where

$$k_1 = f(x,y)\Delta x \tag{A2.60a}$$

$$k_2 = f(x+\tfrac{1}{2}\Delta x,\, y+\tfrac{1}{2}k_1)\Delta x \tag{A2.60b}$$

$$k_3 = f(x+\tfrac{1}{2}\Delta x,\, y+\tfrac{1}{2}k_2)\Delta x \tag{A2.60c}$$

$$k_4 = f(x+\Delta x,\, y+k_3)\Delta x \tag{A2.60d}$$

Therefore, if we know the functional form of $f(x,y)$ and $y(0)$, we can use eqns A2.60(a–d) to calculate values of y for a range of x values. The process can be automated easily with an electronic spreadsheet or with mathematical software. The accuracy of the calculation increases with decreasing values of the increment Δx.

(c) Partial differential equations

A **partial differential equation** is a differential in more than one variable. An example is

$$\frac{\partial^2 y}{\partial t^2} = a\frac{\partial^2 y}{\partial x^2} \tag{A2.61}$$

with y a function of the two variables x and t. In certain cases, partial differential equations may be separated into ordinary differential equations. Thus, the Schrödinger equation for a particle in a two-dimensional square well (Section 9.2) may be separated by writing the wavefunction, $\psi(x,y)$, as the product $X(x)Y(y)$, which results in the separation of the second-order partial differential equation into two second-order differential equations in the variables x and y. A good guide to the likely success of such a **separation of variables** procedure is the symmetry of the system.

Statistics and probability

Throughout the text, but especially in Chapters 16, 17, 19, and 21, we use several elementary results from two branches of mathematics: **probability theory**, which deals with quantities and events that are distributed randomly, and **statistics**, which provides tools for the analysis of large collections of data. Here we introduce some of the fundamental ideas from these two fields.

A2.10 Random selections

Combinatorial functions allow us to express the number of ways in which a system of particles may be configured; they are especially useful in statistical thermodynamics (Chapters 16 and 17). Consider a simple coin-toss problem. If n coins are tossed, the number $N(n,i)$ of outcomes that have i heads and $(n-i)$ tails, regardless of the order of the results, is given by the coefficients of the **binomial expansion** of $(1+x)^n$:

$$(1+x)^n = 1 + \sum_{i=1}^{n} N(n,i)x^i, \qquad N(n,i) = \frac{n!}{(n-i)!i!} \tag{A2.62}$$

The numbers $N(n,i)$, which are sometimes denoted $\begin{pmatrix} n \\ i \end{pmatrix}$, are also called **binomial coefficients**.

Suppose that, unlike the coin-toss problem, there are more than two possible results for each event. For example, there are six possible results for the roll of a die. For n rolls of the die, the number of ways, W, that correspond to n_1 occurrences of the number 1, n_2 occurrences of the number 2, and so on, is given by

$$W = \frac{n!}{n_1!n_2!n_3!n_4!n_5!n_6!}, \qquad n = \sum_{i=1}^{6} n_i$$

This is an example of a **multinomial coefficient**, which has the form

$$W = \frac{n!}{n_1!n_2!\ldots n_m!}, \qquad n = \sum_{i=1}^{m} n_i \tag{A2.63}$$

where W is the number of ways of achieving an outcome, n is the number of events, and m is the number of possible results. In Chapter 16 we use the multinomial coefficient to determine the number of ways to configure a system of identical particles given a specific distribution of particles into discrete energy levels.

In chemistry it is common to deal with a very large number of particles and outcomes and it is useful to express factorials in different ways. We can simplify factorials of large numbers by using **Stirling's approximation**:

$$n! \approx (2\pi)^{1/2} n^{n+\frac{1}{2}} \mathrm{e}^{-n} \tag{A2.64}$$

The approximation is in error by less than 1 per cent when n is greater than about 10. For very large values of n, it is possible to use another form of the approximation:

$$\ln n! \approx n \ln n - n \tag{A2.65}$$

A2.11 Some results of probability theory

Here we develop two general results of probability theory: the mean value of a variable and the mean value of a function. The calculation of mean values is useful in the description of random coils (Chapter 19) and molecular diffusion (Chapter 21).

The mean value (also called the *expectation value*) $\langle X \rangle$ of a variable X is calculated by first multiplying each discrete value x_i that X can have by the probability p_i that x_i occurs and then summing these products over all possible N values of X:

$$\langle X \rangle = \sum_{i=1}^{N} x_i p_i$$

When N is very large and the x_i values are so closely spaced that X can be regarded as varying continuously, it is useful to express the probability that X can have a value between x and $x + \mathrm{d}x$ as

$$\text{Probability of finding a value of } X \text{ between } x \text{ and } x + \mathrm{d}x = f(x)\mathrm{d}x$$

where the function $f(x)$ is the *probability density*, a measure of the distribution of the probability values over x, and $\mathrm{d}x$ is an infinitesimally small interval of x values. It follows that the probability that X has a value between $x = a$ and $x = b$ is the integral of the expression above evaluated between a and b:

$$\text{Probability of finding a value of } X \text{ between } a \text{ and } b = \int_a^b f(x)\mathrm{d}x$$

The mean value of the continuously varying X is given by

$$\langle X \rangle = \int_{-\infty}^{+\infty} x f(x)\mathrm{d}x \tag{A2.66}$$

This expression is similar to that written for the case of discrete values of X, with $f(x)\mathrm{d}x$ as the probability term and integration over the closely spaced x values replacing summation over widely spaced x_i.