7 Operators and Matrices

The notion of an operator has already been developed and employed in Section 5.3. There, the operator $\hat{\mathcal{D}} \equiv \mathrm{d}/\mathrm{d}x$ was used in the solution of ordinary differential equations. In Chapter 5 the vector operator "del", represented by the symbol ∇, was introduced. It was shown that its algebraic form is dependent on the choice of curvilinear coordinates.

It is the objective of the present chapter to define matrices and their algebra – and finally to illustrate their direct relationship to certain operators. The operators in question are those which form the basis of the subject of quantum mechanics, as well as those employed in the application of group theory to the analysis of molecular vibrations and the structure of crystals.

7.1 THE ALGEBRA OF OPERATORS

The addition of operators follows the general rule of addition,

$$(\hat{\alpha} + \hat{\beta})f = \hat{\alpha}f + \hat{\beta}f; \tag{1}$$

that is, addition is distributive. Furthermore,

$$(\hat{\alpha} + \hat{\beta})f = (\hat{\beta} + \hat{\alpha})f. \tag{2}$$

Thus, addition is commutative.

The multiplication of two or more operators is accomplished by their successive application on a function. The order of the operations is by convention from right to left. Thus, the expression $\hat{\alpha}\hat{\beta}f$ implies that the operation $\hat{\beta}$ is carried out before the operation $\hat{\alpha}$. The multiplication of operators is associative, *viz.*

$$\hat{\alpha}\hat{\beta}f = \hat{\alpha}(\hat{\beta}f) = (\hat{\alpha}\hat{\beta})f. \tag{3}$$

However, it is not commutative, so that

$$\hat{\alpha}\hat{\beta}f \neq \hat{\beta}\hat{\alpha}f \tag{4}$$

in general.

As a simple example of the above principles, consider the operator $\hat{X}$, defined as multiplication of the following function by the independent variable, say, x. Thus,

$$\hat{X}f(x) = xf(x). \tag{5}$$

If a second operator is defined by the relation

$$\hat{\mathcal{D}}f(x) = \frac{\mathrm{d}f}{\mathrm{d}x} = f'(x), \tag{6}$$

as in Section 4.3, the products of these operators can be evaluated as

$$\hat{\mathcal{D}}\hat{X}f(x) = \hat{\mathcal{D}}(\hat{X}f) = \hat{\mathcal{D}}(x\ f) = xf' + f \tag{7}$$

and

$$\hat{X}\hat{\mathcal{D}}f(x) = \hat{X}(\hat{\mathcal{D}}f) = \hat{X}f' = xf'. \tag{8}$$

The difference yields the relation

$$(\hat{\mathcal{D}}\hat{X} - \hat{X}\hat{\mathcal{D}})f(x) = f(x). \tag{9}$$

The corresponding operator relation is

$$\hat{\mathcal{D}}\hat{X} - \hat{X}\hat{\mathcal{D}} = 1. \tag{10}$$

However, such a relation is meaningless unless it is understood that the operators are followed by a function upon which they operate.

The commutation relations involving operators are expressed by the so-called commutator, a quantity which is defined by

$$\hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha} = \left[\hat{\alpha}, \hat{\beta}\right]. \tag{11}$$

Thus, for the example presented above, the commutator is given by

$$\left[\hat{\mathcal{D}}, \hat{X}\right] = 1 \tag{12}$$

and the operators $\hat{\mathcal{D}}$ and $\hat{X}$ do not commute. This result is of fundamental importance in quantum mechanics, as will be demonstrated at the end of this chapter.

The operators that are involved in quantum mechanics are linear. An example of a linear operator is given by

$$\hat{\alpha}[c_1 f_1(x) + c_2 f_2(x)] = c_1\hat{\alpha}f_1(x) + c_2\hat{\alpha}f_2(x). \tag{13}$$

On the other hand, if an operator $\hat{\beta}$ is defined by

$$\hat{\beta} f(x) = [f(x)]^2, \tag{14}$$

it should be apparent that

$$\hat{\beta} f_1(x) + \hat{\beta} f_2(x) \neq \hat{\beta}[f_1(x) + f_2(x)]. \tag{15}$$

Such an operator is nonlinear, and it will not appear in quantum-mechanical applications.

So far, nothing has been said concerning the nature of the functions, such as $f(x)$ in the above examples, upon which the operators operate. In practical problems the functions are said to be "well behaved"! This expression means that the functions are:

(i) continuous
(ii) single-valued
(iii) finite.*

These restrictions are in general the origin of the boundary conditions imposed on the solutions of the Schrödinger equation, as illustrated in Chapter 5.

7.2 HERMITIAN OPERATORS AND THEIR EIGENVALUES

It is important to note that all operators of interest in quantum mechanics are Hermitian (or self-adjoint). This property is defined by the relation

$$\int \eta^{\star}(\hat{\alpha}\xi)\,\mathrm{d}\tau = \int \xi(\hat{\alpha}^{\star}\eta^{\star})\,\mathrm{d}\tau, \tag{16}$$

where $\hat{\alpha}$ is an operator and the functions η and ξ are well-behaved, as defined above. The importance of this property will become more apparent in later sections of this chapter.

As an example, consider the quantum mechanical operator for the linear momentum in one dimension,

$$p_x \longrightarrow \frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x} = \hat{p}_x,$$

which was employed in Section 6.3.2. It, and the coordinate x are mutually conjugate, as illustrated earlier. The Hermitian property follows from

*This condition is too severe, as it is the integral $\int f^{\star} f\,\mathrm{d}\tau$ that must remain finite.

the relations

$$\int \eta^{\star}(x)\left(\frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x}\right)\xi(x)\,\mathrm{d}x = -i\hbar\int \eta^{\star}\frac{\mathrm{d}\xi}{\mathrm{d}x}\,\mathrm{d}x \tag{17}$$

$$= -i\hbar\eta^{\star}\xi\Big|_{-\infty}^{+\infty} + i\hbar\int \xi\frac{\mathrm{d}}{\mathrm{d}x}\eta^{\star}\,\mathrm{d}x$$

$$= i\hbar\int \xi\frac{\mathrm{d}}{\mathrm{d}x}\eta^{\star}\,\mathrm{d}x. \tag{18}$$

The first term in Eq. (18) is equal to zero at each limit for the assumed well-behaved functions. Thus, Eqs. (17) and (18) lead to

$$\int \eta^{\star}(x)\hat{p}\xi(x)\,\mathrm{d}x = \int \xi(x)\hat{p}^{\star}\eta^{\star}(x)\,\mathrm{d}x, \tag{19}$$

in agreement with Eq. (16).

The characteristic-value problem – more often referred to as the eigenvalue problem – is of extreme importance in many areas of physics. Not only is it the very basis of quantum mechanics, but it is employed in many other applications. Given a Hermitian operator $\hat{\alpha}$, if their exists a function (or functions) ς such that

$$\hat{\alpha}\varsigma = a\varsigma, \tag{20}$$

the values of a are known as the eigenvalues of $\hat{\alpha}$. The functions ς are the corresponding eigenfunctions.

It is important to note that the eigenvalues of a Hermitian operator are real. If Eq. (20) is multiplied by $\varsigma^{\star}$ and the integration is carried out over all space, the result is

$$\int \varsigma^{\star}\hat{\alpha}\varsigma\,\mathrm{d}\tau = a\int \varsigma^{\star}\varsigma\,\mathrm{d}\tau. \tag{21}$$

The complex conjugate of Eq. (20) can be written as

$$\hat{\alpha}^{\star}\varsigma^{\star} = a^{\star}\varsigma^{\star}. \tag{22}$$

Multiplication of Eq. (22) by ς and integration over all space yields the relation

$$\int \varsigma\hat{\alpha}^{\star}\varsigma^{\star}\,\mathrm{d}\tau = a^{\star}\int \varsigma\varsigma^{\star}\,\mathrm{d}\tau. \tag{23}$$

As $\hat{\alpha}$ is Hermitian, the left-hand side of Eq. (21) is equal to the left-hand side of Eq. (23). Therefore,

$$a\int \varsigma^{\star}\varsigma\,\mathrm{d}\tau = a^{\star}\int \varsigma\varsigma^{\star}\,\mathrm{d}\tau \tag{24}$$

and $a = a^{\star}$. Thus, the eigenvalues of Hermitian operators are real. It can be shown that the inverse is true. Since the eigenvalues correspond to physically observable quantities, they are real and their operators are Hermitian.

As an example, consider Eq. (6-61), which can be written as

$$\frac{\mathrm{d}^2}{\mathrm{d}\varphi^2}\Phi = -m^2\Phi. \tag{25}$$

In this form it can be compared to Eq. (20), where the result of the operation $\mathrm{d}^2/\mathrm{d}\varphi^2$ is to multiply the function Φ by the eigenvalues $-m^2$. Clearly, the eigenfunctions are of the form $\Phi = e^{im\varphi}$. As shown in Section 6.4.2, the quantization of m, *viz.* $m = 0, \pm 1, \pm 2, \ldots$ is the result of the conditions imposed on the solutions. In this case it is the requirement that they be single-valued. It will be shown in Section 9.2.4 that the operator $\hat{L}_z = (\hbar/i)(\mathrm{d}/\mathrm{d}\varphi)$ corresponds to the z component of the angular momentum of the system. That is, for the hydrogen atom it is the vertical component of the angular momentum of the electron. Equation (25) is then equivalent to

$$\hat{L}_z^2\Phi = -\hbar^2\frac{\mathrm{d}^2}{\mathrm{d}\varphi^2}\Phi = m^2\hbar^2\Phi. \tag{26}$$

7.3 MATRICES

A matrix is an array of numbers. For most practical purposes it is rectangular. Thus, a matrix is an array such as

$$\boldsymbol{A} = \begin{bmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \vdots & \vdots & & \vdots \\ a_{m1} & a_{m2} & \cdots & a_{mn} \end{bmatrix}, \tag{27}$$

where the elements a_{ij} are numbers or functions, which may be real or complex. The subscripts i and j of the element a_{ij} identify the row and the column, respectively, of the matrix in which it is located. The matrix given in Eq. (27) consists of m rows and n columns. If the matrix is square, $m = n$, and the matrix is said to be of order n. In a square matrix of order n the elements $a_{11}, a_{22}, \ldots, a_{nn}$ constitute the main diagonal of $\boldsymbol{A}$. The sum of the diagonal elements of a matrix is called the trace (German: *Spur*). In group theory it is known as the character, *i.e.* the quantity that characterizes a matrix representation (see Chapter 8). If all of the nondiagonal elements in a matrix are equal to zero, the matrix is diagonal.

Two matrices $\boldsymbol{A}$ and $\boldsymbol{B}$ are equal if they are identical. That is, $a_{ij} = b_{ij}$ for every pair of subscripts. The addition of two matrices can be defined by the sum $\boldsymbol{A} + \boldsymbol{B}$, which is the matrix of elements $[(a_{ij} + b_{ij})]_{mn}$. That is, the sum of two matrices of the same order is found by adding their corresponding elements. Note that the two matrices must be congruent, that is, have the same number of rows and columns. The product of a number c and a matrix $\boldsymbol{A}$ is defined as the matrix $\boldsymbol{B}$ whose elements are the elements of $\boldsymbol{A}$ multiplied by c. Namely, $\boldsymbol{B} = c\boldsymbol{A}$ if $b_{ij} = ca_{ij}$.

The multiplication of matrices requires a bit more reflection. The product $\boldsymbol{C}$ of two matrices $\boldsymbol{A}$ and $\boldsymbol{B}$ is usually defined by $\boldsymbol{C} = \boldsymbol{AB}$ if

$$c_{ij} = \sum_k a_{ik} b_{kj}. \tag{28}$$

The sum in Eq. (28) is over the number of columns of $\boldsymbol{A}$, which must of course be equal to the number of rows of $\boldsymbol{B}$. The result is the matrix $\boldsymbol{C}$, whose number of rows is equal to the number of rows of $\boldsymbol{A}$ and whose number of columns is equal to the number of columns of $\boldsymbol{B}$.

It is important to note that the product of two square matrices, given by $\boldsymbol{AB}$ is not necessarily equal to $\boldsymbol{BA}$. In other words, matrix multiplication is not commutative. However, the trace of the product does not depend on the order of multiplication. From Eq. (28) it is apparent that

$$Tr(\boldsymbol{AB}) = \sum_i (\boldsymbol{AB})_{ii} = \sum_i \sum_k a_{ik} b_{ki} = \sum_k \sum_i b_{ki} a_{ik} = Tr(\boldsymbol{BA}). \tag{29}$$

While the matrix multiplication defined by Eq. (28) is the more usual one in matrix algebra, there is another way of taking the product of two matrices. It is known as the direct product and is written here as $\boldsymbol{A} \otimes \boldsymbol{B}$. If $\boldsymbol{A}$ is a square matrix of order n and $\boldsymbol{B}$ is a square matrix of order m, then $\boldsymbol{A} \otimes \boldsymbol{B}$ is a square matrix of order nm. Its elements consist of all possible pairs of elements, one each from $\boldsymbol{A}$ and $\boldsymbol{B}$, *viz.*

$$[\boldsymbol{A} \otimes \boldsymbol{B}]_{ik,jl} = a_{ij} b_{kl}. \tag{30}$$

The arrangement of the elements in the direct-product matrix follows certain conventions. They are illustrated in the following chapter, where the direct product of matrices is employed in the theory of groups.

The unit matrix $\boldsymbol{E}$ (German: *Einheit*) is one which is diagonal with all of the diagonal elements equal to one. It plays the role of unity in matrix algebra. Clearly, the unit matrix multiplied by a constant yields a diagonal matrix with all of the diagonal elements equal to the value of the constant. If the constant is equal to zero, the matrix is the null matrix $\boldsymbol{0}$, with all elements equal to zero.

In many applications in physics and chemistry there appear systems of linear equations of the general form

$$\begin{aligned} a_{11}x_1 + a_{12}x_2 + \cdots + a_{1n}x_n &= b_1 \\ a_{21}x_1 + a_{22}x_2 + \cdots + a_{2n}x_n &= b_2 \\ &\vdots \\ a_{m1}x_1 + a_{m2}x_2 + \cdots + a_{mn}x_n &= b_m, \end{aligned} \tag{31}$$

where the number m of equations is not necessarily equal to the number n of unknowns. Following the definition of matrix multiplication, as given in Eq. (28), this system of equations can be written as the matrix equation

$$\begin{bmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \vdots & \vdots & & \vdots \\ a_{m1} & a_{m2} & \cdots & a_{mn} \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{bmatrix} = \begin{bmatrix} b_1 \\ b_2 \\ \vdots \\ b_m \end{bmatrix}. \tag{32}$$

Then, with $\boldsymbol{A} = [a_{ij}]$, $\boldsymbol{X} = [x_j]$ and $\boldsymbol{B} = [b_i]$ Eq. (32) becomes simply

$$\boldsymbol{AX} = \boldsymbol{B}. \tag{33}$$

The bold-face characters employed in Eq. (33) imply that each symbol represents a matrix. The problem of the resolution of simultaneous linear equations will be discussed in Section 7.8, as certain properties of matrices must first be explained.

The matrices such as $\boldsymbol{X}$ and $\boldsymbol{B}$ in Eq. (33), which are composed of a single column, are usually referred to as vectors. In fact, the vectors introduced in Chapter 4 can be written as column matrices in which the elements are the corresponding components. Of course the vector $\boldsymbol{X} = [x_j]$ in Eq. (33) is of dimension n, while those in Chapter 4 were in three-dimensional space. It is apparent that the matrix notation introduced here is a more general method of representing vector algebra in multidimensional spaces. This idea is developed further in Section 7.7.

The transpose of a matrix $\boldsymbol{A}$ is a matrix $\tilde{\boldsymbol{A}}$, which is obtained from $\boldsymbol{A}$ by interchanging rows and columns, *viz.* $[\tilde{\boldsymbol{A}}]_{ij} = a_{ji}$. Clearly, the transpose of a column matrix, a vector, is a row matrix. The complex conjugate of $\boldsymbol{A}$ is the matrix $\boldsymbol{A}^{\star}$ whose elements are the complex conjugates of the corresponding elements of $\boldsymbol{A}$. The conjugate transpose is the matrix $\boldsymbol{A}^{\dagger}$, which is the complex conjugate of the transpose of $\boldsymbol{A}$; that is, $\boldsymbol{A}^{\dagger} = \tilde{\boldsymbol{A}}^{\star}$.

The inverse, $\boldsymbol{A}^{-1}$, of a matrix $\boldsymbol{A}$ is defined by the relation $\boldsymbol{A}\boldsymbol{A}^{-1} = \boldsymbol{E}$. If $\boldsymbol{A}$ is a square matrix, its inverse may exist – although not necessarily so. This question is addressed later in this section. Rectangular, nonsquare, matrices may

Table 1 Special matrices.

Description	Condition	Elements
Real	$\boldsymbol{A}^{\star} = \boldsymbol{A}$	$a_{ij}^{\star} = a_{ij}$
Symmetric	$\tilde{\boldsymbol{A}} = \boldsymbol{A}$	$a_{ji} = a_{ij}$
Hermitian	$\boldsymbol{A}^{\dagger} = \boldsymbol{A}$ or $\boldsymbol{A}^{\star} = \tilde{\boldsymbol{A}}$	$a_{ji}^{\star} = a_{ij}$
Orthogonal	$\boldsymbol{A}^{-1} = \tilde{\boldsymbol{A}}$ or $\boldsymbol{A}\tilde{\boldsymbol{A}} = \boldsymbol{E}$	$\left[\boldsymbol{A}^{-1}\right]_{ji} = a_{ij}$
Unitary	$\boldsymbol{A}^{-1} = \boldsymbol{A}^{\dagger}$ or $\boldsymbol{A}\boldsymbol{A}^{\dagger} = \boldsymbol{E}$	$\left[\boldsymbol{A}^{-1}\right]_{ji}^{\star} = a_{ij}$

also possess inverses, although this question is somewhat more complicated (see problem 4).

Several special matrices are defined in Table 1. The Hermitian matrix is of particular importance in quantum-mechanical applications, as outlined in Section 7.13.

It is often necessary to take the transpose of a product of matrices. Thus, if $\boldsymbol{A}\boldsymbol{B} = \boldsymbol{C}, c_{ij} = \sum_k a_{ik}b_{kj}$, where in the general case all three matrices are rectangular [see Eq. (28)]. If both $\boldsymbol{A}$ and $\boldsymbol{B}$ are transposed, their product is taken in the order $\tilde{\boldsymbol{B}}\tilde{\boldsymbol{A}}$, as the number of columns of $\tilde{\boldsymbol{B}}$ must be equal to the number of rows of $\tilde{\boldsymbol{A}}$. The result is the transpose of $\boldsymbol{C}$, namely, $\tilde{\boldsymbol{C}} = \tilde{\boldsymbol{B}}\tilde{\boldsymbol{A}}$. This principle holds for any number of factors; thus, when a matrix product is transposed, the sequence of the matrices forming the product must be reversed, *e.g.*

$$\boldsymbol{F} = \boldsymbol{A}\boldsymbol{B}\boldsymbol{C}\ldots\boldsymbol{X}, \quad \tilde{\boldsymbol{F}} = \tilde{\boldsymbol{X}}\ldots\tilde{\boldsymbol{C}}\tilde{\boldsymbol{B}}\tilde{\boldsymbol{A}}. \tag{34}$$

A similar relation applies to the inverse of the product of matrices. For example, define the product of three matrices by $\boldsymbol{A}\boldsymbol{B}\boldsymbol{C} = \boldsymbol{W}$. If the inverse of $\boldsymbol{W}$ exists, it is given by $\boldsymbol{W}^{-1} = (\boldsymbol{A}\boldsymbol{B}\boldsymbol{C})^{-1}$. Now consider the product

$$(\boldsymbol{C}^{-1}\boldsymbol{B}^{-1}\boldsymbol{A}^{-1})\boldsymbol{A}\boldsymbol{B}\boldsymbol{C} = (\boldsymbol{C}^{-1}\boldsymbol{B}^{-1}\boldsymbol{A}^{-1})\boldsymbol{W}, \tag{35}$$

where it is assumed that the inverse of each matrix, $\boldsymbol{A}$ $\boldsymbol{B}$ and $\boldsymbol{C}$ exists. As the associative law holds and $\boldsymbol{A}^{-1}\boldsymbol{A} = \boldsymbol{E}$, *etc.*, the left-hand side of Eq. (35) is equal to the identity; then,

$$\boldsymbol{E} = \boldsymbol{C}^{-1}\boldsymbol{B}^{-1}\boldsymbol{A}^{-1}\boldsymbol{W} \tag{36}$$

and

$$\boldsymbol{W}^{-1} = \boldsymbol{C}^{-1}\boldsymbol{B}^{-1}\boldsymbol{A}^{-1} = (\boldsymbol{A}\boldsymbol{B}\boldsymbol{C})^{-1}. \tag{37}$$

This result can be easily generalized to include the inverse of the product of any number of factors.

7.4 THE DETERMINANT

For most students, their first encounter with matrices is in the study of determinants. However, a determinant is a very special case in which a given square matrix has a specific numerical value. If the matrix $\boldsymbol{A}$ is of order two, its determinant can be written in the form

$$|\boldsymbol{A}| = Det \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \equiv \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = a_{11}a_{22} - a_{21}a_{12}. \tag{38}$$

For a matrix of order three, its determinant can be developed in the form

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} = a_{11} \begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix} - a_{12} \begin{vmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{vmatrix} + a_{13} \begin{vmatrix} a_{21} & a_{22} \\ a_{31} & a_{32} \end{vmatrix}. \tag{39}$$

Clearly, each determinant of order two in Eq. (39) can be evaluated following Eq. (38). These determinants of order two are called the minors of the determinant of order three. Note that the minor of a_{11} is obtained by elimination of the row and column in which it appears. Similarly, that of the element a_{12} is obtained by eliminating its row and column. Furthermore, the second term in Eq. (39) is negative because the sum of the subscripts of a_{12} is odd. The sign is positive if the sum of the subscripts is even. A minor with its appropriate sign is referred to as a cofactor. The principles outlined in this paragraph are general and can thus be applied to determinants of higher order.

Although the development of determinants of any order can be made, as illustrated in Eq. (39), in the special case of matrices of third order there is another, often useful, method. It is shown in Fig. 1. The solid arrows, starting with elements a_{11}, a_{12} and a_{13} pass through elements which form the products $a_{11}a_{22}a_{33}$, $a_{21}a_{32}a_{13}$ and $a_{31}a_{23}a_{12}$, respectively. Similarly, following the dotted arrows, the products $a_{31}a_{22}a_{13}$, $a_{21}a_{12}a_{33}$ and $a_{11}a_{23}a_{32}$ are obtained.

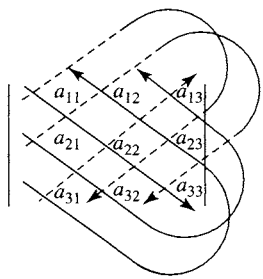

Fig. 1 The development of a third-order determinant.

Addition of these six products, with negative signs for those obtained from the dotted arrows, yields the result

$$|\boldsymbol{A}| = a_{11}a_{22}a_{33} + a_{21}a_{32}a_{13} + a_{31}a_{23}a_{12} - (a_{31}a_{22}a_{13} + a_{21}a_{12}a_{33} + a_{11}a_{23}a_{32}), \tag{40}$$

which can be easily verified by comparison with Eq. (39). It must be emphasized that the method illustrated in Fig. 1 is only applicable to determinants of order three.

The matrix represented in this chapter by $\overline{\boldsymbol{A}}$ is usually called the adjoint matrix. It is obtained by constructing the matrix which is composed of all of the cofactors of the elements a_{ij} in $|\boldsymbol{A}|$ and then taking its transpose. With the basic definition of matrix multiplication [Eq. (29)] and some patience, the reader can verify the relation

$$\boldsymbol{A}\overline{\boldsymbol{A}} = \overline{\boldsymbol{A}}\boldsymbol{A} = |\boldsymbol{A}|\boldsymbol{E} \tag{41}$$

(see problem 8). If the determinant $|\boldsymbol{A}|$ is equal to zero, $\boldsymbol{A}$ is said to be singular and $\boldsymbol{A}\overline{\boldsymbol{A}} = \overline{\boldsymbol{A}}\boldsymbol{A} = \boldsymbol{0}$. If $\boldsymbol{A}$ is nonsingular, Eq. (41) can be divided by $|\boldsymbol{A}|$ to yield a matrix $\boldsymbol{A}^{-1}$ which is the inverse of $\boldsymbol{A}$, or,

$$\boldsymbol{A}^{-1} = \frac{\overline{\boldsymbol{A}}}{|\boldsymbol{A}|} \tag{42}$$

and $\boldsymbol{A}\boldsymbol{A}^{-1} = \boldsymbol{A}^{-1}\boldsymbol{A} = \boldsymbol{E}$. Thus, the inverse of a square matrix exists only if it is nonsingular.

7.5 PROPERTIES OF DETERMINANTS

Some general properties of determinants can be summarized as follows.

(i) The value of a determinant is unchanged if its rows and columns are interchanged, *viz.*

$$|\boldsymbol{A}| = |\tilde{\boldsymbol{A}}|. \tag{43}$$

(ii) The sign of a determinant changes when two rows (or columns) are interchanged, *e.g.*

$$\begin{vmatrix} a_{12} & a_{11} & a_{13} \\ a_{22} & a_{21} & a_{23} \\ a_{32} & a_{31} & a_{33} \end{vmatrix} = - \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix}, \tag{44}$$

as is easily shown by expansion of the two determinants.

(iii) If the elements of a given row (or column) are multiplied by the same quantity, say, c, it can be removed as a common factor, *viz.*

$$\begin{vmatrix} ca_{11} & ca_{12} & ca_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} = c \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix}. \tag{45}$$

(iv) If two rows (or columns) of a determinant are identical, the value of the determinant is zero; thus,

$$\begin{vmatrix} a_{21} & a_{22} & a_{23} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} = 0. \tag{46}$$

(v) The product of two determinants is equal to the determinant of the matrix product of the two, *e.g.*

$$\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} \begin{vmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{vmatrix} = \begin{vmatrix} a_{11}b_{11} + a_{12}b_{21} & a_{11}b_{12} + a_{12}b_{22} \\ a_{21}b_{11} + a_{22}b_{21} & a_{21}b_{12} + a_{22}b_{22} \end{vmatrix}. \tag{47}$$

The proof of (v) constitutes problem 7.

7.6 JACOBIANS

Partial derivatives, as introduced in Section 2.12 are of particular importance in thermodynamics. The various state functions, whose differentials are exact (see Section 3.5), are related *via* approximately 10^{10} expressions involving 720 first partial derivatives! Although some of these relations are not of practical interest, many are. It is therefore useful to develop a systematic method of deriving them. The method of Jacobians is certainly the most widely applied to the solution of this problem. It will be only briefly described here. For a more advanced treatment of the subject and its application to thermodynamics, the reader is referred to specialized texts.

Consider two functions $x(u, v)$ and $y(u, v)$, where u and v are independent variables. In this case the Jacobian can be defined by the determinant

$$J(x, y|u, v) \equiv \begin{vmatrix} \left(\frac{\partial x}{\partial u}\right)_v & \left(\frac{\partial x}{\partial v}\right)_u \\ \left(\frac{\partial y}{\partial u}\right)_v & \left(\frac{\partial y}{\partial v}\right)_u \end{vmatrix}, \tag{48}$$

whose expansion yields

$$J(x, y|u, v) = \left(\frac{\partial x}{\partial u}\right)_v \left(\frac{\partial y}{\partial v}\right)_u - \left(\frac{\partial x}{\partial v}\right)_u \left(\frac{\partial y}{\partial u}\right)_v. \tag{49}$$

A number of significant properties of the Jacobian can be easily derived:

$$
\begin{aligned}
&\text{(i)} \quad J(x, v|u, v) = (\partial x/\partial u)_v \\
&\text{(ii)} \quad J(x, y|x, y) = 1 \\
&\text{(iii)} \quad J(x, x|u, v) = 0 \\
&\text{(iv)} \quad J(x, c|u, v) = 0, \text{ where } c \text{ is a constant.} \\
&\text{(v)} \quad J(x, y|u, v) = -J(x, y|v, u) \\
&\text{(vi)} \quad J(x, y|u, v) = -J(y, x|u, v) \\
&\text{(vii)} \quad J(x, y|u, v)J(u, v|s, t) = J(x, y|s, t) \\
&\text{(viii)} \quad J(x, y|u, v) = 1/[J(u, v|x, y)].
\end{aligned} \tag{50}
$$

Relation (i) is evident, as

$$\left(\frac{\partial v}{\partial u}\right)_v = 0 \text{ and } \left(\frac{\partial v}{\partial v}\right)_u = 1.$$

It allows any partial derivative to be expressed as a Jacobian. Equations (iii) to (vi) follow directly from the properties of the determinant described in the previous section, while (ii) and (viii) are the result of the general expressions for partial derivatives (Section 2.12). Finally, relation (vii) requires a bit more thought. With the use of the definition of the Jacobian and property (v) of determinants [Eq. (50)], the 1-1 element of the resulting Jacobian is

$$\left(\frac{\partial x}{\partial u}\right)_v \left(\frac{\partial u}{\partial s}\right)_t + \left(\frac{\partial x}{\partial v}\right)_u \left(\frac{\partial v}{\partial s}\right)_t = \left(\frac{\partial x}{\partial s}\right)_t, \tag{51}$$

where the chain rule has been applied. The other elements can be found in a similar manner.

In Section 2.13 it was shown that for bulk systems the various thermodynamic functions are related by the system of equations

$$
\begin{aligned}
T &= \left(\frac{\partial E}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P, \; P = -\left(\frac{\partial E}{\partial V}\right)_S = -\left(\frac{\partial F}{\partial V}\right)_T \\
V &= \left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T, \; S = -\left(\frac{\partial F}{\partial T}\right)_V = -\left(\frac{\partial G}{\partial T}\right)_P.
\end{aligned} \tag{52}
$$

In the Jacobian notation these relations become

$$
\begin{aligned}
T &= J(E, V|S, V) = J(H, P|S, P), \\
P &= J(E, S|S, V) = J(F, T|T, V), \\
V &= J(H, S|P, S) = J(G, T|P, T),
\end{aligned}
$$

and

$$S = J(F, V|V, T) = J(G, P|P, T). \tag{53}$$

In this notation Maxwell's relations take the form

$$J(T, S|V, S) = J(P, V|V, S),$$
$$J(T, S|P, S) = J(P, V|P, S),$$
$$J(T, S|T, V) = J(P, V|T, V),$$

and

$$J(T, S|T, P) = J(P, V|T, P). \tag{54}$$

As an example of the use of Jacobians to obtain thermodynamic relationships, consider the quantity

$$\left(\frac{\partial V}{\partial T}\right)_S = J(V, S|T, S) = \frac{J(V, S|T, V)}{J(T, S|T, V)}, \tag{55}$$

where T and V are taken as independent variables and rule (vii) has been used to obtain the second equality. With use of rule (vi) and Maxwell's relations,

$$\left(\frac{\partial V}{\partial T}\right)_S = -\frac{J(S, V|T, V)}{J(T, S|T, V)} = -\frac{J(S, V|T, V)}{J(P, V|T, V)}. \tag{56}$$

Finally, as

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

under adiabatic and reversible conditions,

$$\left(\frac{\partial V}{\partial T}\right)_S = -\frac{C_V}{T\left(\frac{\partial P}{\partial T}\right)_V}. \tag{57}$$

The partial derivative is now expressed in terms of the heat capacity and the equation of state, which are experimental quantities.

7.7 VECTORS AND MATRICES

As indicated above, if the components of a vector $\boldsymbol{X}$ in n-dimensional space are real, the vector can be written as a column matrix with n rows. Similarly, a second vector $\boldsymbol{Y}$ in the same space can be written as a column matrix of the

same order. The scalar product of these two vectors $\boldsymbol{X}$ and $\boldsymbol{Y}$ written in matrix notation, becomes

$$\tilde{\boldsymbol{X}}\boldsymbol{Y} = \sum_{i=1}^{n} X_i Y_i, \tag{58}$$

where in Eq. (5-12) $n = 3$. The result given in Eq. (58) should be evident if it is understood that the transpose of a column matrix is a row matrix.

When $n > 3$ in Eq. (58), the space cannot be visualized. However, the analogy with three-dimensional space is clear. Thus an n-dimensional coordinate system consists of n mutually perpendicular axes. A point requires n coordinates for its location and, which is equivalent, a vector is described by its n components.

If $\boldsymbol{A}$ is a square matrix and $\boldsymbol{X}$ is a column matrix, the product $\boldsymbol{AX}$ is also a column. Therefore, the product $\tilde{\boldsymbol{X}}\boldsymbol{AX}$ is a number. This matrix expression, which is known as a quadratic form, arises often in both classical and quantum mechanics (Section 7.13). In the particular case in which $\boldsymbol{A}$ is Hermitian, the product $\boldsymbol{X}^{\dagger}\boldsymbol{AX}$ is called a Hermitian form, where the elements of $\boldsymbol{X}$ may now be complex.

The vector product $\boldsymbol{X} \times \boldsymbol{Y}$ is somewhat more complicated in matrix notation. In the three-dimensional case, an antisymmetric (or skew symmetric) matrix can be constructed from the elements of the vector $\boldsymbol{X}$ in the form

$$\boldsymbol{X} = \begin{bmatrix} 0 & -x_3 & x_2 \\ x_3 & 0 & -x_1 \\ -x_2 & x_1 & 0 \end{bmatrix}. \tag{59}$$

The vector product is then obtained by ordinary matrix multiplication,

$$\begin{bmatrix} 0 & -x_3 & x_2 \\ x_3 & 0 & -x_1 \\ -x_2 & x_1 & 0 \end{bmatrix} \begin{bmatrix} y_1 \\ y_2 \\ y_3 \end{bmatrix} = \begin{bmatrix} x_2y_3 - x_3y_2 \\ x_3y_1 - x_1y_3 \\ x_1y_2 - x_2y_1 \end{bmatrix}. \tag{60}$$

The column matrix on the left-hand side of Eq. (60) is a vector, whose elements are the coefficients of $\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k}$, respectively, in the notation of Chapter 5. Thus,

$$\boldsymbol{X} \times \boldsymbol{Y} = \begin{bmatrix} \boldsymbol{i} & \boldsymbol{j} & \boldsymbol{k} \end{bmatrix} \begin{bmatrix} 0 & -x_3 & x_2 \\ x_3 & 0 & -x_1 \\ -x_2 & x_1 & 0 \end{bmatrix} \begin{bmatrix} y_1 \\ y_2 \\ y_3 \end{bmatrix} = \begin{bmatrix} x_1 & x_2 & x_3 \\ y_1 & y_2 & y_3 \\ \boldsymbol{i} & \boldsymbol{j} & \boldsymbol{k} \end{bmatrix}, \tag{61}$$

as in Eq. (4-24).

7.8 LINEAR EQUATIONS

In general, Eq. (32) represents a system of inhomogeneous linear equations. It is assumed that $\boldsymbol{A}$ and $\boldsymbol{B}$ are known and the elements of the vector $\boldsymbol{X}$ are the unknowns. For simplicity, the following arguments will be limited to the case in which $\boldsymbol{A}$ is square, that is, $n = m$. If all elements of the vector $\boldsymbol{B}$ are equal to zero, the equations are homogeneous and Eq. (33) becomes $\boldsymbol{AX} = \boldsymbol{0}$.

The solution of a system of linear equations depends on certain conditions, *viz.*

(i) If $\boldsymbol{B} \neq \boldsymbol{0}$ and $|\boldsymbol{A}| \neq 0$, then $\boldsymbol{A}^{-1}$ exists and the unique solutions are given by

$$\boldsymbol{X} = \boldsymbol{A}^{-1}\boldsymbol{B} = \frac{\bar{\boldsymbol{A}}\boldsymbol{B}}{|\boldsymbol{A}|}. \tag{62}$$

(ii) If $\boldsymbol{B} = \boldsymbol{0}$ and $|\boldsymbol{A}| \neq 0$, the only solution is the trivial one, with $\boldsymbol{X} = \boldsymbol{0}$; that is, all of the unknowns are equal to zero.

(iii) However, if $\boldsymbol{B} = \boldsymbol{0}$, a nontrivial solution to these homogeneous equations exists if $|\boldsymbol{A}| = 0$. This condition is usually referred to as Cramer's rule.* It should be noted, however, that because the equations are homogeneous, only ratios of the unknowns can be evaluated. Thus, an additional relation among the unknowns must be invoked in order to obtain unique solutions. This problem is of great importance in many applications, in particular in the classical theory of molecular vibrations and in quantum mechanics. It will be developed in more detail in Chapter 9.

7.9 PARTITIONING OF MATRICES

It is often useful to partition matrices, either square or rectangular, into submatrices, as indicated by the following examples:

$$\boldsymbol{A} = \left[\begin{array}{ccc:cc} a_{11} & a_{12} & a_{13} & a_{14} & a_{15} \\ a_{21} & a_{22} & a_{23} & a_{24} & a_{25} \\ \hdashline a_{31} & a_{32} & a_{33} & a_{34} & a_{35} \end{array}\right] = \left[\begin{array}{c:c} \boldsymbol{A}_{11} & \boldsymbol{A}_{12} \\ \hdashline \boldsymbol{A}_{21} & \boldsymbol{A}_{22} \end{array}\right], \tag{63}$$

where the bold-faced letters with subscripts identify the corresponding submatrices. Thus, with the use of one or more dashed lines a matrix can be

*Gabriel Cramer, Swiss mathematician (1704–1752).

partitioned into submatrices whose positions in the original matrix are specified by the subscripts.

The addition of two or more partitioned matrices is straightforward, providing of course that they are partitioned in the same way. Then, for example,

$$\boldsymbol{A}+\boldsymbol{B}=\left[\begin{array}{c:c}\boldsymbol{A}_{11} & \boldsymbol{A}_{12}\\ \hdashline \boldsymbol{A}_{21} & \boldsymbol{A}_{22}\end{array}\right]+\left[\begin{array}{c:c}\boldsymbol{B}_{11} & \boldsymbol{B}_{12}\\ \hdashline \boldsymbol{B}_{21} & \boldsymbol{B}_{22}\end{array}\right]$$

$$=\left[\begin{array}{c:c}\boldsymbol{A}_{11}+\boldsymbol{B}_{11} & \boldsymbol{A}_{12}+\boldsymbol{B}_{12}\\ \hdashline \boldsymbol{A}_{21}+\boldsymbol{B}_{21} & \boldsymbol{A}_{22}+\boldsymbol{B}_{22}\end{array}\right]. \tag{64}$$

The product of partitioned matrices can be obtained in a similar manner if the columns of $\boldsymbol{A}$ match the rows of $\boldsymbol{B}$, *e.g.*

$$\boldsymbol{AB}=\left[\boldsymbol{A}_{11}\quad \boldsymbol{A}_{12}\quad \boldsymbol{A}_{13}\right]\left[\begin{array}{c}\boldsymbol{B}_{11}\\ \boldsymbol{B}_{12}\\ \boldsymbol{B}_{22}\end{array}\right]=\left[\boldsymbol{A}_{11}\boldsymbol{B}_{11}\quad \boldsymbol{A}_{12}\boldsymbol{B}_{12}\quad \boldsymbol{A}_{13}\boldsymbol{B}_{13}\right]. \tag{65}$$

This result should be obvious from the definition of matrix multiplication [Eq. (28)].

7.10 MATRIX FORMULATION OF THE EIGENVALUE PROBLEM

The eigenvalue problem was introduced in Section 7.3, where its importance in quantum mechanics was stressed. It arises also in many classical applications involving coupled oscillators. The matrix treatment of the vibrations of polyatomic molecules provides the quantitative basis for the interpretation of their infrared and Raman spectra.* This problem will be addressed more specifically in Chapter 9.

The eigenvalue problem can be described in matrix language as follows. Given a matrix $\boldsymbol{H}$, determine the scalar quantities λ and the nonzero vectors $\boldsymbol{L}_i$ which satisfy simultaneously the equation

$$\boldsymbol{H}\boldsymbol{L}_i=\lambda\boldsymbol{L}_i. \tag{66}$$

In all physical applications, although both $\boldsymbol{H}$ and $\boldsymbol{L}_i$ may contain complex elements, the eigenvalues λ, are real (see Section 7.2). Equation (66) can be

*Sir Chandrasekhara Venkata Raman, Indian physicist (1886–1970).

written in the form

$$(\boldsymbol{H} - \lambda \boldsymbol{E})\boldsymbol{L}_i = \boldsymbol{0}. \tag{67}$$

If the unit matrix $\boldsymbol{E}$ is of order n, Eq. (67) represents a system of n homogeneous, linear equations in n unknowns. They are usually referred to as the secular equations. According to Cramer's rule [see (iii) of Section 7.8], nontrivial solutions exist only if the determinant of the coefficients vanishes. Thus, for the solutions of physical interest,

$$|\boldsymbol{H} - \lambda \boldsymbol{E}| = 0; \tag{68}$$

that is, the secular determinant vanishes. It is perhaps useful to write out Eq. (68) as,

$$\begin{vmatrix} h_{11} - \lambda & h_{12} & \cdots & h_{1n} \\ h_{21} & h_{22} - \lambda & \cdots & h_{2n} \\ \vdots & \vdots & & \\ h_{n1} & h_{n2} & \cdots & h_{nn} - \lambda \end{vmatrix} = 0. \tag{69}$$

This relation is equivalent to an algebraic equation of degree n in the unknown λ and therefore has n roots, some of which may be repeated (degenerate). These roots are the characteristic values or eigenvalues of the matrix $\boldsymbol{H}$.

When the determinant of Eq. (69) is expanded, the result is the polynomial equation

$$(-\lambda)^n + c_1(-\lambda)^{n-1} + c_2(-\lambda)^{n-2} + \ldots + c_n = 0. \tag{70}$$

The coefficients c_i are given by

$$c_1 = \sum_i h_{ii} = Tr\boldsymbol{H} = \sum_i \lambda_i,$$

$$c_2 = \sum_{j,i<j} (h_{ii}h_{jj} - h_{ij}h_{ji}) = \sum_{j,i<j} \lambda_i \lambda_j,$$

$$\vdots$$

and

$$c_n = |\boldsymbol{H}| = \prod_{i=1}^{n} \lambda_i. \tag{71}$$

The equalities in Eqs. (71) are the result of a well-known theorem of algebra. As $\boldsymbol{H}$ is nonsingular, the expression for c_n shows that no eigenvalue can be equal to zero.

Now if λ_1 is one of the eigenvalues of $\boldsymbol{H}$, Eq. (66) is satisfied and the equation

$$(\boldsymbol{H} - \lambda_1 \boldsymbol{E})\boldsymbol{L}_1 = \boldsymbol{0} \tag{72}$$

has nontrivial solutions for the vector $\boldsymbol{L}_1$. If n eigenvectors $\boldsymbol{L}_i$ have been found, they may be assembled into a square matrix $\boldsymbol{L} = [\boldsymbol{L}_1 \vdots \boldsymbol{L}_2 \vdots \boldsymbol{L}_3 \vdots \cdots \vdots \boldsymbol{L}_n]$. Then, Eq. (66) becomes

$$\boldsymbol{HL} = \boldsymbol{L\Lambda} \tag{73}$$

or

$$\boldsymbol{L}^{-1}\boldsymbol{HL} = \boldsymbol{\Lambda}, \tag{74}$$

where $\boldsymbol{\Lambda}$ is a diagonal matrix whose elements are the eigenvalues $\lambda_1, \lambda_2, \ldots \lambda_n$ of $\boldsymbol{H}$. From Eq. (74) it is apparent that the eigenvalues are obtained by diagonalization of $\boldsymbol{H}$ by a similarity transformation, *e.g.* premultiplication by $\boldsymbol{L}^{-1}$, followed by postmultiplication by $\boldsymbol{L}$. A transformation of this type, the similarity transformation, will take on a considerable importance in the applications of group theory presented in the following chapter.

7.11 COUPLED OSCILLATORS

A simple eigenvalue problem can be demonstrated by the example of two coupled oscillators. The system is illustrated in Fig. 2. It should be compared with the classical harmonic oscillator that was treated in Section 5.2.2. Here also, the system will be assumed to be harmonic, namely, that both springs obey Hooke's law. The potential energy can then be written in the form

$$V = \tfrac{1}{2}\kappa_1 x_1^2 + \tfrac{1}{2}\kappa_2 (x_2 - x_1)^2, \tag{75}$$

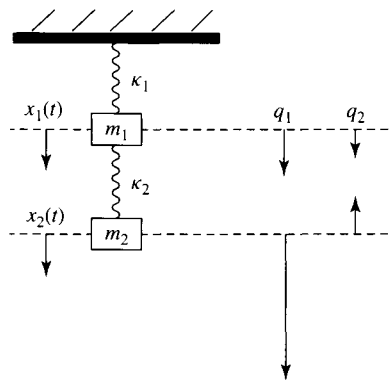

Fig. 2 System of two coupled oscillators.

where κ_1 and κ_2 are the force constants. The corresponding expression for the kinetic energy is given simply by

$$T = \tfrac{1}{2}m_1\dot{x}_1^2 + \tfrac{1}{2}m_2\dot{x}_2^2. \tag{76}$$

Then, applying Newton's law in the form

$$\frac{\mathrm{d}}{\mathrm{d}t}p_i = f_i, \tag{77}$$

where $p_i = m_i\dot{x}_i$ and f_i is the force acting on mass m_i. In terms of the potential and kinetic energies given by Eqs. (75) and (76), respectively,

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial T}{\partial \dot{x}_i}\right) = -\frac{\partial V}{\partial x_i}, \tag{78}$$

and the equations of motion become

$$m_1\ddot{x}_1 + \kappa_1 x_1 - \kappa_2(x_2 - x_1) = 0 \tag{79}$$

and

$$m_2\ddot{x}_2 + \kappa_2(x_2 - x_1) = 0. \tag{80}$$

The introduction of periodic solutions of the form

$$x_i = a_i \cos[\sqrt{\lambda}t + \eta], \tag{81}$$

leads to the pair of simultaneous equations

$$\frac{a_1(\kappa_1 + \kappa_2)}{m_1} - \frac{a_2\kappa_2}{m_1} = a_1\lambda \tag{82}$$

and

$$-\frac{a_1\kappa_2}{m_2} + \frac{a_2\kappa_2}{m_2} = a_2\lambda \tag{83}$$

for the unknown amplitudes a_1 and a_2. It should be noted that $\sqrt{\lambda}$ can be identified with $\omega = 2\pi\nu^0$, the angular frequency. In matrix form Eqs. (82) and (83) can be written as

$$\begin{bmatrix} \dfrac{\kappa_1 + \kappa_2}{m_1} & -\dfrac{\kappa_2}{m_1} \\ -\dfrac{\kappa_2}{m_2} & \dfrac{\kappa_2}{m_2} \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = \begin{bmatrix} \lambda & 0 \\ 0 & \lambda \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} \tag{84}$$

or

$$\begin{bmatrix} \dfrac{\kappa_1 + \kappa_2}{m_1} - \lambda & -\dfrac{\kappa_2}{m_1} \\ -\dfrac{\kappa_2}{m_2} & \dfrac{\kappa_2}{m_2} - \lambda \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = \mathbf{0}, \tag{85}$$

which is a system of linear, homogeneous equations. According to Cramer's rule, for a nontrivial solution to be obtained, the determinant of the coefficients must vanish; then,

$$\begin{vmatrix} \dfrac{\kappa_1 + \kappa_2}{m_1} - \lambda & -\dfrac{\kappa_2}{m_1} \\ -\dfrac{\kappa_2}{m_2} & \dfrac{\kappa_2}{m_2} - \lambda \end{vmatrix} = 0, \tag{86}$$

leading to a quadratic equation for the two eigenvalues. This result corresponds to the general form given by Eq. (68).

For simplicity, the following development of this example will be limited to the special case in which $m_1 = m_2 = m$ and $\kappa_1 = \kappa_2 = \kappa$. Then, the expansion of the secular determinant of Eq. (86) yields

$$\lambda^2 - \frac{3\kappa}{m}\lambda + \frac{\kappa^2}{m^2} = 0, \tag{87}$$

whose roots are

$$\lambda = \frac{\kappa}{2m}(3 \pm \sqrt{5}). \tag{88}$$

By choosing arbitrarily one of the roots as the eigenvalue λ_1 and substituting it in the secular equations, a relation between the amplitudes can be obtained, namely,

$$a_{21} = \tfrac{1}{2}(1 + \sqrt{5})a_{11}, \tag{89}$$

where the second subscript has been added to specify that this relation between the amplitudes was obtained with the use of the first, arbitrarily chosen eigenvalue.

As pointed out above, the homogeneous secular equations can only yield expressions for the ratios of the amplitudes. The additional condition necessary to resolve this ratio is the normalization, which in this example is

$$a_{21}^2 + a_{11}^2 = 1. \tag{90}$$

In general, the normalization of the amplitudes is very useful, as will be indicated below – and developed in more detail in the treatment of molecular vibrations (see Chapter 9). The normalized amplitudes obtained by combination of Eqs. (89) and (90) are $\ell_{11} = \sqrt{2}(5 + \sqrt{5})^{-1/2}$ and $\ell_{21} = (1 + \sqrt{5})[2(5 + \sqrt{5})]^{-1/2}$. The repetition of the procedure employed in the

last paragraph with the use of the second eigenvalue results in the normalized amplitudes $\ell_{12} = \sqrt{2}(5 - \sqrt{5})^{-1/2}$ and $\ell_{22} = (1 - \sqrt{5})[2(5 - \sqrt{5})]^{-1/2}$. Thus, the matrix $\boldsymbol{L}$ takes the form

$$\boldsymbol{L} = \begin{bmatrix} \sqrt{2}(5 + \sqrt{5})^{-1/2} & \sqrt{2}(5 - \sqrt{5})^{1/2} \\ (1 + \sqrt{5})[2(5 + \sqrt{5})]^{-1/2} & (1 - \sqrt{5})[2(5 - \sqrt{5})]^{-1/2} \end{bmatrix}. \tag{91}$$

It should be noted that this matrix is orthogonal, *viz.* $\tilde{\boldsymbol{L}} = \boldsymbol{L}^{-1}$ and thus, $\tilde{\boldsymbol{L}}\boldsymbol{L} = \boldsymbol{E}$.

With a bit of patience it can be verified that Eq. (74) becomes in this case

$$\boldsymbol{L}^{-1}\boldsymbol{H}\boldsymbol{L} = \tilde{\boldsymbol{L}}\boldsymbol{H}\boldsymbol{L} = \boldsymbol{\Lambda}, \tag{92}$$

where

$$\boldsymbol{H} = \begin{bmatrix} 2\kappa/m & -\kappa/m \\ -\kappa/m & \kappa/m \end{bmatrix} \tag{93}$$

and

$$\boldsymbol{\Lambda} = \begin{bmatrix} \frac{\kappa}{2m}(3 - \sqrt{5}) & 0 \\ 0 & \frac{\kappa}{2m}(3 + \sqrt{5}) \end{bmatrix} \tag{94}$$

(see problem 11).

A quantitative physical picture of the vibrations of the system illustrated in Fig. 2 can be obtained with the use of normal coordinates. However, it is first customary to introduce the so-called mass-weighted coordinates by $s_i = \sqrt{m_i}x_i$, where of course $m_1 = m_2 = m$ in this example. The normal coordinates $\boldsymbol{Q}$ can then be defined by the relation

$$\boldsymbol{S} = \begin{bmatrix} \sqrt{m}x_1 \\ \sqrt{m}x_2 \end{bmatrix} = \boldsymbol{L}\begin{bmatrix} q_1 \\ q_2 \end{bmatrix} = \boldsymbol{L}\boldsymbol{Q}. \tag{95}$$

They have the property of allowing both the potential and the kinetic energies to be written as sums of square terms; that is, all cross terms vanish. This result can be demonstrated by substituting for x_1 and x_2 in Eq. (95) into Eqs. (75) and (76). The results are

$$V = \tfrac{1}{2}(\lambda_1 q_1^2 + \lambda_2 q_2^2) \tag{96}$$

and

$$T = \tfrac{1}{2}(\dot{q}_1^2 + \dot{q}_2^2) \tag{97}$$

(see problem 12).

As $\boldsymbol{L}$ is orthogonal, the normal coordinates can be found from Eq. (95) as

$$\boldsymbol{Q} = \tilde{\boldsymbol{L}}\boldsymbol{S} = \sqrt{m}\tilde{\boldsymbol{L}}\boldsymbol{X}. \tag{98}$$

The relative displacements of the masses in the two normal modes of this coupled oscillator are shown to the right in Fig. 2. This method of representing the form of the normal modes is particularly useful in the analysis of molecular vibrations (see Chapter 9).

7.12 GEOMETRIC OPERATIONS

The trivial geometric operation is known as the identity. If it is applied to an arbitrary vector in, say, three-dimensional space, the result is to leave the vector ξ unchanged. In Cartesian coordinates this operation can be expressed in matrix form as

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix}, \tag{99}$$

The unit matrix is a representation of the trivial operation of "doing nothing". Equation (99) can be written more compactly as $\hat{\boldsymbol{E}}\xi = \xi$. The circumflex over $\boldsymbol{E}$ indicates that it is an operator, although in practice this mark is often omitted.

Other operations on a vector include reflections. Consider, for example, the operation of reflection in the x,y plane. The result of this operation is to change the sign of the z component of the vector. Thus, a reflection in the x, y plane can be represented by

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ -z \end{bmatrix}. \tag{100}$$

This operation can be considered to be an inversion of the single coordinate z, as shown in the following chapter. The symbol $\hat{\boldsymbol{\sigma}}(xy)$, which is often used for this operation, is that of Schönflies.* Clearly, the other two reflections in the Cartesian planes correspond to the matrix relations

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix} \tag{101}$$

*Arthur Moritz Schönflies, German mathematician (1853–1928). The Schönflies symbols are employed in spectroscopic applications, while in crystallography the international, or Hermann-Maugin notation is used.

and

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ y \\ z \end{bmatrix}, \tag{102}$$

with the symbols $\hat{\sigma}(zx)$ and $\hat{\sigma}(yz)$, respectively.

The operation which changes the signs of all three components of ξ is called the inversion. Its representation is obviously a negative unit matrix. Then,

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ -z \end{bmatrix}. \tag{103}$$

The Schönflies notation for this operation is $\hat{i}$, although the circumflex is usually omitted.

To find the representation of a simple or "proper" rotation it is convenient to choose the rotation axis along a Cartesian direction. For a rotation of the coordinates by an arbitrary angle about, say, the z axis, that component of any vector will be unchanged. However, the x and y components will be converted into linear combinations, as can be seen by reference to Fig. 3. Here, for simplicity, a unit vector $\boldsymbol{1}$ has been chosen. When the coordinates undergo a counter-clockwise rotation about the z axis by an angle φ the components of the unit vector become $x' = cos(\alpha - \varphi) = cos\,\alpha\, cos\,\varphi + sin\,\alpha\, sin\,\varphi$ and $y' = sin(\alpha - \varphi) = -cos\,\alpha\, sin\,\varphi + sin\,\alpha\, cos\,\varphi$. In matrix notation the result is

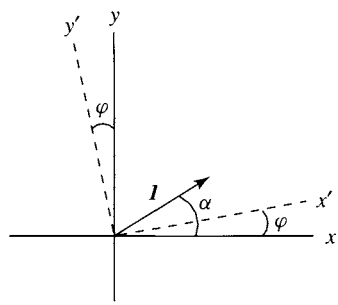

Fig. 3 The effect of a counter-clockwise coordinate rotation about the z axis.

expressed in the form*

$$\begin{bmatrix} \cos\varphi & \sin\varphi & 0 \\ -\sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix}. \tag{104}$$

The Schönflies symbol for a rotation by an angle φ is $C_{2\pi/\varphi}$. If, for example, $\varphi = \pi/2$, the symbol becomes C_4 (see the following chapter).

If a proper rotation is combined with a reflection with respect to the axis of rotation, it is called an improper rotation The matrix representation of such an operation is found simply by replacing 1 by -1 in Eq. (104). The Schönflies symbol for an improper rotation by φ is $S_{2\pi/\varphi}$. Hence, matrix the representation of an improper counter-clockwise rotation by φ is of the form†

$$S_{2\pi/\varphi} = \begin{bmatrix} \cos\varphi & \sin\varphi & 0 \\ -\sin\varphi & \cos\varphi & 0 \\ 0 & 0 & -1 \end{bmatrix}. \tag{105}$$

It should be noted that the trace of a matrix that represents a given geometric operation is equal to $2\cos\varphi \pm 1$, the choice of signs is appropriate to proper or improper operations. Furthermore, it should be noted that the arbitrary direction of rotation has no effect on the value of the trace, as a rotation in the inverse sense corresponds only to a change in sign of the element $\sin\varphi$. These operations and their matrix representations will be employed in the following chapter, where the theory of groups is applied to the analysis of molecular symmetry.

7.13 THE MATRIX METHOD IN QUANTUM MECHANICS

In classical mechanics the kinetic energy of a particle of mass m is written in the form

$$T = \tfrac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2), \tag{106}$$

where $\dot{x}$, $\dot{y}$ and $\dot{z}$ are the Cartesian components of its velocity. The corresponding momentum components are given by

$$p_x = \frac{\partial T}{\partial \dot{x}} = m\dot{x}, \tag{107}$$

*The linear transformation expressed by Eq. (104) has the same form if the vector is rotated in the ***clockwise*** direction by the angle φ while the coordinate axes remain fixed.

†The Schönflies symbols are usually not written in bold-face type, although they are represented by matrices such as given in Eqs. (104) and (105).

and similarly in the y and z directions. Substitution for the velocity components in Eq. (106) yields the kinetic energy expression

$$T = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) = \frac{\boldsymbol{p}^2}{2m}. \tag{108}$$

In quantum mechanics the vector $\boldsymbol{p}$ is replaced by the operator $(\hbar/i)\nabla$. Thus, the operator for the kinetic energy becomes

$$\hat{T} = \frac{\hat{\boldsymbol{p}}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2. \tag{109}$$

The operator for the total energy of the system is then obtained by adding the potential energy, V, which is a function of the appropriate coordinates. The result, which is known as the Hamiltonian, is then

$$\hat{H} = \hat{T} + V = -\frac{\hbar^2}{2m}\nabla^2 + V. \tag{110}$$

This principle was employed earlier (see Sections 5.4 and 6.3.2).

The operators of interest in quantum mechanics such as the Hamiltonian, as well as the linear and angular momenta, are Hermitian (see Section 7.2). Their eigenvalues are then real, as they correspond to quantities that are measurable.

Another fundamental property concerns the orthogonality of eigenfunctions. Given that

$$\hat{\alpha} f_1 = a_1 f_1 \text{ and } \hat{\alpha} f_2 = a_2 f_2, \tag{111}$$

the relation

$$\int f_1^{\star} \hat{\alpha} f_2 \, d\tau = a_2 \int f_1^{\star} f_2 \, d\tau \tag{112}$$

is easily established. And, as a_1 is real and $\hat{\alpha}$ is Hermitian,

$$\int f_1^{\star} \hat{\alpha} f_2 \, d\tau = \int f_2 \hat{\alpha}^{\star} f_1^{\star} \, d\tau = a_1^{\star} \int f_1^{\star} f_2 \, d\tau = a_1 \int f_1^{\star} f_2 \, d\tau. \tag{113}$$

Therefore, the difference, Eqs. (112) minus (113) yields

$$(a_2 - a_1) \int f_1^{\star} f_2 \, d\tau = 0, \tag{114}$$

and either $a_2 - a_1 = 0$ or $\int f_1^{\star} f_2 \, d\tau = 0$, or both. In the former case the system is degenerate, as two eigenvalues are the same; or, if $\int f_1^{\star} f_2 \, d\tau = 0$, the functions f_1 and f_2 are orthogonal. It can be concluded, then, that the eigenfunctions in a nondegenerate system are orthogonal. However, it can be

shown that in the case of a degenerate system, orthogonal eigenfunctions can be constructed as linear combinations.

A basic theorem of quantum mechanics, which will be presented here without proof, is: If $\hat{\alpha}$ and $\hat{\beta}$ commute, namely $[\hat{\alpha}, \hat{\beta}] = 0$, there exists an ensemble of functions that are eigenfunctions of both $\hat{\alpha}$ and $\hat{\beta}$ – and inversely.

In many applications of quantum mechanics in physics and chemistry, interest is primarily in the description of the stationary, or time-independent, states of a system. Thus, it is sufficient to determine the energies and wavefunctions with the use of the Schrödinger equation in the form

$$\hat{H}\psi_n = \varepsilon_n \psi_n. \tag{115}$$

Equation (115) is a special case of the more general Schrödinger equation which includes the time as an independent variable (see Section 12.3). The function ψ_n, is the eigenfunction for the state n with corresponding energy ε_n. Since the eigenfunctions are orthonormal (or can be made so), Eq. (115) can be multiplied by $\psi_m^{\bigstar}$ and integrated over all space. The result is given by

$$\int \psi_m^{\bigstar} \hat{H} \psi_n \, d\tau = \varepsilon_n \delta_{m,n}, \tag{116}$$

where $d\tau$ is the element of volume and $\delta_{m,n}$ is the Kronecker delta [see Eq. (5-105)]. The integrals on the left-hand side of Eq. (116) can be arranged in the form of a square matrix $\boldsymbol{H}$, whose order is equal to the number of independent eigenfunctions in the set. As the functions ψ are in this case the eigenfunctions for the problem, the matrix $\boldsymbol{H}$ is diagonal and equal to the right-hand side of Eq. (116), whose elements are the eigenvalues – that is, the values of the energies of the different stationary states. The diagonal matrix composed of elements $\varepsilon_n \, \delta_{m,n}$ is often represented by the symbol $\boldsymbol{\Lambda}$, as in Eq. (73).

If another set of orthonormal functions, say $\chi = \chi_1, \chi_2, \chi_3, \ldots$ is used to calculate $\boldsymbol{H}$, the result is a matrix composed of elements $\int \chi_i^{\bigstar} \hat{H} \chi_j \, d\tau$. It will not in general be in diagonal form. However, the set of functions χ can serve as a basis for the expression of the unknown wavefunctions. In general, a given function such as ψ_n can be expanded in a complete set of orthonormal functions. A Fourier series such as Eq. (6-15) is an example. If the complete set of orthonormal (and often complex) functions χ is available, the wavefunction appearing in Eq. (115) can be written as

$$\psi_n = \sum_j c_j \chi_j, \tag{117}$$

where the summation extends over all members of the set.* As each function χ_j is assumed to be known, and orthonormal in a given region, a knowledge of all of the coefficients c_j is sufficient to evaluate the correct eigenfunctions. If these coefficients are now written as a vector, namely,

$$\zeta_n = \begin{bmatrix} c_1 \\ c_2 \\ \vdots \end{bmatrix} \tag{118}$$

for each state n. These eigenvectors are collected as described in Section 7.10 to form a square matrix ζ. Then, the eigenvalue problem is that defined by Eqs. (73) and (74), namely,

$$\boldsymbol{H}\zeta = \zeta\boldsymbol{\Lambda}, \tag{119}$$

or

$$\zeta^{-1}\boldsymbol{H}\zeta = \boldsymbol{\Lambda}. \tag{120}$$

As the matrix ζ is unitary, $\zeta^{-1} = \zeta^{\dagger} = \tilde{\zeta}^{\star}$.

7.14 THE HARMONIC OSCILLATOR

The harmonic oscillator has already been presented in several forms. It is defined by the potential function $V = \frac{1}{2}\kappa\xi^2$ in one dimension. The corresponding quantum-mechanical problem, which leads to the wavefunctions presented in Table 5-1, yielded the expression for the energy: $\varepsilon = h\nu^0\left(v + \frac{1}{2}\right) = \hbar\omega(v + \frac{1}{2})$, with $v = 0, 1, 2, \ldots$ [Eq. (5-92)].

The energy of the one-dimensional, classical harmonic oscillator can be written in the form

$$H = T + V = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2, \tag{121}$$

where, following conventions, q is the independent variable and p is its conjugate momentum. The quantum-mechanical operators do not commute, as $[\hat{p}, \hat{q}] = -i\hbar$ (problem 13). This result is easily generalized, namely,

$$\hat{p}_j\hat{q}_k - \hat{q}_k\hat{p}_j = -i\hbar\delta_{j,k} \tag{122}$$

in more than one dimension.

*If the functions χ are continuous in a given region, the summation in Eq. (117) implies integration over that region.

In the matrix formulation of quantum mechanics Eq. (121) is transformed. If $\boldsymbol{P}$ and $\boldsymbol{Q}$ are matrices, the Hamiltonian becomes by analogy

$$\boldsymbol{H}(\boldsymbol{P}, \boldsymbol{Q}) = \frac{1}{2m}(\boldsymbol{P}^2 + m^2\omega^2\boldsymbol{Q}^2). \tag{123}$$

If it is assumed that the matrices $\boldsymbol{P}$ and $\boldsymbol{Q}$ have been chosen so that $[\boldsymbol{P}, \boldsymbol{Q}] = -i\hbar\boldsymbol{E}$, a given element of $\boldsymbol{H}$ is of the form

$$H_{j,k} = \frac{1}{2m}(\boldsymbol{P}^2 + m^2\omega^2\boldsymbol{Q}^2)_{j,k} = \varepsilon_j\delta_{j,k}. \tag{124}$$

Thus, the Hamiltonian has been diagonalized and the diagonal elements correspond to the energies of the system.

To obtain explicit expressions for the energies, define two matrices $\boldsymbol{A}$ and $\boldsymbol{B}$ by

$$\boldsymbol{A} = \boldsymbol{P} - im\omega\boldsymbol{Q}, \tag{125}$$

and

$$\boldsymbol{B} = \boldsymbol{P} + im\omega\boldsymbol{Q}. \tag{126}$$

Their products are given by

$$\boldsymbol{AB} = 2m\boldsymbol{H} + m\omega\hbar\boldsymbol{E} \tag{127}$$

and

$$\boldsymbol{BA} = 2m\boldsymbol{H} - m\omega\hbar\boldsymbol{E}. \tag{128}$$

The matrix product $\boldsymbol{ABA}$ is then equal to

$$\boldsymbol{A}(2m\boldsymbol{H} + m\omega\hbar\boldsymbol{E}) = (2m\boldsymbol{H} - m\omega\hbar\boldsymbol{E})\boldsymbol{A} \tag{129}$$

or,

$$\sum_i A_{k,i}\left(\varepsilon_i\delta_{i,j} - \frac{1}{2}\omega\hbar\delta_{i,j}\right) = \sum_i(\varepsilon_k\delta_{k,i} + \omega\hbar\delta_{k,i})A_{i,j}. \tag{130}$$

Thus,

$$A_{k,j}(\varepsilon_j - \varepsilon_k - \omega\hbar) = 0 \tag{131}$$

and $A_{k,j}$ vanishes unless

$$\varepsilon_j - \varepsilon_k = \hbar\omega. \tag{132}$$

The same result can be obtained from the product $\boldsymbol{BAB}$.

From Eq. (128)

$$(BA)_{jj} = \sum_k B_{j,k}A_{k,j} = 2m(\varepsilon_j - \tfrac{1}{2}\omega\hbar). \tag{133}$$

However, each term in the sum over k vanishes unless Eq. (132) is satisfied. Then, for a particular value of ε_j, either $\varepsilon_j - \varepsilon_k = \hbar\omega$ or there is no eigenvalue below ε_j, by an amount $\hbar\omega$. In the latter case the sum in Eq. (133) vanishes and $\varepsilon_j = \frac{1}{2}\hbar\omega$, which is the lowest eigenvalue. It can be concluded from this argument that the eigenvalues form a sequence, $\frac{1}{2}\hbar\omega$, $\frac{3}{2}\hbar\omega$, $\frac{5}{2}\hbar\omega$ *etc.*, in agreement with the values given by Eq. (5-92).

It should be emphasized that the development presented in this section yielded the same result for the energies of the harmonic oscillator as obtained by application of the Schrödinger equation. However, the notion of a wavefunction is absent. The matrix approach, as invented by Heisenberg, provides a direct method of obtaining the values of measurable quantities in a given system – in this case the energies of a one-dimensional harmonic oscillator. It must be admitted that the matrix formulation is more abstract than Schrödinger's method and its success often depends on judicious guesses.

PROBLEMS

1. Given the matrix

$$\boldsymbol{A} = \begin{pmatrix} 1 & 0 & 2 \\ 3 & 4 & 5 \\ 0 & 1 & 2 \end{pmatrix}$$

(a) What is the value of the trace of $\boldsymbol{A}$? Ans. 7

(b) Calculate the value of the determinant: $|\boldsymbol{A}|$. Ans. 9

(c) What are the values of the determinants $\begin{vmatrix} 1 & 2 & 0 \\ 3 & 5 & 4 \\ 0 & 2 & 1 \end{vmatrix}$ and $\begin{vmatrix} 1 & 2 & 0 \\ 3 & 5 & 0 \\ 0 & 2 & 0 \end{vmatrix}$? Ans. $-9, 0$

(d) Find the inverse of $\boldsymbol{A}$. Ans. $\begin{pmatrix} \frac{1}{3} & \frac{2}{9} & -\frac{8}{9} \\ -\frac{2}{3} & \frac{2}{9} & \frac{1}{9} \\ \frac{1}{3} & -\frac{1}{9} & \frac{4}{9} \end{pmatrix}$

2. Given the vector $\boldsymbol{B} = \begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix}$,

(a) Calculate the product $\boldsymbol{AB} = \boldsymbol{C}$, where $\boldsymbol{A}$ is given in problem 1.

Ans. $\begin{pmatrix} 7 \\ 26 \\ 8 \end{pmatrix}$

(b) Evaluate the product $\tilde{\boldsymbol{B}}\boldsymbol{A}$ (where $\tilde{\boldsymbol{B}}$ is the transpose of $\boldsymbol{B}$). Ans. $\begin{pmatrix} 7 \\ 11 \\ 18 \end{pmatrix}$

3. Given the system of simultaneous equations

$$\begin{aligned} 3v - w + 2x + 6y &= 0 \\ 2v + 3w + 5x + 4y &= 0 \\ 4v - 2w + 2x + 7y &= 0 \\ -3v + 2w - x - 3y &= 0 \end{aligned}$$

Does a nontrivial solution exist? Explain. Ans. Yes, Section 7.8

4. Find an inverse of the matrix

$\begin{pmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \end{pmatrix}$. Ans. $\begin{pmatrix} 1 & 1 \\ -4 & -1 \\ \frac{8}{3} & \frac{1}{3} \end{pmatrix}$, *etc.*

5. Calculate the eigenvalues of the matrix $\begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix}$. Ans. $\dfrac{5 \pm \sqrt{33}}{2}$

6. Given the matrix: $\boldsymbol{H} = \begin{pmatrix} 1 & \frac{\sqrt{7}}{2} \\ \frac{\sqrt{7}}{2} & 1 \end{pmatrix}$:

(a) Calculate the eigenvalues λ_1 and λ_2. Ans. $\frac{9}{2}, \frac{1}{2}$

(b) Find the normalized eigenvectors $\boldsymbol{L}_1$ and $\boldsymbol{L}_2$. Ans. $\begin{pmatrix} \frac{1}{\sqrt{8}} \\ \frac{\sqrt{7}}{\sqrt{8}} \end{pmatrix}, \begin{pmatrix} -\frac{\sqrt{7}}{\sqrt{8}} \\ \frac{1}{\sqrt{8}} \end{pmatrix}$

(c) To verify the results of (a) and (b), show that $\boldsymbol{HL} = \boldsymbol{L\Lambda}$, where

$$\boldsymbol{L} = [\boldsymbol{L}_1 | \boldsymbol{L}_2] \text{ and } \boldsymbol{\Lambda} = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix}.$$

(d) Find the inverse $\boldsymbol{L}^{-1}$. Ans. $\begin{pmatrix} \frac{1}{\sqrt{8}} & \sqrt{\frac{7}{8}} \\ -\sqrt{\frac{7}{8}} & \frac{1}{\sqrt{8}} \end{pmatrix}$

(e) Show that $\boldsymbol{H}$ is diagonalized by the similarity transformation, *viz.*

$$\boldsymbol{L}^{-1}\boldsymbol{H}\boldsymbol{L} = \boldsymbol{\Lambda}.$$

7. Prove property (v) of determinants (Section 7.5).

8. Verify Eq. (41).

9. Derive the properties of Jacobians, as given by Eqs. (50).

10. Verify Eq. (57).

11. Verify Eqs. (93) and (94).

12. Verify Eqs. (96) and (97).

13. Show that $[\hat{p}, \hat{q}] = -i\hbar$.