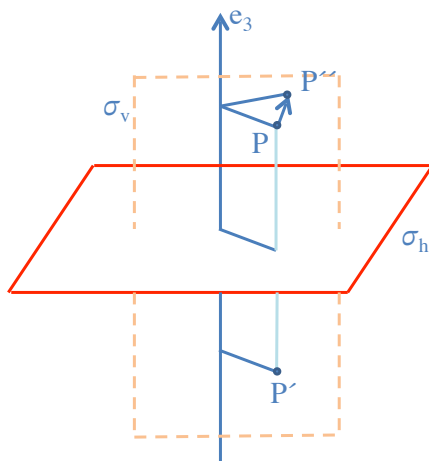


Figure 4.7: Reflections.  $P$  is taken into  $P'$  by  $\sigma_h$ , into  $P''$  by  $\sigma_v$ .

The repetition of any reflection restores a structure to its original position. Therefore, a reflection is also its own inverse, so that

$$\sigma^2 = E, \quad \sigma^{-1} = \sigma. \quad (4.57)$$

So far the geometrical operations we have discussed in no way relate to the specific geometric shape of a particular molecule. However,

among all these operations of rotations, reflections, etc. one might find certain special ones that have the property of bringing the equilibrium framework of a specific molecule *into coincidence with itself*, that is, one is unable to tell whether these operations have been performed or not by just examining the molecular framework before and after the operation. Such operations are called *symmetry operations* and the corresponding symmetry in the molecule that admits them a *symmetry element* of the molecule. One thus has symmetry elements consisting of axes of rotation, planes of reflection, etc., depending on the equilibrium structure of the molecule being examined.

Take, for example, the  $X_3$  molecule of Sec. 4-5. Considered as a plane structure in two dimensions its structure admits as symmetry operations (Fig. 4.8) (i) rotations by  $\pm 2\pi/3$  (symbols  $C_3$  and  $C_3^{-1}$ ) about an axis  $\mathbf{e}$  perpendicular to the molecular plane and passing through the center-of-mass and (ii) reflections in three "vertical" planes (symbols  $\sigma_1, \sigma_2, \sigma_3$ ) intersecting along  $\mathbf{e}$  and bisecting the bond angles at each  $X$  atom. The set of symmetry operations

$$E, C_3, C_3^{-1}, \sigma_1, \sigma_2, \sigma_3 \quad (4.58)$$

that includes the identity operation  $E = C_3^3$  form a group, the so-called *symmetry group of the molecule*  $X_3$  (Prob. 4-6). We will see that this symmetry group already predetermines to a large extent how a molecule can vibrate.

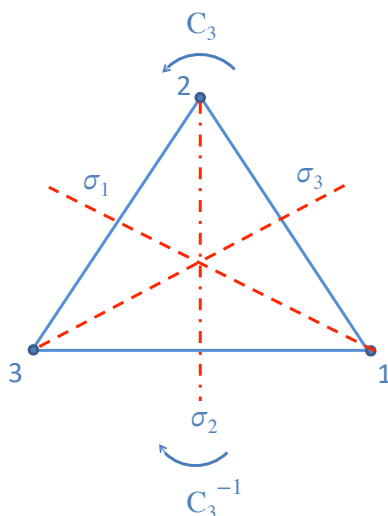


Figure 4.8: Symmetry operations for the  $X_3$  molecule.

Returning to the symmetry group of  $X_3$  in (4.58), (usually denoted by  $C_{3v}$  in the literature) we record in Table 4.3 its character table from D. Schonland<sup>60</sup>, p.281. According to Table 4.3 the group  $C_{3v}$  has three classes consisting of the identity operation  $E$ , the two rotations  $C_3$  and

<sup>60</sup> D. Schonland  
*Molecular Symmetry*,  
D. van Nostrand  
Company Ltd.,  
London and New  
York, 1965.

$C_3^{-1}$ , and the three reflections  $\sigma_1, \sigma_2$ , and  $\sigma_3$  respectively. Therefore this group has three irreducible representations (theorem IV). Calling their dimensions  $n_1, n_2$  and  $n_3$  we know that

$$n_1^2 + n_2^2 + n_3^2 = 6,$$

since the group has six elements (theorem III). This relation can be satisfied in only one way, viz.

$$n_1 = n_2 = 1, \quad n_3 = 2.$$

	$E$	$2C_3$	$3\sigma_v$
$A_1$	1	1	1
$A_2$	1	1	-1
$E$	2	-1	0
$\Gamma$	6	0	0
$\Gamma_t$	2	-1	0
$\Gamma_r$	1	1	-1
$\Gamma_{vib}$	3	0	1

Table 4.3: Character table for  $C_{3v}$ .

Therefore, two of the irreducible representations of  $C_{3v}$ , are one dimensional (called  $A_1$  and  $A_2$  in Table 4.3), the third one has dimension two (called  $E$  in Table 4.3 and *not* to be confused with the identity operation!).

The knowledge that  $X_3$  has the symmetry group  $C_{3v}$  and that this group has three irreducible representations plays an important role in the analysis of the normal modes of  $X_3$ . But to appreciate the procedure we need to know more about group representations and how they are found.

#### 4-10 Group Representations.

We pointed out in Chap. 3 that the rotation of any vector  $\mathbf{Q}$  into a new vector  $\mathbf{q}$  by an operator  $A$  could be written

$$q_i = \sum_j A_{ij} Q_j, \tag{4.59}$$

where the matrix array

$$A_{ij} = \begin{pmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{pmatrix}$$

was called a representation of  $A$  in the basis vectors used as coordinate directions for the components of  $\mathbf{Q}$  and  $\mathbf{q}$ . A second rotation  $B$  carries  $\mathbf{q}$  into  $\mathbf{q}'$ , or

$$q'_i = \sum_j B_{ij} q_j = \sum_{jk} B_{ij} A_{jk} Q_k.$$

Thus the single rotation that carries  $\mathbf{Q}$  directly over into  $\mathbf{q}'$  is represented by the matrix product

$$C_{ik} = \sum_j B_{ij} A_{jk}$$

in terms of the individual representations of  $A$  and  $B$ . This relation shows that matrix arrays like (4.59) qualify as *matrix representations* for the group of operators  $A, B, C, \dots$  in the sense of Sec. 4-6 (iii).

The representations of rotations are now very easily found by choosing for  $\mathbf{Q}$  the position vector  $\mathbf{r} = (x, y, z)$  of a point  $P$  in space and observing how  $P$  moves under a rotation. In fact we unwittingly found a representation of the rotation described by the three Euler angles  $(\phi, \theta, \psi)$  by this method in (3.34) of Chap. 3. With one important difference. Here we are moving the vector, not the coordinate system so that the angles in (3.31) *et seq.* must be replaced by their negatives for use in the present chapter. Let us find two important representations by considering the displacement of a point  $P$  in two dimensions.

(a) Representation of a rotation through an angle  $\alpha$  about the  $z$  axis (the  $\mathbf{e}_3$  direction). This operation is shown in Fig. 4.9.

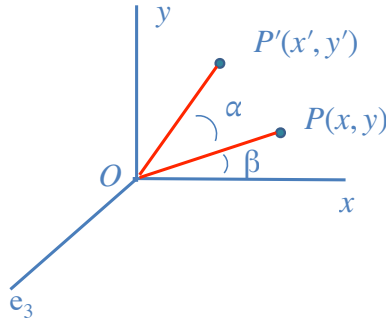


Figure 4.9: A rotation of the point  $P$  through an angle  $\alpha$  in the  $x - y$  plane.

The operation  $C_z(\alpha)$  carries the point  $P(x, y)$  into the point  $P'(x', y')$  where

$$x' = OP \cos(\alpha + \beta), \quad y' = OP \sin(\alpha + \beta),$$

$\beta$  being the angle  $OP$  makes with the  $x$  axis, or

$$x' = x \cos \alpha - y \sin \alpha, \quad y' = x \sin \alpha + y \cos \alpha.$$

Writing these equations in matrix form,

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} \cos \alpha & -\sin \alpha \\ \sin \alpha & \cos \alpha \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

one finds a two-dimensional representation of  $C_z(\alpha)$ , viz.

$$C_z(\alpha) = \begin{pmatrix} \cos \alpha & -\sin \alpha \\ \sin \alpha & \cos \alpha \end{pmatrix}. \tag{4.60}$$

(b) Representation of a reflection in a plane  $\sigma$  passing through  $\mathbf{e}_3$  and making an angle  $\alpha$  with the  $x$  axis. The operation is shown in Fig. 4.10.

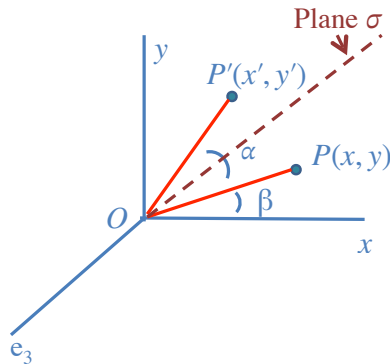


Figure 4.10: Reflection of the point  $P$  through a plane passing through  $\mathbf{e}_3$ .

Defining the angle  $\beta$  as before one finds

$$x' = OP \cos(2\alpha - \beta), \quad y' = OP \sin(2\alpha - \beta),$$

or

$$x' = x \cos 2\alpha + y \sin 2\alpha, \quad y' = x \sin 2\alpha - y \cos 2\alpha,$$

so that

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} \cos 2\alpha & \sin 2\alpha \\ \sin 2\alpha & -\cos 2\alpha \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix},$$

leading to the representation

$$\sigma(\alpha) = \begin{pmatrix} \cos 2\alpha & \sin 2\alpha \\ \sin 2\alpha & -\cos 2\alpha \end{pmatrix} \quad (4.61)$$

for the reflection in the plane  $\sigma$ .

Instead of considering the transformation of the coordinates of a single point in two dimensions we may consider the transformation of all the displacement coordinates of an  $N$ -particle molecule. These coordinates generate a  $3N \times 3N$  representation of the symmetry group of the molecule, the so-called *configuration space* representation. Because of its size, this representation is almost always reducible. Its reduction into the irreducible representations of the molecular symmetry group reveals important information about the nature of the normal modes of the molecule.

The preceding sentence is an important general statement that provides the link between abstract group theory and the small oscillations problem for molecules. While exploring its consequences, we carry along  $X_3$  as an illustrative example. The symmetry group for  $X_3$  is  $\mathcal{C}_{3v}$  (considered as a plane molecule in two dimensional space). Let us develop the

configuration space representation  $\Gamma$  for  $C_{3v}$  in the configuration space of  $X_3$ . Looking back at Fig. 4.3 where we assigned the positions 1, 2 and 3 to the three  $X$  atoms and described the displacements of the atom in each of these positions by  $(x_1, y_1)$ ,  $(x_2, y_2)$  and  $(x_3, y_3)$ , we now consider an arbitrary displacement of  $X_3$  as in Fig. 4.11(a) (the arrows denote the extent and direction of displacement suffered by each  $X$  atom). "Freeze" the molecule in this displaced position and apply the operators of the group  $C_{3v}$ . Fig. 4.11(b) shows what the rotation  $C_3$  about a  $z$  axis point out of the page does. After rotation, the atom in position 1 is endowed with the displacement that atom 3 had, 2 with the displacement 1 had, and 3 with the displacement 2 had, before rotation. Notice that the *labelling* of the three vertices is not altered by the symmetry operation.

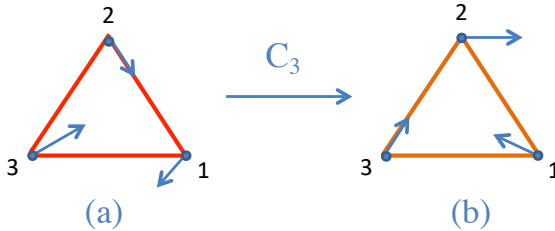


Figure 4.11: Action of  $C_3$  on  $X_3$  in a displaced configuration.

The effect of the rotation  $C_3$  on the coordinates of each atom can be expressed analytically by means of the matrix (4.60) with  $\alpha = 2\pi/3$ . For instance if  $x'_1, y'_1$  are the coordinates of the atom in position 1 after  $C_3$  has acted, then

$$C_3 \begin{pmatrix} x_1 \\ y_1 \end{pmatrix} = \begin{pmatrix} x'_1 \\ y'_1 \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & -\frac{1}{2}\sqrt{3} \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} x_3 \\ y_3 \end{pmatrix}.$$

Similar relations hold for the atoms in positions 2 and 3 before and after rotation so we can write

$$C_3 \begin{pmatrix} x_1 \\ y_1 \\ x_2 \\ y_2 \\ x_3 \\ y_3 \end{pmatrix} = \begin{pmatrix} x'_1 \\ y'_1 \\ x'_2 \\ y'_2 \\ x'_3 \\ y'_3 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \\ -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ x_2 \\ y_2 \\ x_3 \\ y_3 \end{pmatrix}.$$

Looking back at (4.59), we see this means that the matrix

$$\Gamma(C_3) = \begin{pmatrix} 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \\ -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 & 0 \end{pmatrix}$$

gives a  $6 \times 6$  representation of the rotation  $C_3$ . The two things that are striking about  $\Gamma(C_3)$  are its "block" form, and the inordinate number of zeros that appear. In fact one can write

$$\Gamma(C_3) = \begin{pmatrix} \mathbf{0} & \mathbf{0} & C_3 \\ C_3 & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & C_3 & \mathbf{0} \end{pmatrix}, \quad C_3 = \begin{pmatrix} -\frac{1}{2} & -\frac{1}{2}\sqrt{3} \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} \end{pmatrix} \quad (4.62)$$

in terms of  $2 \times 2$  submatrices  $\mathbf{0}$  and  $C_3$ , where  $\mathbf{0}$  is a  $2 \times 2$  null matrix and  $C_3$  the  $\alpha = 2\pi/3$  version of (4.60). In a similar vein, we obtain the representations for the remaining operators of the group  $\mathcal{C}_{3v}$ :

$$\begin{aligned} \Gamma(C_3^{-1}) &= \begin{pmatrix} \mathbf{0} & C_3^{-1} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & C_3^{-1} \\ C_3^{-1} & \mathbf{0} & \mathbf{0} \end{pmatrix}, \quad C_3^{-1} = \begin{pmatrix} -\frac{1}{2} & \frac{1}{2}\sqrt{3} \\ -\frac{1}{2}\sqrt{3} & -\frac{1}{2} \end{pmatrix} \\ \Gamma(\sigma_1) &= \begin{pmatrix} \sigma_1 & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \sigma_1 \\ \mathbf{0} & \sigma_1 & \mathbf{0} \end{pmatrix}, \quad \sigma_1 = \begin{pmatrix} \frac{1}{2} & -\frac{1}{2}\sqrt{3} \\ -\frac{1}{2}\sqrt{3} & -\frac{1}{2} \end{pmatrix} \\ \Gamma(\sigma_2) &= \begin{pmatrix} \mathbf{0} & \mathbf{0} & \sigma_2 \\ \mathbf{0} & \sigma_2 & \mathbf{0} \\ \sigma_2 & \mathbf{0} & \mathbf{0} \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \\ \Gamma(\sigma_3) &= \begin{pmatrix} \mathbf{0} & \sigma_3 & \mathbf{0} \\ \sigma_3 & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \sigma_3 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} \frac{1}{2} & \frac{1}{2}\sqrt{3} \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} \end{pmatrix} \\ \Gamma(E) &= \begin{pmatrix} I & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & I & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & I \end{pmatrix}, \quad I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \end{aligned} \quad (4.63)$$

The matrices for  $\sigma_1, \sigma_2$  and  $\sigma_3$  follow on setting  $\alpha = -\pi/6, \pi/2$  and  $\pi/6$  respectively in (4.61), and the matrix  $C_3^{-1}$  on setting  $\alpha = -2\pi/3$  in (4.60). The representation  $\Gamma(E)$  for the identity operation is quite obvious, but also formally follows on setting  $\alpha = 0$  (or  $2\pi$ ) in (4.60).

The collection of matrices  $\Gamma = \{\Gamma(E), \Gamma(C_3), \dots\}$  is clearly reducible since  $\mathcal{C}_{3v}$  only has one and two dimensional irreducible representations. Let us examine this reduction in some detail. First, we know that  $\Gamma$  must

be reducible into translational, rotational and vibrational representations  $\Gamma_t, \Gamma_r$  and  $\Gamma_{vib}$  generated by the translational, rotational and vibrational coordinates of the molecule. This is so because any one of these motions can be performed without exciting the others. We can thus write

$$\Gamma = \Gamma_t + \Gamma_r + \Gamma_{vib} \quad (4.64)$$

as a first step in the reduction of  $\Gamma$ . The representations on the right hand side of this equation are usually still further reducible. Of these, the reduction of  $\Gamma_{vib}$  is the important one since here we find information relating to the vibrational modes of the molecule.

To effect the reduction of  $\Gamma_{vib}$  we need to know the characters  $\chi_{vib}(R)$  of this representation, see (4.46). But these are most easily found by subtraction, knowing the characters of  $\Gamma, \Gamma_t$  and  $\Gamma_r$ :

$$\chi_{vib}(R) = \chi(R) - \chi_t(R) - \chi_r(R) \quad (4.65)$$

in an obvious notation.

The characters  $\chi(R)$  of the total representation  $\Gamma$  are read off directly from (4.62) and (4.63):

$$\chi(E) = 6, \quad \chi(C_3) = 0, \quad \chi(\sigma_1) = 0,$$

taking a typical element of each class. These numbers are appended to Table 4.3 next to the representation  $\Gamma$ .

The characters of  $\Gamma_t$  and  $\Gamma_r$  are also simple to calculate. Consider translations first. We take the center-of-mass coordinates of the molecule

$$\mathbf{X} = \frac{1}{\mu} \sum_p m_p \mathbf{x}_p \quad (4.66)$$

( $\mathbf{x}_p$  is the displacement of the atom in the  $p^{\text{th}}$  position,  $m_p$  its mass and  $\mu = \sum_p m_p$  the total molecular mass) and subject it to any symmetry operation  $R$ . Then, since  $R$  does not act on the symbol  $P$ ,

$$\begin{aligned} RX_i &= \frac{1}{\mu} \sum_p m_p (Rx_{pi}) = \frac{1}{\mu} \sum_p \sum_{j=1}^3 \Gamma_t(R)_{ij} x_{pj} \\ &= \sum_{j=1}^3 \Gamma_t(R)_{ij} X_j, \quad i = 1, 2, 3. \end{aligned}$$

Thus,  $\mathbf{X}$  transforms like the three dimensional vector that it is and the matrices  $\Gamma_t(R)$ , with matrix elements  $\Gamma_t(R)_{ij}$ , constitute a matrix representation of  $R$ . Its trace is

$$\chi_t(R) = \sum_{i=1}^3 \Gamma_t(R)_{ii}. \quad (4.67)$$

For  $X_3$  there are six matrices  $\Gamma_t(R)$  given by  $C_3, C_3^{-1}, \sigma_1, \sigma_2, \sigma_3$  and  $\mathbf{I}$  in (4.62) through (4.63). The traces  $\chi_t(R)$  of typical elements from each class are

$$\chi_t(E) = 2, \quad \chi_t(C_3) = -1, \quad \chi_r(\sigma_1) = 0$$

for  $X_3$ . These numbers appear in Table 4.3 next to the representation  $\Gamma_t$ .

The representation  $\Gamma_r$  generated by the rotational coordinates is more tricky. Here, one must first decide how such a "coordinate" is defined. We know from our discussions of rigid body rotations that it is not generally possible to find coordinates such that their vanishing time derivatives implies that the body does not rotate. However, we can characterize a lack of rotation of the molecular framework by the vanishing of the angular momentum

$$\mathbf{L} = \sum_p m_p (\mathbf{r}_p \times \dot{\mathbf{x}}_p)$$

about its center-of-mass. Here  $\mathbf{r}_p$  measures the instantaneous position of the atom in position  $p$  from the center-of-mass and the  $\mathbf{x}_p$  have the same meaning as in (4.67). But  $\mathbf{r}_p = \mathbf{r}_{op} + \mathbf{x}_p$  in terms of the equilibrium positions  $\mathbf{r}_{op}$  of each atom, so that one has

$$\mathbf{L} \simeq \sum_p m_p (\mathbf{r}_{op} \times \dot{\mathbf{x}}_p) = \frac{d}{dt} \sum_p m_p (\mathbf{r}_{op} \times \mathbf{x}_p)$$

to first order in the displacements  $\mathbf{x}_p$ . In this order, a vanishing  $\mathbf{L}$  means that the time derivative of

$$\mathbf{R} = \sum_p m_p (\mathbf{r}_{op} \times \mathbf{x}_p) \quad (4.68)$$

vanishes, thus placing  $\mathbf{R}$  on the same footing as  $\mathbf{X}$ , but for rotational instead of translational motion. We take  $\mathbf{R}$  as our "rotational" coordinate. It is an ordinary vector under rotation, but a *pseudovector* under reflections. In the present instance the single rotational coordinate  $R_z$  is found by direct calculation to be proportional to

$$(y_1 - y_3 - \sqrt{3}x_3),$$

which changes sign under  $\sigma_1$  but is left unaffected by  $C_3$  and  $E$ .

Hence

$$\chi_r(E) = 1, \quad \chi_r(C_3) = -1, \quad \chi_r(\sigma_1) = -1.$$

These numbers also appear in Table 4.3. The characters for the representation  $\Gamma_{vib}$  are now found by subtraction as

$$\chi_{vib} = 2, \quad \chi_{vib}(C_3) = 2, \quad \chi_{vib}(\sigma_1) = 1. \quad (4.69)$$

According to (4.46) the reduction of  $\Gamma_{vib}$  thus proceeds as follows:

$$\begin{aligned} \Gamma_{vib}(X_3) &= \frac{1}{6}(3+0+3)A_1 + \frac{1}{6}(3+0-3)A_2 + \frac{1}{6}(6+0+0)E \\ &= A_1 + E, \end{aligned} \quad (4.70)$$

if we use the relation (4.52) repeatedly.

Of what avail is this knowledge? We return to the dynamical description of a vibrating system to find out. The link to group theory is provided by the fact that the Lagrange function (see (4.7))

$$L = \sum_k \frac{1}{2} \dot{x}_k'^2 - \sum_k \frac{1}{2} W_{kl} x_k' x_l'$$

(notice the use of mass-scaled coordinates) is *invariant* under the symmetry operations of the molecular symmetry group. (This statement is of course equally true for the original Lagrangian given in the displacement coordinates but the theory is simpler to implement in the mass-scaled set as given above). To take our standard example of  $X_3$  again, it is clear that the potential energy in the displacements pictured in Fig. 4.11 (a) and (b) is the same: all that has happened is that the physically equivalent  $X$ -atoms have changed places. Similarly, the kinetic energy term stays invariant under all symmetry operations of the group and therefore also  $L$ .

The same remarks are true if  $L$  is expressed in normal coordinates instead:  $L$  must be an invariant under all group operations. This requirement places certain restrictions on the way normal coordinates must transform under group operations and this in turn leads us directly to the information on the number and types of vibrational modes that a molecule has.

There are two cases:

(i) The system has no degenerate eigenfrequencies. This means that  $V$  has the form (the sum only includes vibrational normal coordinates, see (4.35))

$$V = \frac{1}{2} \Omega_1^2 \zeta_1^2 + \frac{1}{2} \Omega_2^2 \zeta_2^2 + \dots$$

when expressed in normal coordinates. The numbers  $\Omega_1, \Omega_2, \dots$  are supposed to be all different. To maintain the same form for  $V$  under any symmetry operation  $R$  means that each normal coordinate must behave like

$$R\zeta_i = \pm \zeta_i \quad (4.71)$$

under a symmetry operation, i.e. they must be either symmetric (+1) or antisymmetric (-1). Thus, non-degenerate normal coordinates generate *one-dimensional* representations of the symmetry group. Such representations are obviously irreducible.

(ii) Some of the eigenfrequencies of the system may be degenerate. This means that some normal coordinates share a common frequency. The potential in this case looks like (again only vibrational coordinates are present)

$$V = \frac{1}{2} \Omega_1^2 \zeta_1^2 + \frac{1}{2} \Omega_2^2 \zeta_2^2 + \dots + \frac{1}{2} \omega_1^2 (\zeta_{11}^2 + \zeta_{12}^2 + \dots + \zeta_{1n_1}^2) \\ + \frac{1}{2} \omega_2^2 (\zeta_{21}^2 + \zeta_{22}^2 + \dots + \zeta_{2n_2}^2) + \dots + \frac{1}{2} \omega_\mu^2 (\zeta_{\mu 1}^2 + \zeta_{\mu 2}^2 + \dots + \zeta_{\mu n_\mu}^2) + \dots$$

where  $n_1$  coordinates share the frequency  $\omega_1$ ,  $n_2$  coordinates the frequency  $\omega_2$ , etc. The non-degenerate coordinates still transform according to (4.71). But for a set of  $n_\mu$  degenerate coordinates,  $\zeta_{\mu 1}, \zeta_{\mu 2}, \dots, \zeta_{\mu n_\mu}$ , all we can say is that

$$R\zeta_{\mu\alpha} = \sum_{\beta=1}^{n_\mu} D^{(\mu)}(R)_{\alpha\beta} \zeta_{\mu\beta}, \quad (4.72)$$

where  $D^{(\mu)}(R)$  is an orthogonal matrix, in order to preserve the form of  $V$ . For (4.72) simply represents a *rotation* in the  $n_\mu$  dimensional space of the normal coordinates  $\{\zeta_{\mu\alpha}\}$ , leaving the sum of squares

$$\zeta_{1\mu}^2 + \zeta_{2\mu}^2 + \dots + \zeta_{n_\mu\mu}^2$$

invariant. Clearly, the matrices with the  $D^{(\mu)}(R)_{\alpha\beta}$  as matrix elements form an  $n_\mu$ -dimensional representation of the molecular symmetry group. A little reflection shows that this must indeed be an *irreducible* representation for the potential energy has been reduced to a sum of squares.

Coordinates like the  $\zeta_{\mu\alpha}$  which obey (4.72) are said to transform like (or belong to) the  $\mu^{\text{th}}$  irreducible representation of the symmetry group. We have then that normal coordinates belonging to non-degenerate frequencies transform like the one dimensional representations of the group, those sharing a common eigenfrequency like multidimensional irreducible representations of the group, the dimension equalling the *multiplicity*  $f_\mu$  of that degenerate eigenfrequency,

$$f_\mu = n_\mu.$$

We stress that these degeneracies are an inherent property of the molecule<sup>61</sup> that cannot be destroyed without also destroying the symmetry of the molecule (by for example placing it in an external field with which it interacts).

Turning all this around now, we can say (i) that since the Lagrange function is brought into normal form by a linear orthogonal transformation (this is where the use of the mass-scaled coordinates is advantageous)  $\mathbf{x}' = U\zeta$ , the matrix  $U$  will likewise *serve to reduce the configuration space representation*  $\Gamma_{vib}$  (for the vibrational motion of the molecule) into *whatever irreducible representations it contains*, and (ii) that the dimensions of these irreducible representations tell us immediately how many non-degenerate and degenerate eigenfrequencies the molecule has, together with their multiplicities  $f_\mu$ .

These remarks, and especially the reduction process, can be illustrated by looking back at (4.39) and (4.40) which show that one vibrational coordinate  $Q_{A_1}$  belongs to the frequency  $\sqrt{3\kappa/m}$ , and two vibrational coordinates  $Q_{E_1}$  and  $Q_{E_2}$  to the frequency  $\sqrt{3\kappa/2m}$ . This is in accord with the information contained in the reduction of  $\Gamma_{vib}$  for  $X_3$  in (4.70).

<sup>61</sup> As opposed to accidental degeneracies that can occur for special values of the coupling constants.

The transformation matrix  $U$  in (4.37) should reduce the configuration representation  $\Gamma$  of  $X_3$  accordingly. This is indeed the case. Taking the representation matrix  $\Gamma(C_3)$  for the rotation  $C_3$  from (4.62) we find that

$$U^{-1}\Gamma(C_3)U = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \quad (4.73)$$

fully reduces  $\Gamma(C_3)$  into one dimensional and two dimensional irreducible representations of  $\mathcal{C}_{3v}$ . This reduced form agrees with the reduction

$$\Gamma = A_1 + A_2 + 2E \quad (4.74)$$

of  $\Gamma$  (see Prob. 4-8) and shows that the irreducible representation of  $C_3$  are

$$D^{(A_1)}(C_3) = 1, \quad D^{(A_2)}(C_3) = 1, \quad \text{and} \quad D^{(E)}(C_3) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}. \quad (4.75)$$

The irreducible representations for the remaining operators in  $\mathcal{C}_{3v}$  can be found in the same way. (Prob. 4-9).

#### 4-11 Symmetry-Adapted Coordinates (SACs)

The appearance of two separate species of coordinates in the Lagrangian (4.29) for the  $X_3$  molecule that are not coupled to each other suggests that coordinates belonging to different species of representation of the symmetry group never couple. This is indeed so. A term

$$(Q_{A_1}Q_{E1})$$

in the Lagrange function (4.39) would be inadmissible since according to (4.72) with  $D^{(E)}(C_3)$  given by the last entry in (4.75) it would change into

$$Q_{A_1}\left(-\frac{1}{2}Q_{E1} - \frac{1}{2}\sqrt{3}Q_{E2}\right)$$

under action of the rotation  $C_3$ , thereby changing the value of  $L$ . In fact, this simple remark leads to a very general discussion of the structure of the potential energy matrix  $U$ .

We introduce some terminology first. Coordinates like the  $Q_{A_1}, Q_{E1}$ , etc., that transform like the irreducible representations of the molecular symmetry group we choose to call *symmetry-adapted coordinates* (or SACs for short). They are not necessarily but can be *normal* coordinates of the system because of the non-uniqueness of the representation

matrices themselves. We restrict our attention for the moment to SACs not involving any linear or angular momentum of the molecule, since coordinates corresponding to such motions cannot occur in the potential function anyway. The symbol  $Q$ , suitably attired, is used to denote these coordinates. The SACs belonging to the  $\mu^{\text{th}}$  irreducible representation respond to a symmetry operation  $R$  as in the equation

$$RQ_{\mu,\alpha} = \sum_{\beta=1}^{n_{\mu}} D^{(\mu)}(R)_{\alpha\beta} Q_{\mu,\beta}, \quad (4.76)$$

where  $n_{\mu}$  is the dimension of the representation matrices  $D^{(\mu)}(R)$ . These coordinates themselves are said to define an *invariant subspace* of dimension  $n_{\mu}$ . But we saw in the previous section that a given irreducible representation can occur more than once in  $\Gamma_v$ . This means there can be more than one *set* of coordinates  $Q_{\mu,\alpha}$  that transform as in (4.76) and hence more than one invariant subspace of dimension  $n_{\mu}$ . Two such subspaces are called *equivalent*. We need a notation to express this fact. Attach a subscript  $i$  to the representation index  $\mu$  on  $Q_{\mu,\alpha}$  thusly:  $Q_{\mu_i,\alpha}$ . If the representation  $\mu$  is repeated  $a_{\mu}$  times then

$$i = 1, 2, \dots, a_{\mu}$$

identifies the different sets of SAC's transforming according to the representation  $\mu$ . Thus, different values of  $\mu$  mean distinct subspaces, different values of  $i$  on the  $\mu_i$  equivalent subspaces in this notation.

Now, to express the potential energy in terms of the set of SAC's

$$Q_{\mu_i,1}, Q_{\mu_i,2}, \dots, Q_{\mu_i,n_{\mu}}$$

where  $i = 1, 2, \dots, a_{\mu}$  runs through all equivalent subspaces  $\mu$ , and  $\mu$  runs through all the distinct invariant subspaces admitted by the problem. We have

$$V = \sum_{\mu,\nu} \sum_{i,j} \sum_{\alpha,\beta} \frac{1}{2} W_{\mu_i,\alpha;\nu_j,\beta} Q_{\mu_i,\alpha} Q_{\nu_j,\beta}, \quad (4.77)$$

where the coefficients  $W_{\mu_i,\alpha;\nu_j,\beta}$ , like the  $W_{kl}$  of (4.5), form a symmetric matrix, but with rows and columns double-indexed by  $\{\mu_i, \alpha\}$ . A symmetry operation of  $V$  leads to

$$\begin{aligned} RV &= \frac{1}{2} W_{\mu_i,\alpha;\nu_j,\beta} D^{(\mu)}(R)_{\alpha'\alpha} D^{(\nu)}(R)_{\beta'\beta} Q_{\mu_i,\alpha'} Q_{\nu_j,\beta'} \\ &= \sum \frac{1}{2} W_{\mu_i,\alpha;\nu_j,\beta} Q_{\mu_i,\alpha} Q_{\nu_j,\beta}, \end{aligned}$$

since  $V$  is supposed to be invariant under all group operations. Therefore it follows that the relation

$$\sum_{\alpha'\beta'} D^{(\mu)}(R)_{\alpha'\alpha} D^{(\nu)}(R)_{\beta'\beta} W_{\mu_i,\alpha';\nu_j,\beta'} = W_{\mu_i,\alpha;\nu_j,\beta}$$

must be satisfied by the coefficients  $U_{\mu_i\alpha;v_j\beta}$ . This result holds for any symmetry operation  $R$ ; in particular it holds for the sum of all such operations. Summing both sides of this equation in  $R$  introduces the orthogonality properties of the  $D^{(\mu)}(R)$  via the great orthogonality theorem, (4.43), (we only deal in *real* coordinates, therefore the matrices  $D^{(\mu)}(R)$  are real and the complex conjugation  $(*)$  in (4.43) is superfluous) and we find

$$g\delta_{\mu\nu}\delta_{\alpha\beta}\frac{1}{n_\mu}\sum_{\alpha=1}^{n_\mu}W_{\mu_i\alpha;v_j\alpha}=gW_{\mu_i\alpha;v_j\beta}.$$

This remarkable result says, first of all, that  $W_{\mu_i\alpha;v_j\beta}$  is zero unless  $\mu_i$  and  $v_j$  are equivalent representations ( $\mu = \nu$ ), and  $\alpha = \beta$ . Furthermore, if these two conditions are satisfied then

$$\frac{1}{n_\mu}\sum_{\alpha=1}^{n_\mu}W_{\mu_i\alpha;\mu_j\alpha}=W_{\mu_i\alpha;\mu_j\alpha},$$

which can only be satisfied if both sides are *independent* of  $\alpha$ . Thus,

$$W_{\mu_i\alpha;\mu_j\alpha}=W_{\mu_i\mu_j}\delta_{\mu\nu}\delta_{\alpha\beta}, \quad (4.78)$$

that is, the matrix elements  $U_{\mu_i\alpha;v_j\beta}$  (a) only couple SACs lying in equivalent subspaces and (b) the coefficients of the cross products of all SACs in such a pair of equivalent subspaces are the same!

The final appearance of the potential in SACs is thus

$$V=\sum_{\mu}\sum_{i,j}\frac{1}{2}W_{\mu_i\mu_j}Q_{\mu_i\alpha}Q_{\mu_j\alpha}. \quad (4.79)$$

A similar reduction occurs for the kinetic energy. Furthermore, since the transformation from the configuration space coordinates to SACs is an orthogonal one if mass-scaled displacement coordinates are employed, the kinetic energy must appear as

$$T=\frac{1}{2}\sum_{\mu,l,\alpha}\dot{Q}_{\mu_l\alpha}^2+\dots \quad (4.80)$$

The ellipsis refers to SACs that describe the translation and rotation of the molecule that do appear in the kinetic energy but not in the potential energy (see (4.35)).

Putting (4.79) and (4.80) together we see that the determinantal equation (4.32) for the vibrational eigenfrequencies *factors* into subdeterminants of dimension equal to the number of equivalent irreducible representations that are present in  $\Gamma_{vib}$ . Furthermore there are as many degenerate eigenfrequencies as the dimension of any one of these equivalent representations, so that a given submatrix must be repeated in  $W$  as often as the dimension of the irreducible representation its SACs belong to.

The generality of these statements obscure their simplicity. An example will suffice as an illustration.

Consider the ammonia molecule  $NH_3$ , the three  $H$  atoms forming an equilateral base triangle for a pyramid with the  $N$  atom at its apex. The symmetry group of  $NH_3$  is clearly  $C_{3v}$  also, but the configuration representation  $\Gamma$  is now twelve dimensional (three degrees of freedom per atom). The characters of the total representation  $\Gamma$  as well as the characters of the translational and rotational representations are shown in Table 4.4 which repeats the character table of  $C_{3v}$  again.

	$E$	$2C_3$	$3\sigma_v$
$A_1$	1	1	1
$A_2$	1	1	-1
$E$	2	-1	0
$\Gamma$	12	0	2
$\Gamma_t$	3	0	1
$\Gamma_r$	3	0	-1
$\Gamma_{vib}$	6	0	2

Table 4.4: Character table for  $C_{3v}$  and characters for the  $NH_3$  molecule.

The reduction of  $\Gamma_{vib}$  is easily found to be

$$\Gamma_{vib} = \frac{1}{6}(6+6)A_1 + \frac{1}{6}(6-6)A_2 + \frac{1}{6}(12)E = 2A_1 + 2E.$$

Therefore,  $NH_3$  possesses two SAC's transforming like  $A_1$  and two pairs of SAC's transforming like  $E$ . The corresponding structure of the  $W$ -matrix of (4.78) is shown in Fig. 4.12, the second and third  $2 \times 2$  submatrices being identical.

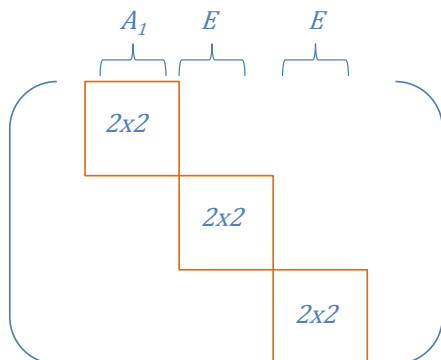


Figure 4.12: Structure of the  $W$  matrix for  $NH_3$ .

Obviously, SACs are appropriate coordinates to employ in complicated vibrational problems. But how does one find them? A *systematic* application of group theoretic techniques provides a powerful method for doing so. We discuss the elements of this method next.

### 4-12 Projection Operators

One method of obtaining coordinates that belong to a prescribed irreducible representation of the molecular symmetry group is to try to construct them by inspection. But such an approach is obviously of limited value, depending as it does on the ingenuity of the user. We now show how a *systematic* procedure for finding SAC's can be developed, using some further results of group theory.

Consider again (4.76). Multiply both sides of this equation by  $D^{(\nu)}(R)_{\gamma\delta}^*$  and then sum on all group operators  $R$ :

$$\sum_R D^{(\nu)}(R)_{\gamma\delta}^* R Q_{\mu,\alpha} = \frac{g}{n_\nu} \delta_{\mu\nu} \delta_{\gamma\alpha} Q_{\nu,\delta},$$

after invoking the great orthogonality theorem once more. Now set  $\delta = \gamma$  on both sides of this expression and sum on  $\gamma = 1, 2, \dots, n_\nu$ . Then

$$\sum_R \sum_\gamma D^{(\nu)}(R)_{\gamma\gamma}^* R Q_{\mu,\alpha} = \sum_R \chi^{(\nu)}(R)^* R Q_{\mu,\alpha} = \frac{g}{n_\nu} \delta_{\mu\nu} Q_{\mu,\alpha},$$

or, writing  $\mu$  for  $\nu$  and  $\nu$  for  $\mu$ ,

$$\begin{aligned} P^{(\mu)} Q_{\nu,\alpha} &= 0, & \mu \neq \nu \\ &= Q_{\mu,\alpha}, & \mu = \nu, \end{aligned}$$

where the combination of operations

$$P^{(\mu)} = \frac{n_\mu}{g} \sum_R \chi^{(\mu)}(R)^* R \quad (4.81)$$

defines  $P^{(\mu)}$ . Thus,  $P^{(\mu)}$  has the value one when operating on a coordinate  $Q_{\mu,\alpha}$  that belongs to the irreducible representation  $\mu$  and zero otherwise, i.e.  $P^{(\mu)}$  is a *projection operator* onto the coordinates  $Q_{\mu,\alpha}$ .

We make use of this property as follows. The displacements  $x_k$  of each atom must be linear combinations of the symmetry-adapted coordinates  $Q_{\mu_i,\alpha'}$ . Moreover, if mass-scaled displacements  $\sqrt{m_k} x_k = \tilde{x}'_k$  are used, it suffices to consider orthogonal transformations only:

$$\mathbf{x}' = U\mathbf{Q}, \quad \text{or} \quad \mathbf{Q} = U^T \mathbf{x}', \quad (4.82)$$

since  $UU^T = I$ . Operating on the  $k^{\text{th}}$  component of  $\mathbf{x}'$  with the projection operator  $P^{(\mu)}$  gives

$$P^{(\mu)}(x'_k) = \sum_{i,\alpha} U_{k;\mu_i,\alpha} Q_{\mu_i,\alpha}, \quad (4.83)$$

containing (no summation on  $\mu$ ); the operator  $P^{(\mu)}$  selects out of all the SAC's  $\mathbf{Q}$  in (4.82) those sets which belong to the  $\mu^{\text{th}}$  irreducible representation only. On the other hand the left hand side of (4.83) can be calculated explicitly. It equals

$$P^{(\mu)}(x'_k) = \frac{n_\mu}{g} \sum_R \chi^{(\mu)*}(R) R x'_k = \frac{n_\mu}{g} \sum_R \sum_l \chi^{(\mu)*}(R) \Gamma(R)_{kl} x'_l, \quad (4.84)$$

where the  $\Gamma(R)$  are the matrix representation of the group generated by the *complete* configuration space of the molecule. Consequently the "coordinates"  $P^{(\mu)}(x'_k)$  that are *linear combinations* of the  $x_k$  may be used to construct a suitable set of  $Q$ 's. However, since each projection operator  $P^{(\mu)}$  generates  $3N$  linear combinations of coordinates that belong to  $\mu$ , that are candidates for  $Q$ 's, and there are certainly less *independent* combinations than this per representation, there is considerable redundancy in the procedure. The problem (and its solution) is best illustrated by way of an example.

The projection operators for the irreducible representations  $A_1, A_2$  and  $E_1$  of  $\mathcal{C}_{3v}$  are

$$\begin{aligned} P^{(A_1)} &= \frac{1}{6}\{E + C_3 + C_3^{-1} + \sigma_1 + \sigma_2 + \sigma_3\} \\ P^{(A_2)} &= \frac{1}{6}\{E + C_3 + C_3^{-1} - \sigma_1 - \sigma_2 - \sigma_3\} \\ P^{(A_3)} &= \frac{1}{6}\{E - C_3 - C_3^{-1}\}, \end{aligned} \quad (4.85)$$

using (4.81) and the character table for  $\mathcal{C}_{3v}$ . Applying these operations in turn to the coordinates  $(x_1, y_1), (x_2, y_2), (x_3, y_3)$  of the  $X_3$  molecule shown in Fig. 4.4 we obtain linear combinations of these coordinates that transform like  $A_1, A_2$  and  $E$ . We choose the following combinations (going over into mass-scaled coordinates):

$$\begin{aligned} P^{(A_1)}(x'_1) &= \frac{\sqrt{3}}{12}\{\sqrt{3}(x'_1 - x'_3) - (y'_1 - 2y'_2 + y'_3)\} \sim Q_{A_1} \quad (i) \\ P^{(A_2)}(x'_1) &= \frac{1}{12}\{\sqrt{3}(y'_1 - y'_3) + (x'_1 - 2x'_2 + x'_3)\} \sim Q_{A_2} \quad (ii) \\ P^{(E)}(x'_1 + x'_2 + x'_3) &= x'_1 + x'_2 + x'_3 = Q'_{E1} \quad (iii) \\ P^{(E)}(y'_1 + y'_2 + y'_3) &= y'_1 + y'_2 + y'_3 = Q'_{E2} \quad (iv) \\ P^{(E)}(x'_1) &= \frac{1}{6}\{4x'_1 + x'_2 + x'_3 - \sqrt{3}(y'_2 - y'_3)\} \sim Q_{E1} \quad (v) \\ P^{(E)}(y'_1) &= \frac{1}{6}\{4y'_1 + y'_2 + y'_3 + \sqrt{3}(x'_2 - x'_3)\} \sim Q_{E2}. \quad (vi) \end{aligned} \quad (4.86)$$

From (4.86) (i) we can construct the first row of  $U$  in the inverse transformation

$$Q_{\mu_i, \alpha} = \sum_k U_{\mu_i, \alpha; k}^T x'_k \quad (4.87)$$

by writing

$$Q_{A_1} = \frac{1}{2\sqrt{3}}(\sqrt{3} \ -1 \ 0 \ 2 \ -\sqrt{3} \ -1)\{x'_1, y'_2, \dots\} \quad (4.88)$$

(the factor  $1/2\sqrt{3}$  normalizes this vector to unity). The second row of  $U$  is obtained from (4.86) (ii) as

$$Q_{A_2} = \frac{1}{2\sqrt{3}}(1 \ \sqrt{3} \ -2 \ 0 \ 1 \ -\sqrt{3})\{x'_1, y'_2, \dots\}. \quad (4.89)$$

The row vectors appearing in  $Q_{A_1}$  and  $Q_{A_2}$  are automatically orthogonal to each other and to the row vectors  $Q_{E1}$  and  $Q_{E2}$ , etc. But the coordinates transforming like  $E$  have row vectors that are not necessarily orthogonal. Starting with

$$Q'_{E1} = \frac{1}{2\sqrt{3}}(2 \ 0 \ 2 \ 0 \ 2 \ 0)\{x'_1, y'_2, \dots\} \quad (4.90)$$

and

$$Q'_{E2} = \frac{1}{2\sqrt{3}}(0 \ 2 \ 0 \ 2 \ 0 \ 2)\{x'_1, y'_2, \dots\} \quad (4.91)$$

that *are* orthogonal to each other, we orthogonalize  $Q_{E1}$  and  $Q_{E2}$  (they are orthogonal to each other) to  $Q'_{E1}$  and  $Q'_{E2}$ . The result is

$$Q_{E1} = \frac{1}{2\sqrt{3}}(2 \ 0 \ -1 \ -\sqrt{3} \ -1 \ \sqrt{3})\{x'_1, y'_2, \dots\}$$

$$Q_{E2} = \frac{1}{2\sqrt{3}}(0 \ -2 \ -\sqrt{3} \ 1 \ \sqrt{3} \ 1)\{x'_1, y'_2, \dots\}$$

so that

$$\begin{pmatrix} Q_{A_1} \\ Q_{A_2} \\ Q_{E1} \\ Q_{E2} \\ Q'_{E1} \\ Q'_{E2} \end{pmatrix} = \frac{1}{2\sqrt{3}} \begin{pmatrix} \sqrt{3} & -1 & 0 & 2 & -\sqrt{3} & -1 \\ 1 & \sqrt{3} & -2 & 0 & 1 & -\sqrt{3} \\ 2 & 0 & -1 & -\sqrt{3} & -1 & \sqrt{3} \\ 0 & -2 & -\sqrt{3} & 1 & \sqrt{3} & 1 \\ 2 & 0 & 2 & 0 & 2 & 0 \\ 0 & 2 & 0 & 2 & 0 & 2 \end{pmatrix} \begin{pmatrix} x'_1 \\ y'_1 \\ x'_2 \\ y'_2 \\ x'_3 \\ y'_3 \end{pmatrix} \quad (4.92)$$

and

$$\begin{pmatrix} x'_1 \\ y'_1 \\ x'_2 \\ y'_2 \\ x'_3 \\ y'_3 \end{pmatrix} = \frac{1}{2\sqrt{3}} \begin{pmatrix} \sqrt{3} & 1 & 2 & 0 & 2 & 0 \\ -1 & \sqrt{3} & 0 & -2 & 0 & 2 \\ 0 & -2 & -1 & -\sqrt{3} & 2 & 0 \\ 2 & 0 & -\sqrt{3} & 1 & 0 & 2 \\ -\sqrt{3} & 1 & -1 & \sqrt{3} & 2 & 0 \\ -1 & -\sqrt{3} & \sqrt{3} & 1 & 0 & 2 \end{pmatrix} \begin{pmatrix} Q_{A_1} \\ Q_{A_2} \\ Q_{E1} \\ Q_{E2} \\ Q'_{E1} \\ Q'_{E2} \end{pmatrix} \quad (4.93)$$

give the relations between the configuration and symmetry-adapted coordinates, the latter relation serving to identify the origin of the matrix  $U$  in (4.38). We have succeeded in constructing the transformation matrix for the  $X_3$  molecular vibration problem on the basis of symmetry arguments alone.

In terms of the SAC's  $Q_{A_1}$ ,  $Q_{A_2}$  etc., the kinetic energy of  $X_3$  assumes the form advertised in (4.80). In this case the potential energy also becomes diagonal, see (4.39), but this is an exception rather than a rule due to the high degree of symmetry  $X_3$  exhibits. Usually some diagonalization among SAC's that belong to the same irreducible representation of the symmetry group of the molecule is necessary (Prob. 4-11).

## 4-13 Vibrations of Continuous Systems

We now inquire what happens to the vibrational modes of a system when the number of particles in it becomes infinite, that is, when it is no longer sensible (or desirable) to describe the motion of individual particles in the system. We restrict for the moment our considerations to linear systems in one dimension for simplicity. As a preamble to taking the limit  $N \rightarrow \infty$ , consider the transverse vibrations of a linear array of  $N$  identical, equally spaced particles that are joined together by identical springs. Particles 1 and  $N$  are attached to fixed points  $A$  and  $B$  by similar springs, Fig. 4.13. We use this system as a model for the vibrations of a continuous string tied down at  $A$  and  $B$ . We will clearly have to be careful about how the limit  $N \rightarrow \infty$  obtains since this will determine the mass density distribution along the length of the string.

Looking at Fig. 4.13, we label the transverse displacement of particle  $k$  by  $y_k$  (we want to reserve  $x$  for measuring the distance *along* the string) and call their spacing  $a$ .

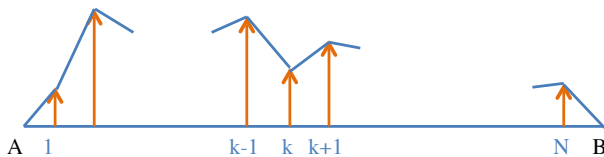


Figure 4.13: Linear chain of vibrating particles.

The points  $A$  and  $B$  are advantageously included in this scheme by calling their displacements  $x_0$  and  $x_{N+1}$  and setting  $y_0 = y_{N+1} = 0$ . With this convention, the potential energy in an arbitrary displacement of the particle array is easily found. It is first of all clear that the potential energy associated with the  $k^{\text{th}}$  spring connecting particles  $k - 1$  and  $k$  is

$$V_{k,k-1} = F\delta l_k \quad (4.94)$$

if  $F$  is the tension in the spring and  $\delta l_k$  its extension. But from Fig. 4.14

$$\delta l_k = a(\sec \theta - 1) \quad (4.95)$$

or

$$\delta l_k \simeq a\left(\frac{1}{2}\theta^2\right) \simeq \frac{a}{2}\left(\frac{y_k - y_{k-1}}{a}\right)^2 \quad (4.96)$$

if we make the small angle approximation for  $\sec \theta$ .

The potential energy of the entire system is thus

$$V = \sum_k V_k = \sum_{k=1}^{N+1} \frac{1}{2} Fa \left(\frac{y_k - y_{k-1}}{a}\right)^2, \quad (4.97)$$

so that the Lagrange function is given by

$$L = \sum_k \frac{1}{2} y_k'^2 - \sum_k \frac{1}{2} \frac{Fa}{m} \left(\frac{y_k' - y_{k-1}'}{a}\right)^2 \quad (4.98)$$

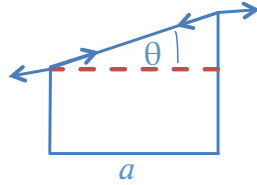


Figure 4.14: Geometry connecting two neighbouring particles.

after reverting to mass-scaled coordinates,  $\sqrt{m_k}y_k = y'_k$ . Hence, the eigenvalue problem (4.17) that is at the heart of the normal mode analysis reads (measure  $\lambda$  in units  $F/ma$ )

$$\begin{pmatrix} 2-\lambda & -1 & 0 & 0 & \dots \\ -1 & 2-\lambda & -1 & 0 & \dots \\ 0 & -1 & 2-\lambda & -1 & \dots \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix} \begin{pmatrix} u_1^\lambda \\ u_2^\lambda \\ \cdot \\ \cdot \\ \cdot \end{pmatrix} = 0 \quad (4.99)$$

or

$$\begin{aligned} (2-\lambda)u_1^{(\lambda)} - u_2^{(\lambda)} &= 0 \\ -u_1^{(\lambda)} + (2-\lambda)u_2^{(\lambda)} - u_3^{(\lambda)} &= 0 \\ &\cdot \\ &\cdot \\ &\cdot \\ -u_{N-1}^{(\lambda)} + (2-\lambda)u_N^{(\lambda)} &= 0. \end{aligned} \quad (4.100)$$

This set of equations can be summarized by the single *recursion relation*

$$-u_{n-1}^{(\lambda)} + (2-\lambda)u_n^{(\lambda)} - u_{n+1}^{(\lambda)} = 0, \quad n = 1, \dots, N \quad (4.101)$$

if the *boundary conditions*

$$u_0^{(\lambda)} = 0, \quad u_{N+1}^{(\lambda)} = 0 \quad (4.102)$$

are obeyed for every  $\lambda$ . The relation (4.101) is obeyed by the set of functions

$$u_n = \sin n\varphi \quad (4.103)$$

where  $n$  is an integer, provided that

$$(2-\lambda) = 2 \cos \varphi, \quad \text{or} \quad \lambda = 2(1 - \cos \varphi). \quad (4.104)$$

The functions  $\sin n\varphi$  automatically obey the first boundary condition in (4.102); the second one determines the allowed values of the angle  $\varphi$  and hence the eigenvalues through (4.104):

$$u_{N+1}^{(\lambda)} = \sin[(N+1)\varphi] = 0 \quad \text{if} \quad \varphi = \frac{m\pi}{N+1}, \quad (4.105)$$

where  $m$  is integral. Furthermore,  $m \leq N$  since values of  $m$  equal to  $N, N + 1, \dots$  just repeat the set of functions (4.103) for  $m = 0, 1, \dots$ . Finally,  $m = 0$  is excluded since this gives the trivial solution  $u_n = 0$  for all  $n$ . Hence the eigenvalues are

$$\lambda_m = 2\left(1 - \cos \frac{m\pi}{N+1}\right), \quad m = 1, 2, \dots, N, \quad (4.106)$$

leading to the eigenfrequencies

$$\omega_m = \sqrt{\frac{2F}{\mu a^2}} \sqrt{1 - \cos\left(\frac{m\pi}{N+1}\right)}, \quad m = 1, 2, \dots, N \quad (4.107)$$

for a string carrying a mass  $\mu = m/a$  per unit length. We notice from this expression that the  $\omega_m$  bunch together as  $m$  increases until a maximum allowable frequency  $\omega_{max} = \omega_N$  is reached at  $m = N$ . Frequencies higher than this cannot be propagated by the string.

The components of the  $m^{\text{th}}$  eigenvector are easily obtained from (4.103). They are

$$u_n^{(m)} = A \sin\left(\frac{m\pi n}{N+1}\right), \quad n = 1, 2, \dots, N, \quad (4.108)$$

where  $A$  is a normalizing constant. Its value follows from the condition

$$\sum_{n=1}^N u_n^{(m)2} = A^2 \sum_{n=1}^N \sin^2\left(\frac{m\pi n}{N+1}\right) = 1. \quad (4.109)$$

According to (4.108) the particles lie on a sine curve of wave length  $2L/m$  in the  $m^{\text{th}}$  normal mode of vibration if the string has length  $L$ . The case for three particles,  $N = 3$ , is illustrated in Fig. 4.15.

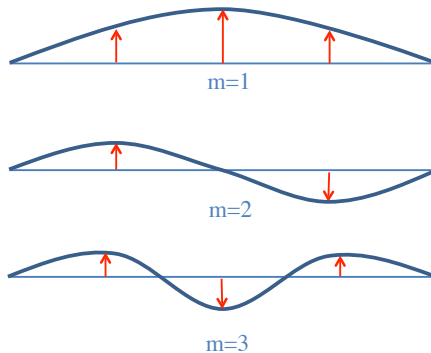


Figure 4.15: Transverse normal modes of three particles in a linear chain.

Consider now what happens as the number of particles increases without limit while the density, or mass per unit length, and the length  $L$  of the string are constant. This limiting procedure is characterized by the limits

$$a \rightarrow 0, \quad N \rightarrow \infty, \quad \text{but} \quad Na \rightarrow L, \quad \frac{m}{a} \rightarrow \mu, \quad (4.110)$$

where  $\mu$  is the mass per unit length of a continuous string. The eigenvalues of the latter system are

$$\begin{aligned}\omega_m^2 &= \frac{F}{ma} \lambda_m = \lim_{a \rightarrow 0, N \rightarrow \infty} \frac{2F}{ma} \left[1 - \cos \frac{m\pi}{N+1}\right] \\ &= \lim_{a \rightarrow 0} \frac{2F}{\mu a^2} \left[1 - \cos \frac{m\pi a}{L}\right] \\ &= \lim_{a \rightarrow 0} \frac{2F}{\mu a^2} \left[1 - \left(1 - \frac{1}{2} \left(\frac{m\pi a}{L}\right)^2 + \dots\right)\right] \\ &= \frac{F}{\mu} \left(\frac{m\pi}{L}\right)^2,\end{aligned}\tag{4.111}$$

or

$$\omega_m = \sqrt{\frac{F}{\mu}} \left(\frac{m\pi}{L}\right), \quad m = 1, 2, \dots, \infty.\tag{4.112}$$

Notice that the frequency  $\omega_m$  increases linearly with the mode number  $m$  *without limit* in contrast with (4.107) for the weighted string. The normal modes of this system are

$$y_k \sim \sin\left(\frac{mk\pi}{N+1}\right) \sim \sin\left(\frac{kam\pi}{L}\right).\tag{4.113}$$

But  $ka = x$  is just the distance of the  $k^{\text{th}}$  particle from the point  $A$ .

Hence,

$$\lim_{a \rightarrow 0, N \rightarrow \infty} y_k \rightarrow y(x) = \sin\left(\frac{x\pi m}{L}\right)\tag{4.114}$$

is the normal mode displacement of the string at each point  $x$  along the length in the limit  $N \rightarrow \infty$ . This is a sine curve of wave length  $2L/m$ . These normal modes resemble the ones found for  $N$  finite in all respects except that there are an infinite number of them.

The result (4.114) is important from another entirely different point of view in that it shows that the displacement  $y(x)$  of the string at  $x$  is the appropriate "coordinate" to use if we want to describe the dynamics of a continuous system directly without the intermediary procedure of passing through the discrete system first.

To see what changes in the Lagrange formalism are implied let us calculate (4.98) for the  $N \rightarrow \infty$  case. Then,

$$\begin{aligned}L &\rightarrow \int \frac{1}{2} \mu \left(\frac{\partial y}{\partial t}\right)^2 dx - \int \frac{1}{2} \frac{F}{\mu} \left(\frac{\partial y}{\partial x}\right)^2 dx \\ &= \int \mathcal{L} dx,\end{aligned}\tag{4.115}$$

where

$$\mathcal{L} = \frac{1}{2} \mu \left(\frac{\partial y}{\partial t}\right)^2 - \frac{1}{2} F \left(\frac{\partial y}{\partial x}\right)^2\tag{4.116}$$

plays the obvious role of a linear density. It is called the *Lagrange density* of the system. Notice that  $\mathcal{L}$  depends on the derivatives  $\partial y/\partial t$  and

$\partial y/\partial x$  of the "coordinate"  $y$  with respect to the parameters  $x$  and  $t$ . We therefore expect a Lagrange density of the form

$$\mathcal{L} = \mathcal{L}\left[y, \frac{\partial y}{\partial x}, \frac{\partial y}{\partial t}, t\right] \quad (4.117)$$

for a one dimensional system.

Such a system is called a *field*, described by the field amplitude  $y(x, t)$ . To find the equations of motion we return to (1.20) and write down the action  $S$  as

$$S = \int \int \mathcal{L} dx dt. \quad (4.118)$$

Variations in the value of  $S$  are now brought about by varying the field coordinates  $y(x, t)$  at particular values of  $x$  and  $t$ . Calling  $\delta y$  the variation in  $y$  we get

$$\delta S = \int \int \left\{ \frac{\partial \mathcal{L}}{\partial y} \delta y + \frac{\partial \mathcal{L}}{\partial(\partial y/\partial x)} \delta\left(\frac{\partial y}{\partial x}\right) + \frac{\partial \mathcal{L}}{\partial(\partial y/\partial t)} \delta\left(\frac{\partial y}{\partial t}\right) \right\} dx dt, \quad (4.119)$$

since variations in  $y$  also induce variations in  $\partial y/\partial x$  and  $\partial y/\partial t$ . In fact,

$$\delta\left(\frac{\partial y}{\partial x}\right) = \frac{\partial}{\partial x}(\delta y), \quad \text{and} \quad \delta\left(\frac{\partial y}{\partial t}\right) = \frac{\partial}{\partial t}(\delta y). \quad (4.120)$$

Therefore

$$\begin{aligned} \int \int \frac{\partial \mathcal{L}}{\partial(\partial y/\partial x)} \delta\left(\frac{\partial y}{\partial x}\right) &= - \int \int \frac{\partial}{\partial x} \frac{\partial \mathcal{L}}{\partial(\partial y/\partial x)} dx dt + \int_{t_1}^{t_2} dt \left[ \frac{\partial \mathcal{L}}{\partial(\partial y/\partial x)} \delta y \right]_{x_1}^{x_2} \\ \int \int \frac{\partial \mathcal{L}}{\partial(\partial y/\partial t)} \delta\left(\frac{\partial y}{\partial t}\right) &= - \int \int \frac{\partial}{\partial t} \frac{\partial \mathcal{L}}{\partial(\partial y/\partial t)} dx dt + \int_{x_1}^{x_2} dx \left[ \frac{\partial \mathcal{L}}{\partial(\partial y/\partial t)} \delta y \right]_{t_1}^{t_2}. \end{aligned} \quad (4.121)$$

The "surface terms" in both these expressions can be made to vanish by placing suitable boundary conditions on the variations  $\delta y$  as a function of  $x$  and  $t$ . In the former expression the time integral vanishes if either  $y(x, t)$  vanishes as  $x_1$  or  $x_2$  approach  $\pm\infty$  or if  $y(x, t)$  obeys "periodic boundary conditions" at  $x_1$  or  $x_2$ <sup>62</sup>; the space integral in the latter expression vanishes if we impose the boundary condition

$$\delta y(x, t_1) = \delta y(x, t_2) = 0 \quad (4.122)$$

for all  $x$ , cf. (1.30). In view of these conditions the variation in the action now reads

$$\delta S = \int \int \left\{ \frac{\partial \mathcal{L}}{\partial y} - \frac{\partial}{\partial x} \frac{\partial \mathcal{L}}{\partial(\partial y/\partial x)} - \frac{\partial}{\partial t} \frac{\partial \mathcal{L}}{\partial(\partial y/\partial t)} \right\} \delta y dx dt, \quad (4.123)$$

which vanishes for an arbitrary variation  $\delta y$  if

$$\frac{\partial \mathcal{L}}{\partial y} - \frac{\partial}{\partial x} \frac{\partial \mathcal{L}}{\partial(\partial y/\partial x)} - \frac{\partial}{\partial t} \frac{\partial \mathcal{L}}{\partial(\partial y/\partial t)} = 0. \quad (4.124)$$

<sup>62</sup> See, for example, L.I. Schiff, *Quantum Mechanics*, McGraw-Hill Book Company, Inc., New York, 1955, p43.

This is the Lagrange equation of motion for a one dimensional field  $y(x, t)$ . Notice that it is a *partial differential* equation, reflecting thereby an infinite number of degrees of freedom possessed by such a field.

If  $\mathcal{L}$  is given by (4.116), we get

$$\frac{\partial \mathcal{L}}{\partial y} = 0, \quad \frac{\partial \mathcal{L}}{\partial(\partial y/\partial x)} = -F\left(\frac{\partial y}{\partial x}\right), \quad \frac{\partial \mathcal{L}}{\partial(\partial y/\partial t)} = \mu\left(\frac{\partial y}{\partial t}\right), \quad (4.125)$$

so

$$-\frac{\partial}{\partial x}\left\{-F\frac{\partial y}{\partial x}\right\} - \frac{\partial}{\partial t}\left\{\mu\frac{\partial y}{\partial t}\right\} = 0, \quad (4.126)$$

or

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 y}{\partial t^2}, \quad v = \sqrt{\frac{F}{\mu}} \quad (4.127)$$

is the equation of motion of a string under a constant tension  $F$ . Equation (4.126) is the one-dimensional "wave equation" for the propagation of waves along such a string with velocity  $v = \sqrt{F/\mu}$ .

#### 4-14 The Oscillating String

As a first illustration of the application of (4.127) let us take a horizontal string under tension  $F$  that is tied down at both ends. The solution to this problem is actually contained in the expressions (4.112) and (4.114) but let us rederive these results directly. Equation (4.127) is a partial differential equation and as such admits solution by the separation of variables technique. Set

$$y(x, t) = u(x)f(t) \quad (4.128)$$

where  $u$  and  $f$  are functions of the variables shown in their arguments. Substituting back into (4.127) leads to

$$\frac{1}{u} \frac{d^2 u}{dx^2} = \frac{1}{v^2} \frac{1}{f} \frac{d^2 f}{dt^2}, \quad (4.129)$$

a relation that can only be satisfied if both sides equal a common constant (the separation constant) since the variables  $x$  and  $t$  have been segregated from each other. Calling the separation constant  $-k^2$ , one is lead to solve two ordinary differential equations

$$\begin{aligned} \frac{d^2 u}{dx^2} + k^2 u &= 0 \\ \frac{d^2 f}{dt^2} + (kv)^2 f &= 0. \end{aligned} \quad (4.130)$$

Assuming  $k^2$  is positive, we find that  $y = uf$  oscillates in both space and time according to

$$y(x, t) = e^{\pm ikx} e^{\pm i\omega t}, \quad \omega = kv. \quad (4.131)$$

The constant  $\omega = kv$  is the *frequency* in time of the oscillation,  $k$  its *wave number*.

Any linear combination of the solutions (4.134) with specific choices of sign before  $k$  and  $\omega$  are of course also solutions and we will make free use of this latitude. However, physical requirements, known as *boundary conditions*, on the system under discussion usually limit one to a particular combination. For example, in the case of the string tied down at both ends, we must require that

$$y(0, t) = y(L, t) = 0 \quad (4.132)$$

for all  $t$ , if  $L$  is the length of the string. This stipulation is said to give rise to a *standing wave* solution of the wave equation. The first boundary condition means that only the linear combination

$$\frac{1}{2i}(e^{ikx} - e^{-ikx}) = \sin kx \quad (4.133)$$

is permissible for the space part of  $y(x, t)$ . The second condition then fixes the value of the wave number  $k$  to be such that

$$\sin kL = 0, \quad \text{or} \quad k = k_m = \frac{m\pi}{L}, \quad m = 1, 2, \dots \quad (4.134)$$

Notice that  $m = 0$  is excluded from this set as it gives a trivial solution to the problem (no displacement). Negative values of  $m$  are also excluded by the positive nature of the wave number  $k_m$ . Condition (4.134) thus gives us the eigenvalues of the vibrating string:

$$\omega_m = \sqrt{\frac{F}{\mu}}k_m = \sqrt{\frac{F}{\mu}}\left(\frac{m\pi}{L}\right), \quad m = 1, 2, \dots \quad (4.135)$$

in agreement with (4.112). The associated *eigenvectors* are

$$u_m(x) = \sin k_m x \quad (4.136)$$

apart from a normalizing constant. The function  $u_m(x)$  is called an *eigenfunction* of the vibrating string. It is the obvious analog of  $u_n^{(m)}$  in (4.108), with the index  $n$  replaced by the continuous index  $x$ , and the  $m$  moved down to agree with common usage. Multiplying  $u_m(x)$  by the appropriate time factor, we get a normal mode of the string:

$$y_m(x, t) = u_m(x)e^{\pm i\omega_m t}. \quad (4.137)$$

We see then that there are an infinite number of such normal modes, so that the *most general* motion of the string tied down at both ends is given by the linear superposition

$$\begin{aligned} y(x, t) &= \sum_{m=1}^{\infty} C_m y_m(x, t) \\ &= \sum_{m=1}^{\infty} |C_m| \sin k_m x \cos(\omega_m t + \delta_m), \end{aligned} \quad (4.138)$$

containing an infinite number of adjustable complex constants  $C_m = |C_m| \exp i\delta_m$ . Clearly, the values of these constants are related to the initial conditions on the motion of the string. As usual, we are at liberty to specify its initial shape  $y(x, 0)$  (the displacement of its constituent particles) and velocity  $(\partial y / \partial t)_{t=0}$  (the velocity of its constituent particles) at  $t = 0$ . These functions are then expressed, according to (4.138) and its time derivative, by the *Fourier sine series*

$$y(x, 0) = \sum_{m=1} |C_m| \cos \delta_m \cdot \sin\left(\frac{m\pi x}{L}\right) \quad (4.139)$$

and

$$\left(\frac{\partial y}{\partial t}\right)_{t=0} = - \sum_m \omega_m |C_m| \sin \delta_m \cdot \sin\left(\frac{m\pi x}{L}\right) \quad (4.140)$$

in the interval  $(0, L)$ . The coefficients  $|C_m| \cos \delta_m$  and  $|C_m| \sin \delta_m$  are found by the usual inversion formulas

$$\begin{aligned} |C_m| \cos \delta_m &= \frac{2}{L} \int_0^L y(x, 0) \sin\left(\frac{m\pi x}{L}\right) dx \\ |C_m| \sin \delta_m &= - \frac{2}{\omega_m L} \int_0^L \left(\frac{\partial y}{\partial t}\right)_{t=0} \sin\left(\frac{m\pi x}{L}\right) dx \end{aligned} \quad (4.141)$$

that depend for their validity on the orthogonal nature

$$\frac{2}{L} \int_0^L \sin\left(\frac{m\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right) dx = \delta_{mn} \quad (4.142)$$

of the set of eigenfunctions  $\sin(m\pi x/L)$ .

As a simple illustration, suppose the string is pulled aside a distance  $h$  at its center and released. The initial shape is thus

$$\begin{aligned} y(x, 0) &= x \frac{2h}{L}, \quad 0 < x < \frac{L}{2} \\ &= (L - x) \frac{2h}{L}, \quad \frac{L}{2} < x < L. \end{aligned}$$

We calculate  $|C_m| \cos \delta_m$  from (4.141) as

$$|C_m| \cos \delta_m = \frac{2}{L} \cdot \frac{2h}{L} \cdot \left\{ \int_0^{L/2} x \sin\left(\frac{m\pi x}{L}\right) dx + \int_{L/2}^L (L - x) \sin\left(\frac{m\pi x}{L}\right) dx \right\}, \quad (4.143)$$

to find

$$\begin{aligned} |C_m| \cos \delta_m &= \frac{4h}{L^2} (1 + (-1)^{m+1}) \int_0^{L/2} x \sin \frac{m\pi x}{L} dx \\ &= \frac{8h}{\pi^2} \frac{(-1)^{(m-1)/2}}{m^2}, \quad m = 1, 3, 5, \dots \end{aligned} \quad (4.144)$$

and zero for even  $m$ . There is no initial velocity distribution along the string, so  $|C_m| \sin \delta_m = 0$ . The motion at subsequent times is therefore

given by the series

$$y(x, t) = \frac{8h}{\pi^2} \left\{ \sin \frac{\pi x}{L} \cos \omega_1 t - \frac{1}{3^2} \sin \frac{3\pi x}{L} \cos 3\omega_1 t + \frac{1}{5^2} \sin \frac{5\pi x}{L} \cos 5\omega_1 t - \dots \right\}, \quad (4.145)$$

containing no even modes.

#### 4-15 Forced motion of a String

Up to now we have only considered the free oscillations of a string - we give the system some initial displacement and / or velocity and watch what it does. The next problem is to have some force (varying in space and time) act on the string. In what follows we shall always suppose that such forces are periodic in time, i.e. carry a time factor  $\exp(i\omega t)$ . The most important physical distinction between free and forced oscillations is then that the system oscillates with the frequency of the applied force rather than with any of its eigenfrequencies. A mathematical difference is that forced motion is described by an *inhomogeneous* differential equation. For suppose the string of Sec. 4-14 is subjected to forces distributed along its length according to  $f^{(e)}(x) \exp(i\omega t)$  per unit length that act transversely. Their effect is included in (4.126) by simply adding this force to the left hand side of that equation. Hence,

$$\frac{\partial}{\partial x} \left\{ F \frac{\partial y}{\partial x} \right\} + f^{(e)}(x) e^{i\omega t} = \mu \frac{\partial^2 y}{\partial t^2} \quad (4.146)$$

describes the forced motion of a string of mass density  $\mu$  under tension  $F$ . Assuming that  $F$  is constant throughout the length of the string, we try a solution

$$y(x, t) = u(x) e^{-i\omega t}, \quad (4.147)$$

and find that  $u(x)$  satisfies

$$\left( \frac{d^2}{dx^2} + k^2 \right) u(x) = -\frac{f^{(e)}(x)}{F}, \quad k = \omega \sqrt{\frac{\mu}{F}}. \quad (4.148)$$

Notice that the dimension of  $f^{(e)}/F$  is that of an inverse length, which agrees with the dimensions on the left.

It turns out that this equation is easily solved if we know the solutions of the *special* differential equation

$$\left( \frac{d^2}{dx^2} + k^2 \right) G_k(x, x') = \delta(x - x'), \quad (4.149)$$

where the forcing term is a delta function<sup>63</sup>  $\delta(x - x')$  and is located at one point  $x'$  along the string. Its solution  $G_k(x, x')$  is called a *Green function*.

<sup>63</sup> The symbol  $\delta(x - x')$  is a mathematical artifice called the *Dirac delta function*. It is defined in such a fashion that

$$\int_a^b f(x) \delta(x - x') dx = f(x'), \quad (4.150)$$

where  $a < x' < b$ , and provided that  $f(x')$  is finite.

From (4.149) we see that a Green function is nothing but the amplitude of displacement of the string under the action of the singular driving force  $f(x) \sim \delta(x - x')$ . To find  $G_k(x, x')$ , we note that as long as  $x \neq x'$  the equation is homogeneous with the usual variety of solutions

$$\sin kx, \quad \cos kx, \quad (4.151)$$

or any combination of two of these. On the other hand, the presence of the delta function divides the  $x$ -axis into two regions,  $0 < x < x'$  and  $x' < x < L$ . This is so because the singularity on the right hand side introduces a *discontinuity of slope* into the function  $G_k(x, x')$  at  $x = x'$ . We see this by integrating both sides of (4.149) over the interval  $x' - \varepsilon$  to  $x' + \varepsilon$  around  $x'$ . Then, taking the limit,

$$\lim_{\varepsilon \rightarrow 0} \int_{x'-\varepsilon}^{x'+\varepsilon} k^2 G_k(x, x') dx = 0, \quad \lim_{\varepsilon \rightarrow 0} \int_{x'-\varepsilon}^{x'+\varepsilon} \delta(x - x') dx = 1, \quad (4.152)$$

but

$$\lim_{\varepsilon \rightarrow 0} \int_{x'-\varepsilon}^{x'+\varepsilon} \frac{d^2 G_k(x, x')}{dx^2} dx = \left( \frac{dG_k}{dx} \right)_{x=x'+\varepsilon} - \left( \frac{dG_k}{dx} \right)_{x=x'-\varepsilon}, \quad (4.153)$$

so that

$$\left( \frac{dG_k}{dx} \right)_{x=x'+\varepsilon} - \left( \frac{dG_k}{dx} \right)_{x=x'-\varepsilon} = 1 \quad (4.154)$$

is the "kink" or discontinuity, inflicted by the singular "function"  $\delta(x - x')$  on  $G_k$  at  $x = x'$ . We now find the function  $G_k$  by patching together solutions of the homogeneous part of (4.149) in the two regions of space mentioned above. For  $0 < x < x'$  we take

$$G_k(x, x') = A \sin k(x' - L) \sin kx \quad \text{for } x < x', \quad (4.155)$$

since  $G_k$  must vanish at end  $x = 0$ . Notice that the factor  $A \sin k(x' - L)$  is a *constant* as far as  $x$  is concerned. Its presence simplifies the joining problem at  $x = x'$ , for this is automatic if we now interchange  $x$  and  $x'$  and take

$$G_k(x, x') = A \sin k(x - L) \sin kx' \quad \text{for } x > x'. \quad (4.156)$$

This also satisfied (4.149) for  $x \neq x'$  and vanishes at the other end of the string  $x = L$ , as it should. The constant  $A$  is now found by requiring that  $G_k(x, x')$  have a unit discontinuity in derivative at  $x = x'$ . The result is  $A = 1/(k \sin kL)$ , so that

$$\begin{aligned} G_k(x, x') &= \frac{1}{k \sin kL} \sin kx \sin k(x' - L), \quad 0 < x < x' \\ &= \frac{1}{k \sin kL} \sin kx' \sin k(x - L) \quad x' < x < L. \end{aligned} \quad (4.157)$$

The steady state displacement of the string under the influence of a general driving force can then be obtained by superposition:

$$y(x, t) = u(x)e^{-i\omega t} = - \int_0^L dx' \frac{f^{(e)}(x')}{F} G_k(x, x') e^{-i\omega t}, \quad (4.158)$$

a form reminiscent of  $\zeta^{(s)}$  in Sec. 4-5. Note in particular that, considered as a function of the wave number  $k$ , the function  $G_k(x, x')$  has poles at the allowed wave numbers  $k_m$  for the eigenvibrations of the *free* system ( $k = 0$  is *not* a pole):

$$\sin kL = 0, \quad \text{or} \quad k = k_m = \frac{m\pi}{L}. \quad (4.159)$$

There is another form for  $G_k(x, x')$  that is much more illuminating in determining the response  $y(x, t)$  to the external field  $f^{(e)}(x) \exp(i\omega t)$ . This is the bilinear expansion of  $G_k$  into eigenfunctions of the homogeneous problem represented by the left hand side of (4.149). We write these eigenfunctions as

$$u_m(x) = \sqrt{\frac{2}{L}} \sin k_m x, \quad k_m = \frac{m\pi}{L}, \quad m = 1, 2, \dots \quad (4.160)$$

in the present case so that they obey the normalization condition (4.146) automatically,

$$\int_0^L u_m(x) u_n(x) dx = 0 \quad (4.161)$$

and suppose that, as a function of  $x$ ,  $G_k(x, x')$  has the expansion

$$G_k(x, x') = \sum_{m=1}^{\infty} a_m(x') u_m(x). \quad (4.162)$$

The expansion coefficients  $a_m(x')$  depend on the *parameter*  $x'$  as indicated. Inserting this expansion into the differential equation (4.149) for  $G_k$  there results

$$\sum_{m=1}^{\infty} (-k_m^2 + k^2) a_m(x') u_m(x) = \delta(x - x'), \quad (4.163)$$

which can be solved for  $a_n(x')$  by multiplying by  $u_n(x)$  and integrating over  $x$ . The result

$$a_n(x') = \frac{u_n(x')}{k^2 - k_n^2}, \quad n = 1, 2, \dots \quad (4.164)$$

provides us with the symmetrical expression

$$G_k(x, x') = \sum_{m=1}^{\infty} \frac{u_m(x) u_m(x')}{k^2 - k_m^2} \quad (4.165)$$

for  $G_k$ . This expression is important because it shows immediately that only force distributions having a non-zero overlap with mode  $m$  can excite this mode:

$$\text{RHS of (4.158)} \sim \int_0^L u_m(x') f^{(e)}(x') dx' \neq 0, \quad (4.166)$$

if the  $m^{\text{th}}$  mode is to be excited.

The pole structure of  $G_k$  mentioned in connection with (4.159) is now self-evident of course and (4.165) is a very convenient formula for obtaining an approximation to  $G_k$  if  $k$  lies near one of the eigenvalues  $k_m$ . Then,

$$\frac{u_m(x)u_m(x')}{k^2 - k_m^2} \quad (4.167)$$

gives the dominant contribution to  $G_k$ . As an aside remark note that this expression has as residue at  $k = k_m$ , the product of the normalized eigenfunctions

$$\frac{1}{2k_m} u_m(x)u_m(x') \quad (4.168)$$

of the homogeneous problem. Therefore, if we know  $G_k(x, x')$  from some other calculation as in (4.157), we can determine these eigenfunctions as the residues of  $G_k$  at the poles  $k = k_m$ . For instance this residue is

$$\lim_{k \rightarrow k_m} (k - k_m)G_k(x, x') = \frac{\sin k_m x \sin k_m x'}{2k_m}, \quad (4.169)$$

or

$$u_m(x)u_m(x') = \sqrt{\frac{2}{L}} \sin k_m x \cdot \sqrt{\frac{2}{L}} \sin k_m x', \quad (4.170)$$

confirming the result (4.160).

A more detailed discussion of the application of Green functions to calculate the response of continuous systems would take us too far afield. The interested reader is referred to P.M. Morse and H. Feshbach, *Methods of Theoretical Physics*, Mc-Graw-Hill Book Company, Inc., New York, 1951, Vol. I, for further details of this method.

### Problems

4-1. Show that the eigenvalues of a real, symmetric matrix are all real.

4-2. Reappraise (4.20) through (4.23) in the event that the matrix  $W$  has two equal roots, say  $\lambda_1 = \lambda_2$ . Test out your considerations on the matrix

$$\begin{pmatrix} 7 & -2 & 1 \\ -2 & 10 & -2 \\ 1 & -2 & 7 \end{pmatrix} \quad (4.171)$$

by explicitly constructing the matrix  $U$  that diagonalizes it.

4-3. Show that each element of a group appears once and once only in any row or column of the group multiplication table. (Hint: assume the converse and show that a violation of the group postulates arises).

4-4. Show that no element of a group can appear in more than one class of the group.

4-5. Show that for an abelian group the number of classes equals the order of the group.

4-6. Prove that operations  $E, C_3, C_3^{-1}, \sigma_1, \sigma_2, \sigma_3$  listed in (4.54) form a group by showing that all the group postulates of Sec. 4-6 are satisfied.

4-7. Verify (4.73).

4-8. Verify that (4.74) gives the correct reduction of the configuration space representation of the  $X_3$  molecule.

4-9. Find the irreducible matrix representation for all the operators of the group  $C_{3v}$  following along the lines leading up to (4.75).

4-10. Verify Table 4.4 in the text as the correct character table for the  $NH_3$  molecule.

4-11. Set up and analyze the eigenvibration problem of a water molecule ( $H_2O$ ) using the methods of group theory. Show that the secular determinant can be broken up in one  $2 \times 2$  determinant and one  $1 \times 1$  determinant. Construct the symmetry adapted coordinates for  $H_2O$  and solve explicitly for the vibrational frequencies under the assumption that the potential energy depends quadratically on both the OH bond extensions and the HOH bond angle increment.

The  $H_2O$  molecule is a prototype of *non-linear*  $XY_2$  molecules. The symmetry group you will come up with is called  $C_{2v}$ . It is an abelian group of order 4.

4-12. Consider, as a working hypothesis, that when the hammer of a piano hits a piano string it creates a "velocity profile"

$$v(x) = \frac{\bar{v}L}{\sqrt{\pi a}} e^{-(\frac{x-d}{a})^2} \quad (4.172)$$

of extent  $a$  about the point of impact  $d$  from one end of the string. Here  $L$  is the length of the string and  $\bar{v}$  its average initial velocity. Assume further that the string is negligibly displaced in the process. Calculate the motion of the string in the limit that  $a \ll 1$  and show that even or odd modes can be suppressed by choosing the ratio  $d/L$  appropriately. Take this opportunity to discuss the energy distribution of the excited modes of the vibrating string. Show that low frequency modes contain most of the energy initially supplied to the string in the present example.

4-13. Consider a horizontal string of length  $L$  and mass density  $\mu_0$  tied down at both ends. In addition, the string carries  $N$  point masses

$m$  equally spaced along the string. Present an analysis of the eigen-vibrations of this system. (Hint: write the mass density as  $\mu(x) = \mu_0 + m \sum_{k=1}^N \delta(x - x_k)$  in the wave equation for a continuous string and construct suitable solutions).