The mean value of a function $g(X)$ can be calculated with a formula similar to that for $\langle X\rangle$:

$$\langle g(X)\rangle = \int_{-\infty}^{+\infty} g(x)f(x)\mathrm{d}x \tag{A2.67}$$

Matrix algebra

A **matrix** is an array of numbers. Matrices may be combined together by addition or multiplication according to generalizations of the rules for ordinary numbers. Most numerical matrix manipulations are now carried out with mathematical software.

Consider a square matrix $\boldsymbol{M}$ of n^2 numbers arranged in n columns and n rows. These n^2 numbers are the **elements** of the matrix, and may be specified by stating the row, r, and column, c, at which they occur. Each element is therefore denoted M_{rc}. For example, in the matrix

$$\boldsymbol{M} = \begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix}$$

the elements are $M_{11} = 1$, $M_{12} = 2$, $M_{21} = 3$, and $M_{22} = 4$. This is an example of a 2×2 matrix. The **determinant**, $|\boldsymbol{M}|$, of this matrix is

$$|\boldsymbol{M}| = \begin{vmatrix} 1 & 2 \\ 3 & 4 \end{vmatrix} = 1\times 4 - 2\times 3 = -2$$

A **diagonal matrix** is a matrix in which the only nonzero elements lie on the major diagonal (the diagonal from M_{11} to M_{nn}). Thus, the matrix

$$\boldsymbol{D} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

is diagonal. The condition may be written

$$M_{rc} = m_r \delta_{rc} \tag{A2.68}$$

where δ_{rc} is the **Kronecker delta**, which is equal to 1 for $r = c$ and to 0 for $r \neq c$. In the above example, $m_1 = 1$, $m_2 = 2$, and $m_3 = 1$. The **unit matrix**, **1** (and occasionally **I**), is a special case of a diagonal matrix in which all nonzero elements are 1.

The **transpose** of a matrix $\boldsymbol{M}$ is denoted $\boldsymbol{M}^{\mathrm{T}}$ and is defined by

$$M^{\mathrm{T}}_{mn} = M_{nm} \tag{A2.69}$$

Thus, for the matrix $\boldsymbol{M}$ we have been using,

$$\boldsymbol{M}^{\mathrm{T}} = \begin{pmatrix} 1 & 3 \\ 2 & 4 \end{pmatrix}$$

Matrices are very useful in chemistry. They simplify some mathematical tasks, such as solving systems of simultaneous equations, the treatment of molecular symmetry (Chapter 12), and quantum mechanical calculations (Chapter 11).

A2.12 Matrix addition and multiplication

Two matrices $\boldsymbol{M}$ and $\boldsymbol{N}$ may be added to give the sum $\boldsymbol{S} = \boldsymbol{M} + \boldsymbol{N}$, according to the rule

$$S_{rc} = M_{rc} + N_{rc} \tag{A2.70}$$

(that is, corresponding elements are added). Thus, with $\boldsymbol{M}$ given above and

$$\boldsymbol{N}=\begin{pmatrix}5 & 6\\ 7 & 8\end{pmatrix}$$

the sum is

$$\boldsymbol{S}=\begin{pmatrix}1 & 2\\ 3 & 4\end{pmatrix}+\begin{pmatrix}5 & 6\\ 7 & 8\end{pmatrix}=\begin{pmatrix}6 & 8\\ 10 & 12\end{pmatrix}$$

Two matrices may also be multiplied to give the product $\boldsymbol{P}=\boldsymbol{MN}$ according to the rule

$$P_{rc}=\sum_n M_{rn}N_{nc} \tag{A2.71}$$

For example, with the matrices given above,

$$\boldsymbol{P}=\begin{pmatrix}1 & 2\\ 3 & 4\end{pmatrix}\begin{pmatrix}5 & 6\\ 7 & 8\end{pmatrix}=\begin{pmatrix}1\times5+2\times7 & 1\times6+2\times8\\ 3\times5+4\times7 & 3\times6+4\times8\end{pmatrix}=\begin{pmatrix}19 & 22\\ 43 & 50\end{pmatrix}$$

It should be noticed that in general $\boldsymbol{MN}\neq\boldsymbol{NM}$, and matrix multiplication is in general non-commutative.

The **inverse** of a matrix $\boldsymbol{M}$ is denoted $\boldsymbol{M}^{-1}$, and is defined so that

$$\boldsymbol{MM}^{-1}=\boldsymbol{M}^{-1}\boldsymbol{M}=\boldsymbol{1} \tag{A2.72}$$

The inverse of a matrix can be constructed by using mathematical software, but in simple cases the following procedure can be carried through without much effort:

1 Form the determinant of the matrix. For example, for our matrix $\boldsymbol{M}$, $|\boldsymbol{M}|=-2$.

2 Form the transpose of the matrix. For example, $\boldsymbol{M}^{\mathrm{T}}=\begin{pmatrix}1 & 3\\ 2 & 4\end{pmatrix}$.

3 Form $\tilde{\boldsymbol{M}}'$, where $\tilde{\boldsymbol{M}}'_{rc}$ is the **cofactor** of the element M_{rc}, that is, it is the determinant formed from $\boldsymbol{M}$ with the row r and column c struck out. For example,

$$\tilde{\boldsymbol{M}}'=\begin{pmatrix}4 & -2\\ -3 & 1\end{pmatrix}$$

4 Construct the inverse as $\boldsymbol{M}^{-1}=\tilde{\boldsymbol{M}}'/|\boldsymbol{M}|$. For example,

$$\boldsymbol{M}^{-1}=\tfrac{1}{-2}\begin{pmatrix}4 & -2\\ -3 & 1\end{pmatrix}=\begin{pmatrix}-2 & 1\\ \frac{3}{2} & -\frac{1}{2}\end{pmatrix}$$

A2.13 Simultaneous equations

A set of n **simultaneous equations**

$$\begin{aligned}
a_{11}x_1+a_{12}x_2+\cdots+a_{1n}x_n&=b_1\\
a_{21}x_1+a_{22}x_2+\cdots+a_{2n}x_n&=b_2\\
&\vdots\\
a_{n1}x_1+a_{n2}x_2+\cdots+a_{nn}x_n&=b_n
\end{aligned} \tag{A2.73}$$

can be written in matrix notation if we introduce the **column vectors** $\boldsymbol{x}$ and $\boldsymbol{b}$:

$$\boldsymbol{x}=\begin{pmatrix}x_1\\ x_2\\ \vdots\\ x_n\end{pmatrix} \qquad \boldsymbol{b}=\begin{pmatrix}b_1\\ b_2\\ \vdots\\ b_n\end{pmatrix}$$

Then, with the $\boldsymbol{a}$ matrix of coefficients a_{rc}, the n equations may be written as

$$\boldsymbol{ax} = \boldsymbol{b} \tag{A2.74}$$

The formal solution is obtained by multiplying both sides of this matrix equation by $\boldsymbol{a}^{-1}$, for then

$$\boldsymbol{x} = \boldsymbol{a}^{-1}\boldsymbol{b} \tag{A2.75}$$

A2.14 Eigenvalue equations

An **eigenvalue equation** is a special case of eqn A2.74 in which

$$\boldsymbol{ax} = \lambda\boldsymbol{x} \tag{A2.76}$$

where λ is a constant, the **eigenvalue**, and $\boldsymbol{x}$ is the **eigenvector**. In general, there are n eigenvalues $\lambda^{(i)}$, and they satisfy the n simultaneous equations

$$(\boldsymbol{a} - \lambda\mathbf{1})\boldsymbol{x} = 0 \tag{A2.77}$$

There are n corresponding eigenvectors $\boldsymbol{x}^{(i)}$. Equation A2.77 has a solution only if the determinant of the coefficients is zero. However, this determinant is just $|\boldsymbol{a} - \lambda\mathbf{1}|$, so the n eigenvalues may be found from the solution of the **secular equation**:

$$|\boldsymbol{a} - \lambda\mathbf{1}| = 0 \tag{A2.78}$$

The n eigenvalues the secular equation yields may be used to find the n eigenvectors. These eigenvectors (which are $n \times 1$ matrices), may be used to form an $n \times n$ matrix $\boldsymbol{X}$. Thus, because

$$\boldsymbol{x}^{(1)} = \begin{pmatrix} x_1^{(1)} \\ x_2^{(1)} \\ \vdots \\ x_n^{(1)} \end{pmatrix} \qquad \boldsymbol{x}^{(2)} = \begin{pmatrix} x_1^{(2)} \\ x_2^{(2)} \\ \vdots \\ x_n^{(2)} \end{pmatrix} \qquad \text{etc.}$$

we may form the matrix

$$\boldsymbol{X} = (\boldsymbol{x}^{(1)}, \boldsymbol{x}^{(2)}, \ldots, \boldsymbol{x}^{(n)}) = \begin{pmatrix} x_1^{(1)} & x_1^{(2)} & \cdots & x_1^{(n)} \\ x_2^{(1)} & x_2^{(2)} & \cdots & x_2^{(n)} \\ \vdots & \vdots & & \vdots \\ x_n^{(1)} & x_n^{(2)} & \cdots & x_n^{(n)} \end{pmatrix}$$

so that $X_{rc} = x_r^{(c)}$. If further we write $\Lambda_{rc} = \lambda_r\delta_{rc}$, so that $\boldsymbol{\Lambda}$ is a diagonal matrix with the elements $\lambda_1, \lambda_2, \ldots, \lambda_n$ along the diagonal, then all the eigenvalue equations $\boldsymbol{ax}^{(i)} = \boldsymbol{\lambda}_i\boldsymbol{x}^{(i)}$ may be confined into the single equation

$$\boldsymbol{aX} = \boldsymbol{X\Lambda} \tag{A2.79}$$

because this expression is equal to

$$\sum_n a_{rn}X_{nc} = \sum_n X_{rn}\Lambda_{nc}$$

or

$$\sum_n a_{rn}x_n^{(c)} = \sum_n x_r^{(n)}\lambda_n\delta_{nc} = \lambda_c x_r^{(c)}$$

as required. Therefore, if we form $\boldsymbol{X}^{-1}$ from $\boldsymbol{X}$, we construct a **similarity transformation**

$$\boldsymbol{\Lambda} = \boldsymbol{X}^{-1}\boldsymbol{aX} \tag{A2.80}$$