# Resumé of mathematics for Chemistry A

If you have followed the Mathematics course in Part IA reasonably diligently, most of the following material should be familiar. Some of it consists of brief exercises (answers at the end) to illustrate the types of manipulation that are needed, and if you can do all these without any difficulty you should have no trouble with the maths in the rest of the course. You need to be fairly proficient with this material, so that you can concentrate on the new ideas in the course without having to struggle with the mathematics. If any of it is unfamiliar or difficult for you, ask your supervisor to take you through it as soon as possible.

## 1 Functions of a complex variable

$$\exp[\pm \mathrm{i}\theta] \equiv \mathrm{e}^{\pm \mathrm{i}\theta} = \cos\theta \pm \mathrm{i}\sin\theta. \tag{1.1}$$

(The notation means that we take *either* the top sign *or* the bottom sign throughout.) Conversely

$$\cos\theta = \frac{1}{2}(\mathrm{e}^{\mathrm{i}\theta} + \mathrm{e}^{-\mathrm{i}\theta}), \qquad \sin\theta = \frac{1}{2i}(\mathrm{e}^{\mathrm{i}\theta} - \mathrm{e}^{-\mathrm{i}\theta}). \tag{1.2}$$

### 1.1 Complex conjugate

The complex conjugate of any expression is constructed by replacing i by $-\mathrm{i}$ throughout. An expression that is equal to its complex conjugate is said to be *real*; one that is equal to minus its complex conjugate is *imaginary*. The complex conjugate is usually denoted by an asterisk; thus $z^*$ is the complex conjugate of $z$.

***Exercise* 1.1** If $z = \mathrm{e}^{\mathrm{i}\theta}$, show that $zz^* = 1$.

***Exercise* 1.2** Use eq. (1.2) to express $\cos^2\theta$ and $\sin^2\theta$ in terms of $\cos 2\theta$.

***Exercise* 1.3** What are the solutions of the equation $z^3 = 1$?

## 2 Spherical polar coordinates

The definition of spherical polar coordinates and the relationship between them and Cartesian coordinates are given in the Data Book. Although they are available for consultation in the examination, you will find it helpful to be familiar with these relationships, as we shall need to switch between Cartesian and polar from time to time.

***Exercise* 2.1** (a) A point is at $x = y = z = a$ in Cartesian coordinates. Find its position in spherical polar coordinates.
(b) A point is at $(r, \theta, \varphi)$ in spherical polar coordinates. Find the position, in spherical polars, of the point obtained by inversion through the origin. (In Cartesians, inversion takes the point $(x, y, z)$ to $(-x, -y, -z)$.)

# 3 Differentiation

***Exercise* 3.1** Differentiate with respect to $x$:

$$(a)\quad \sin x, \qquad (b)\quad \sin^2 x, \qquad (c)\quad \exp(-x^2).$$

***Exercise* 3.2** Evaluate

$$(a)\quad \frac{\mathrm{d}^2}{\mathrm{d}x^2}\exp(-x^2), \qquad (b)\quad \frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}r^2\frac{\mathrm{d}}{\mathrm{d}r}\mathrm{e}^{-r}, \qquad (c)\quad \frac{1}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\sin\theta\frac{\mathrm{d}}{\mathrm{d}\theta}\cos\theta.$$

(In the more complicated expressions each differential operator applies to everything to its right. Start at the right-hand end and work to the left.)

## 3.1 Chain Rule

If $f$ is a function of $g$ which is a function of $x$, then

$$\frac{\mathrm{d}}{\mathrm{d}x}f(g(x)) = \frac{\mathrm{d}g}{\mathrm{d}x}\frac{\mathrm{d}f}{\mathrm{d}g}. \tag{3.3}$$

If $f$ is a function of several variables $u$, $v$ and $w$ which are each functions of $x$, $y$ and $z$, then

$$\frac{\partial f}{\partial x} = \frac{\partial u}{\partial x}\frac{\partial f}{\partial u} + \frac{\partial v}{\partial x}\frac{\partial f}{\partial v} + \frac{\partial w}{\partial x}\frac{\partial f}{\partial w}. \tag{3.4}$$

This most commonly arises when $u$, $v$ and $w$ are the spherical polar coordinates $r$, $\theta$ and $\varphi$.

***Exercise* 3.3** If $r = \sqrt{x^2+y^2+z^2}$, evaluate

$$(a)\quad \frac{\mathrm{d}}{\mathrm{d}x}r \quad \text{(use (3.4) with } u = x^2+y^2+z^2\text{, so that } r=\sqrt{u}\text{)}, \qquad (b)\quad \frac{\mathrm{d}}{\mathrm{d}x}\mathrm{e}^{-r}.$$

# 4 Stationary points

At a maximum or minimum (a stationary point) of a function $f(x)$, $\mathrm{d}f/\mathrm{d}x = 0$. For a function of several variables $x_1, x_2, \ldots$, the condition for a stationary point is

$$\partial f/\partial x_1 = \partial f/\partial x_2 = \cdots = 0. \tag{4.5}$$

***Exercise* 4.1** Find the values of $r$ at which $f(r) = r^2\exp(-2r)$ has a maximum or minimum.

***Exercise* 4.2** Find the maximum of $f(r,\theta) = r^4\cos^2\theta\exp(-r)$, where $r$ and $\theta$ are spherical polar coordinates.

# 5 Integration

We only need *definite* integrals, almost always taken over the full range of the variable.

***Exercise* 5.1** Evaluate

$$(a) \quad \int_0^{2\pi} \sin^2\varphi \, d\varphi, \qquad (b) \quad \int_0^a \sin^2 \frac{\pi x}{a} \, dx.$$

## 5.1 Integration by parts

$$\int_a^b u \, dv = \left[uv\right]_a^b - \int_a^b v \, du \tag{5.6}$$

***Exercise* 5.2** Evaluate

$$(a) \quad \int_0^{\pi} x \sin x \, dx, \qquad (b) \quad \int_0^{\infty} r^2 e^{-2r} \, dr, \qquad (c) \quad \int_0^a x^2 \sin^2 \frac{\pi x}{a} \, dx.$$

***Exercise* 5.3** Some of the more difficult integrals are tabulated in the Data Book. Use the tabulated formulae to evaluate

$$(a) \quad \int_{-\infty}^{\infty} x^2 \exp\left(-\frac{km}{\hbar^2} x^2\right) dx, \qquad (b) \quad \int_0^{\pi} \cos^2\theta \sin^3\theta \, d\theta.$$

***Exercise* 5.4** Sometimes it isn't necessary to evaluate an integral at all because the negative parts cancel the positive parts. Sketch the integrands of the following integrals and satisfy yourself that the integral is zero in each case.

$$(a) \quad \int_{-\infty}^{\infty} x e^{-ax^2} \, dx, \qquad (b) \quad \int_0^{\pi} \sin^2\theta \cos\theta \, d\theta.$$

***Exercise* 5.5** Integrals involving spherical polar coordinates have to include the volume element $dV = r^2 \sin\theta \, dr \, d\theta \, d\varphi$. Leaving out the $r^2 \sin\theta$ factor is a very common source of error. Using spherical polar coordinates, evaluate

$$(a) \quad \int \exp(-2r) \, dV, \qquad (b) \quad \int x^2 \exp(-r) \, dV.$$

Refer to the Data Book if you are uncertain about the range of integration.

# 6 Differential equations

## 6.1 Ordinary differential equations

***Exercise* 6.1** Solve for $y$:

$$(a) \quad \frac{d^2 y}{dx^2} = -m^2 y, \qquad (b) \quad \frac{dy}{dx} = -xy$$

## 6.2 Partial differential equations

***Exercise* 6.2** If $y(r, \varphi)$ satisfies the partial differential equation

$$\frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial y}{\partial r} + \frac{1}{r^2} \frac{\partial^2 y}{\partial \varphi^2} = 0,$$

show that a possible solution is $y = R(r) \exp(im\varphi)$. Find the equation satisfied by $R(r)$ and find its solutions. (Hint: try $R = r^k$.)

## 7 Probability distributions

Some of you may not have met this topic at A level or in Part IA, so here is a brief summary. If it's unfamiliar you should probably refer to a textbook for a more detailed account; if it's familiar just read through it to remind yourself of the main points, and do the exercises to check your understanding.

If a quantity $x$ doesn't always have the same value, but is different each time it's measured, its behaviour can usually be described by a probability density $P(x)$. Examples: height of a person chosen at random; length of a vibrating chemical bond. $P(x)\,\mathrm{d}x$ is the probability that a measurement of $x$ yields a value between $x$ and $x+\mathrm{d}x$.

The probability that a particular measured value of $x$ lies in the finite range between $a$ and $b$ is $\int_a^b P(x)\,\mathrm{d}x$. Since $x$ must be somewhere (probability 1), the probability density has to satisfy $\int P(x)\,\mathrm{d}x = 1$, where the integral sign without explicit limits means that we are to integrate over the full range of $x$, which might be 0 to $\infty$, or $-\infty$ to $\infty$, or some other range, depending on the problem. (This notation must not be confused with the indefinite integral, but it is useful in applications like quantum mechanics where the indefinite integral doesn't usually occur.)

The average or *mean* of a series of measurements is the sum of all of them divided by the number of measurements. In a very long series of $N$ measurements ($N \to \infty$) values in the range $x$ to $x+\mathrm{d}x$ occur $NP(x)\mathrm{d}x$ times, so the mean is $\langle x\rangle = (1/N)\int x \times NP(x)\,\mathrm{d}x = \int xP(x)\,\mathrm{d}x$.

In the same way, the average or *expectation value* of some function of $x$, such as $x^2$, is obtained by adding up the values of $x^2$ and dividing by the total number of measurements. In terms of the probability distribution this gives $\langle x^2\rangle = \int x^2 P(x)\,\mathrm{d}x$. An important quantity is the *variance*, which is the mean square deviation from the mean, that is the average value of $\big(x-\langle x\rangle\big)^2$. This is

$$\begin{aligned}
\mathrm{var}_x &= \int \big(x-\langle x\rangle\big)^2 P(x)\,\mathrm{d}x \\
&= \int \big(x^2 - 2x\langle x\rangle + \langle x\rangle^2\big)P(x)\,\mathrm{d}x \\
&= \langle x^2\rangle - \langle x\rangle^2.
\end{aligned} \tag{7.7}$$

In practice it is more convenient to work with the square root of the variance, which is known as the *standard deviation* in probability theory, and as the *uncertainty* in quantum mechanics:

$$\sigma_x = \Delta x = \sqrt{\mathrm{var}_x} = \big(\langle x^2\rangle - \langle x\rangle^2\big)^{1/2}. \tag{7.8}$$

***Exercise* 7.1** If $P(r) = 4r^2\exp(-2r)$ $(0 \le r < \infty)$, show that

$$(a)\quad \int P(r)\,\mathrm{d}r = 1, \qquad (b)\quad \langle r\rangle = 3/2, \qquad (c)\quad \langle r^2\rangle = 3, \qquad (d)\quad \Delta r = \sqrt{\tfrac{3}{4}}.$$

(Remember that the integrals are in the data book.)

***Exercise* 7.2** If $P(J) = (1/Q)(2J+1)\exp(-BJ(J+1)/kT)$ and $E(J) = BJ(J+1)$, where $B$ is a constant, then
(a) Find the value of $Q$ for which $\int_0^\infty P(J)dJ = 1$;
(b) Find $\langle E \rangle$.
(Hint: use the substitution $u = J(J+1)$.)

# 8 Determinants

The determinant of a $2 \times 2$ matrix is defined by

$$\begin{vmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{vmatrix} = A_{11}A_{22} - A_{12}A_{21}. \tag{8.9}$$

The determinant of a square $n \times n$ matrix with elements $A_{ij}$ can be defined recursively as follows:

$$\begin{aligned} \det(A) \equiv & \begin{vmatrix} A_{11} & A_{12} & \dots & A_{1n} \\ A_{21} & A_{22} & \dots & A_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ A_{n1} & A_{n2} & \dots & A_{nn} \end{vmatrix} \\ = A_{11} & \begin{vmatrix} A_{22} & A_{23} & \dots & A_{2n} \\ A_{32} & A_{33} & \dots & A_{3n} \\ \vdots & \vdots & \ddots & \vdots \\ A_{n2} & A_{n3} & \dots & A_{nn} \end{vmatrix} - A_{12} \begin{vmatrix} A_{21} & A_{23} & \dots & A_{2n} \\ A_{31} & A_{33} & \dots & A_{3n} \\ \vdots & \vdots & \ddots & \vdots \\ A_{n1} & A_{n3} & \dots & A_{nn} \end{vmatrix} \\ & + A_{13} \begin{vmatrix} A_{21} & A_{22} & A_{24} & \dots & A_{2n} \\ A_{31} & A_{32} & A_{34} & \dots & A_{3n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ A_{n1} & A_{n2} & A_{n4} & \dots & A_{nn} \end{vmatrix} - \cdots. \end{aligned} \tag{8.10}$$

In this formula, each element of the first row is multiplied by the determinant of an $(n-1) \times (n-1)$ matrix (the *cofactor*) obtained by crossing out the row and column containing that element, and multiplying by $(-1)^{i+j}$, where $i$ and $j$ label the row and column. Any row or column can be used — it doesn't have to be the first row.

This defines an $n \times n$ determinant in terms of smaller ones, and formally we can repeat the process, eventually reaching $2 \times 2$ determinants where we can use (8.9). Fortunately we shall only need to carry out this procedure in practice for a $3 \times 3$ determinant:

$$\begin{aligned} \begin{vmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{vmatrix} &= A_{11} \begin{vmatrix} A_{22} & A_{23} \\ A_{32} & A_{33} \end{vmatrix} - A_{12} \begin{vmatrix} A_{21} & A_{23} \\ A_{31} & A_{33} \end{vmatrix} + A_{13} \begin{vmatrix} A_{21} & A_{22} \\ A_{31} & A_{32} \end{vmatrix} \\ &= A_{11}(A_{22}A_{33} - A_{23}A_{32}) - A_{12}(A_{21}A_{33} - A_{23}A_{31}) \\ &\quad + A_{13}(A_{21}A_{32} - A_{22}A_{31}) \end{aligned} \tag{8.11}$$

The only other property that we need is that exchanging any two columns of a determinant changes its sign. This can be seen immediately for (8.9), and with rather more effort for (8.10), but you do not need to be able to prove it. It follows from this that a determinant with two identical columns, or two identical rows, is zero, and also that any multiple of any row (column) can be added to any other row (column) without affecting the value of the determinant.

***Exercise* 8.1** Evaluate

$$(a)\quad \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix}, \qquad (b)\quad \begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{vmatrix},$$

and in each case find the values of $x$ that make the determinant zero.

# 9 Matrices

A reminder of some definitions. For a square $n \times n$ matrix **A** with elements $A_{ij}$,

- An *identity* or *unit* matrix is a square matrix with every diagonal element equal to 1 and the remaining elements zero. That is, $A_{ij} = 1$ if $i = j$ and 0 otherwise.
- The product **AB** of two matrices **A** and **B** is a matrix **C** whose elements are

$$C_{ij} = \sum_k A_{ik} B_{kj}. \tag{9.12}$$

  That is, $C_{ij}$ is the scalar product of the $i$th row of **A** with the $j$th column of **B**.
- The *inverse* $\mathbf{A}^{-1}$ of an $n \times n$ matrix **A** is another $n \times n$ matrix such that the product $\mathbf{A}^{-1}\mathbf{A} = \mathbf{I}$, where **I** is the $n \times n$ unit matrix.
- The *transpose* of a matrix **A** is a matrix $\mathbf{A}^T$ whose elements are $(A^T)_{ij} = A_{ji}$.
- A *symmetric* matrix is a square matrix which is unchanged by reflection in its leading diagonal (top left to bottom right). That is, $A_{ij} = A_{ji}$, or $\mathbf{A}^T = \mathbf{A}$.
- The *Hermitian conjugate* of a matrix **A** is a matrix $\mathbf{A}^\dagger$ whose elements are $(A^\dagger)_{ij} = (A_{ji})^*$.
- The elements of a *Hermitian* matrix satisfy $A_{ij} = A^*_{ji}$. That is, $\mathbf{A} = \mathbf{A}^\dagger$.
- A matrix is *orthogonal* if its inverse is equal to its transpose: $\mathbf{A}^{-1} = \mathbf{A}^T$.
- A matrix is *unitary* if its inverse is equal to its Hermitian conjugate: $\mathbf{A}^{-1} = \mathbf{A}^\dagger$.

- The *trace* of a matrix is the sum of its diagonal elements: $\mathrm{trace}(\mathbf{A}) = \sum_i A_{ii}$.

A *column vector* is an $n \times 1$ matrix, and a *row vector* is a $1 \times n$ matrix. The transpose $\mathbf{x}^T$ of a column vector is a row vector. Two vectors $\mathbf{u}$ and $\mathbf{v}$ are said to be *orthogonal* if $\mathbf{u}^T \mathbf{v} = 0$.

If a column vector $\mathbf{x}$ satisfies

$$\mathbf{A}\mathbf{x} = \lambda \mathbf{x} \tag{9.13}$$

it is said to be an *eigenvector* of the matrix $\mathbf{A}$ with *eigenvalue* $\lambda$. An $n \times n$ symmetric or Hermitian matrix has $n$ eigenvectors, which are mutually orthogonal. The eigenvalues satisfy $\det(\mathbf{A} - \lambda \mathbf{I}) = 0$.

***Exercise* 9.1** Find the eigenvalues and eigenvectors of the matrices

$$(a) \quad \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \qquad (b) \quad \begin{pmatrix} 0 & 1 & 0 \\ 1 & 1 & 1 \\ 0 & 1 & 0 \end{pmatrix}.$$

## 10 Permutations and Combinations

The number of possible arrangements of $N$ distinguishable objects (the number of permutations) is $N!$. The number of distinct ways of selecting $k$ objects from $N$, if the order of the $k$ selected objects does not matter (the number of combinations of $k$ objects from $N$) is $N!/k!(N-k)!$.

If $N$ is very large, Stirling's approximation is useful:

$$\ln N! \approx N \ln N - N. \tag{10.14}$$

The error in this approximation is of the order of $\ln N$, which is negligible compared with $N$ when $N$ is of the order of $10^{23}$.

***Exercise* 10.1** Write down the probability of winning the lottery (i.e. of guessing correctly six different numbers between 1 and 49). Evaluate it (a) exactly, (b) using Stirling's approximation for the large factorials.

***Exercise* 10.2** If $A = -kT \ln(q^N/N!)$, use Stirling's approximation to express it in the form $A = -NkT \ln(q\mathrm{e}/N)$.

***Exercise* 10.3** Find the number of ways of putting $Q$ indistinguishable balls in $N$ distinguishable boxes.

Hint: imagine the boxes arranged in order from 1 on the left to $N$ on the right, separated by partitions, and with balls in some of the boxes:

$$\begin{array}{c|c|c|c|c|c|c|c} 1 & 2 & 3 & 4 & 5 & \dots & N-1 & N \\ & \bullet & & \bullet\bullet & \bullet & & & \end{array}$$

How many ways are there of arranging the $N-1$ (indistinguishable) partitions and the $Q$ indistinguishable balls?

# 11 Dimensional Analysis

The magnitude of a physical quantity is expressed as a multiple of some unit, which in turn can be expressed in terms of basic units of length $L$, mass $M$, time $T$, electric current $J$, temperature $K$, amount of substance $N$ and luminous intensity $I$. The *dimensions* of a physical quantity specify the power to which each of these basic units occurs. Thus velocity might be measured in units of $\mathrm{m\,s^{-1}}$, but its dimensions are $LT^{-1}$ — length over time — whatever system of units is used. Square brackets are conventionally used to denote the dimensions of a quantity, so we can write $[\text{velocity}] = LT^{-1}$. The dimensions of other quantities can be found by analysing expressions for them. For example the dimensions of energy can be derived by considering the expression $\frac{1}{2}mv^2$ for kinetic energy, from which we see that $[\text{energy}] = [\text{mass}]\times[\text{velocity}]^2 = ML^2T^{-2}$. A quantity for which all the factors of $L$, $M$, $T$, etc. cancel out is said to be *dimensionless*, and has the same value in any system of units.

Every term in an equation must have the same dimensions. The argument of a mathematical function such as log or exp must be dimensionless, so for instance $\log(V)$ is not a legitimate expression if $V$ is a volume, but $\log(V/V_0)$ might be.

***Exercise* 11.1** Find the dimensions of the following expressions:

$$(a)\quad \left(\frac{8k_BT}{\pi m}\right)^{1/2} \qquad (b)\quad \left(\frac{2\pi m k_BT}{h^2}\right)^{3/2} V \qquad (c)\quad -\frac{e^4 m}{8\hbar^2 n^2 (4\pi\varepsilon_0)^2}$$

where the symbols have the following meanings:

| | |
|---|---|
| $k_B$ | is Boltzmann's constant; |
| $T$ | is a temperature; |
| $m$ | is a mass; |
| $e$ | is the elementary charge (proton charge); |
| $h$ | is Planck's constant, and $\hbar = h/2\pi$; |
| $V$ | is a volume; |
| $n$ | is an integer; |
| $\varepsilon_0$ | is the permittivity of the vacuum. |

Hint: For $(c)$, note that $[\text{charge}^2/(4\pi\varepsilon_0 \times \text{distance})]$ =[energy].

***Exercise* 11.2** Which of the following are dimensionally legitimate expressions?

$$(a)\quad \exp\left(-\frac{E}{k_BT}\right) \qquad (b)\quad \exp\left(-\frac{1}{2}\frac{\sqrt{km}}{\hbar}x^2\right) \qquad (c)\quad \exp\left(-\frac{n^2h^2}{8ml^2k_BT}\right),$$

where the symbols have the same meanings as above, and also:

| | |
|---|---|
| $E$ | is an energy in $\mathrm{kJ\,mol^{-1}}$; |
| $k$ | is a force constant; |
| $x$ and $l$ | are lengths. |

## Answers

**1.1** If $z = \mathrm{e}^{\mathrm{i}\varphi}$, then $zz^* = \mathrm{e}^{\mathrm{i}\varphi}\mathrm{e}^{-\mathrm{i}\varphi} = \mathrm{e}^0 = 1$.

**1.2**

$$\cos^2\theta = \tfrac{1}{4}(\mathrm{e}^{\mathrm{i}\theta} + \mathrm{e}^{-\mathrm{i}\theta})^2 = \tfrac{1}{4}(\mathrm{e}^{2\mathrm{i}\theta} + \mathrm{e}^{-2\mathrm{i}\theta} + 2) = \tfrac{1}{2}(1 + \cos 2\theta)$$
$$\sin^2\theta = \frac{1}{(2\mathrm{i})^2}(\mathrm{e}^{\mathrm{i}\theta} - \mathrm{e}^{-\mathrm{i}\theta})^2 = -\tfrac{1}{4}(\mathrm{e}^{2\mathrm{i}\theta} + \mathrm{e}^{-2\mathrm{i}\theta} - 2) = \tfrac{1}{2}(1 - \cos 2\theta)$$

**1.3** Since $\exp(2\pi n\mathrm{i}) = 1$ for any integer $n$, the possible solutions of $z^3 = 1$ are $\exp(2\pi n\mathrm{i}/3)$, for any $n$. However $n+3$ gives the same solution as $n$, so there are 3 distinct solutions, corresponding to $n = 0$, 1, and 2.

**2.1** (a) $r = \sqrt{x^2+y^2+z^2} = a\sqrt{3}$; $\theta = \arccos(z/r) = \arccos\sqrt{\tfrac{1}{3}} = 54.74^\circ$; $\varphi = \arctan(y/x) = \arctan 1 = 45^\circ$.
(b) $r = \sqrt{x^2+y^2+z^2}$, so after inversion we have $r' = r$, and $\cos\theta' = z'/r' = -z/r = -\cos\theta$, so that $\theta' = \pi - \theta$. (This is the only possible value for $\theta$ because $0 < \theta < \pi$.) For $\varphi$, we have $\tan\varphi' = y'/x' = (-y)/(-x) = \tan\varphi$, so $\varphi' = \varphi$ or $\varphi + \pi$. From geometrical considerations the latter is the correct answer.

**3.1**

$$(a) \quad \cos x, \qquad (b) \quad 2\sin x\cos x, \qquad (c) \quad -2x\exp(-x^2).$$

**3.2**

$$(a) \quad \frac{\mathrm{d}^2}{\mathrm{d}x^2}\exp(-x^2) = \frac{\mathrm{d}}{\mathrm{d}x}\big(-2x\exp(-x^2)\big) = (4x^2-2)\exp(-x^2);$$
$$(b) \quad \frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}r^2\frac{\mathrm{d}}{\mathrm{d}r}\mathrm{e}^{-r} = \frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}r^2(-\mathrm{e}^{-r}) = -\frac{1}{r^2}(2r\mathrm{e}^{-r} - r^2\mathrm{e}^{-r}) = \left(1 - \frac{2}{r}\right)\mathrm{e}^{-r};$$
$$(c) \quad \frac{1}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\sin\theta\frac{\mathrm{d}}{\mathrm{d}\theta}\cos\theta = -\frac{1}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\sin^2\theta = -\frac{1}{\sin\theta}2\sin\theta\cos\theta = -2\cos\theta.$$

**3.3** Writing $u = r^2 = x^2+y^2+z^2$,

$$(a) \quad \frac{\mathrm{d}}{\mathrm{d}x}r = \frac{\mathrm{d}}{\mathrm{d}x}\sqrt{u} = \frac{\mathrm{d}u}{\mathrm{d}x}\tfrac{1}{2}u^{-1/2} = \frac{x}{r},$$
$$(b) \quad \frac{\mathrm{d}}{\mathrm{d}x}\mathrm{e}^{-r} = \frac{\mathrm{d}r}{\mathrm{d}x}\frac{\mathrm{d}}{\mathrm{d}r}\mathrm{e}^{-r} = -\frac{x}{r}\mathrm{e}^{-r}.$$

**4.1**

$$\frac{\mathrm{d}}{\mathrm{d}r}\big(r^2\exp(-2r)\big) = (2r - 2r^2)\exp(-2r),$$

which is zero when $r = 0$, $r = 1$ or $r = \infty$. By inspection, $r = 1$ is a maximum.

**4.2**

$$\frac{\mathrm{d}}{\mathrm{d}r}\big(r^4\cos^2\theta\exp(-r)\big) = (4r^3 - r^4)\exp(-r)\cos^2\theta,$$
$$\frac{\mathrm{d}}{\mathrm{d}\theta}\big(r^4\cos^2\theta\exp(-r)\big) = -2\cos\theta\sin\theta r^4\exp(-r).$$

Both derivatives are zero for any $\theta$ when $r = 0$ or $r = \infty$, or for any $r$ when $\theta = \frac{1}{2}\pi$. In all these cases the function is zero. The only other possibilities are $r = 4$, $\theta = 0$ or $\pi$; at these points the function has its maximum value.

**5.1**

$$(a) \quad \int_0^{2\pi} \sin^2\varphi\,\mathrm{d}\varphi = \int_0^{2\pi} \tfrac{1}{2}(1-\cos 2\varphi)\,\mathrm{d}\varphi = \left[\tfrac{1}{2}(\varphi - \tfrac{1}{2}\sin 2\varphi)\right]_0^{2\pi} = \pi.$$

$$(b) \quad \int_0^{a} \sin^2\frac{\pi x}{a}\,\mathrm{d}x = \frac{a}{\pi}\int_0^{\pi} \sin^2\varphi\,\mathrm{d}\varphi = a/2,$$

using the substitution $\varphi = \pi x/a$.

**5.2**

$$(a) \quad \int_0^{\pi} x\sin x\,\mathrm{d}x = \Big[-x\cos x\Big]_0^{\pi} + \int_0^{\pi}\cos x\,\mathrm{d}x = \pi + \Big[\sin x\Big]_0^{\pi} = \pi;$$

$$\begin{aligned}(b) \quad \int_0^{\infty} r^2\mathrm{e}^{-2r}\,\mathrm{d}r &= \left[\frac{r^2\mathrm{e}^{-2r}}{-2}\right]_0^{\infty} + \tfrac{1}{2}\int_0^{\infty} 2r\mathrm{e}^{-2r}\,\mathrm{d}r \\ &= 0 + \left[\frac{r\mathrm{e}^{-2r}}{-2}\right]_0^{\infty} + \tfrac{1}{2}\int_0^{\infty}\mathrm{e}^{-2r}\,\mathrm{d}r = 0 + \tfrac{1}{2}\left[\frac{\mathrm{e}^{-2r}}{-2}\right]_0^{\infty} = \tfrac{1}{4};\end{aligned}$$

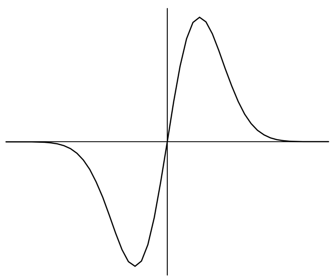
$$\begin{aligned}(c) \quad \int_0^{a} x^2\sin^2\frac{\pi x}{a}\,\mathrm{d}x &= \tfrac{1}{2}\int_0^{a} x^2\left(1-\cos\frac{2\pi x}{a}\right)\mathrm{d}x \\ &= \left[\frac{x^3}{6}\right]_0^{a} - \tfrac{1}{2}\int_0^{2\pi}\frac{a^3}{8\pi^3}\varphi^2\cos\varphi\,\mathrm{d}\varphi \qquad (\text{setting } \varphi = 2\pi x/a) \\ &= \frac{a^3}{6} - \frac{a^3}{16\pi^3}\left\{\Big[\varphi^2\sin\varphi\Big]_0^{2\pi} - \int_0^{2\pi} 2\varphi\sin\varphi\,\mathrm{d}\varphi\right\} \\ &= \frac{a^3}{6} + \frac{a^3}{8\pi^3}\left\{\Big[\varphi(-\cos\varphi)\Big]_0^{2\pi} + \int_0^{2\pi}\cos\varphi\,\mathrm{d}\varphi\right\} \\ &= a^3\left(\frac{1}{6} - \frac{1}{4\pi^2}\right).\end{aligned}$$

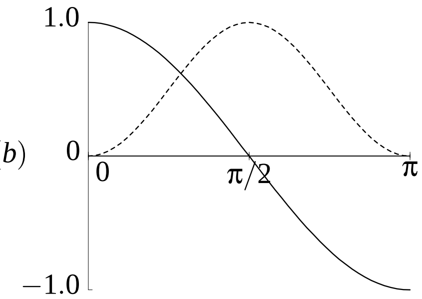
**5.3**

$$(a) \quad \frac{\sqrt{\pi}}{2}\frac{\hbar^3}{(km)^{3/2}}; \qquad (b) \quad 4/15.$$

**5.4** $(a)$ The function $f(x) = x\exp(-\frac{1}{2}x^2)$ is odd; that is, $f(-x) = -f(x)$. Consequently the contribution to the integral from $-x$ cancels the contribution from $+x$.

$(b)$ Rather than sketching the complete function, it is easier and more helpful to sketch the separate factors $\cos x$ (solid curve) and $\sin^2 x$ (dashed curve). The two halves of the integral cancel because $\cos(\pi - x) = -\cos x$.

$(a)$ 

$(b)$ 

**5.5**

$$(a)\quad \int \exp(-2r)\,\mathrm{d}V = \int_{r=0}^{\infty} r^2\exp(-2r)\,\mathrm{d}r \int_{\theta=0}^{\pi}\sin\theta\,\mathrm{d}\theta\int_{\varphi=0}^{2\pi}\mathrm{d}\varphi$$
$$= (2!/2^3)\times\Big[-\cos\theta\Big]_0^{\pi}\times 2\pi = \pi;$$
$$(b)\quad \int x^2\exp(-r)\,\mathrm{d}V = \int r^2\sin^2\theta\cos^2\varphi\exp(-r)r^2\sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\varphi$$
$$= 4!\times 2\times\tfrac{2}{3}\times\pi = 32\pi$$

using the formulae in the Data Book. An alternative for $(b)$ is to note that $x$, $y$ and $z$ are equivalent, so that

$$\int x^2\exp(-r)\,\mathrm{d}V = \tfrac{1}{3}\int r^2\exp(-r)4\pi r^2\,\mathrm{d}r = \tfrac{1}{3}\times 4\pi\times 4! = 32\pi,$$

since we can use the volume element $4\pi r^2\,\mathrm{d}r$ for a purely radial integral.

**6.1** $(a)$ Try $y = e^{kx}$. This leads to $k^2 = -m^2$, or $k = \pm\mathrm{i}m$, so the solutions are $e^{\pm\mathrm{i}mx}$, or equivalently (see eq. (1.1)) $\sin(mx)$ or $\cos(mx)$.

$(b)$ Rearrange the equation into the form

$$\frac{\mathrm{d}y}{y} = -x\mathrm{d}x,$$

and integrate to get $\ln y = -\frac{1}{2}x^2 + c$, *i.e.* $y = A\exp(-\frac{1}{2}x^2)$.

**6.2** Substituting $y = R(r)\exp(\mathrm{i}m\varphi)$ into the equation gives

$$\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial R}{\partial r} - \frac{m^2}{r^2}R = 0$$

as the equation to be satisfied by $R$. Substituting $R = r^k$ into this shows that it is a solution provided that $k^2 = m^2$, *i.e.*, $k = \pm m$. Thus the solutions are $y(r,\varphi) = r^{\pm m}\exp\mathrm{i}m\varphi$.

(The equation is Laplace's equation in 2-dimensional polar coordinates. If the solutions are to be single-valued, *i.e.*, $y(r,\varphi) = y(r,\varphi+2\pi)$, then $m$ must be an integer.)

**7.2** Using the substitution $u = J(J+1)$, so that $\mathrm{d}u = (2J+1)\mathrm{d}J$,

$$(a)\qquad Q = \int_0^{\infty}(2J+1)\exp\left(-\frac{BJ(J+1)}{kT}\right)\mathrm{d}J = \int_0^{\infty}\exp\left(-\frac{Bu}{kT}\right)\mathrm{d}u = \frac{kT}{B},$$
$$(b)\quad \langle E\rangle = \frac{1}{Q}\int_0^{\infty}(2J+1)BJ(J+1)\left(-\frac{BJ(J+1)}{kT}\right)\mathrm{d}J$$
$$= \frac{B}{kT}\int_0^{\infty}Bu\exp\left(-\frac{Bu}{kT}\right)\mathrm{d}u = \frac{B}{kT}\times B\times\frac{k^2T^2}{B^2} = kT.$$

**8.1**

$$(a)\quad \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = x(x^2-1) - 1\times x = x^3 - 2x = 0 \text{ when } x = 0 \text{ or } x = \pm\sqrt{2}.$$

$$(b)\quad \begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{vmatrix} = x(x^2-1) - 1\times(x-1) + 1\times(1-x) = x^3 - 3x + 2$$
$$= (x-1)^2(x+2).$$

**9.1** $(a)$ The equation for the eigenvalues is $\det(\mathbf{A} - \lambda\mathbf{I}) = 0$, *i.e.*,

$$\begin{vmatrix} -\lambda & 1 & 0 \\ 1 & -\lambda & 1 \\ 0 & 1 & -\lambda \end{vmatrix} = -\lambda^3 + 2\lambda,$$

(see ex. 8.1), so $\lambda = 0$ or $\pm\sqrt{2}$. For $\lambda = \sqrt{2}$ we have

$$\begin{pmatrix} -\sqrt{2} & 1 & 0 \\ 1 & -\sqrt{2} & 1 \\ 0 & 1 & -\sqrt{2} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = 0,$$

That is,

$$\begin{aligned} -\sqrt{2}x_1 \quad + x_2 \qquad\quad &= 0, \\ x_1 - \sqrt{2}x_2 \quad + x_3 &= 0, \\ x_2 - \sqrt{2}x_3 &= 0, \end{aligned}$$

so if $x_3 = c$ we find $x_2 = c\sqrt{2}$ and $x_1 = c$. For the eigenvector to be normalized $(x_1^2 + x_2^2 + x_3^2 = 1)$, we need $c = \frac{1}{2}$. Finding the remaining eigenvectors in the same way gives

$$\lambda = \sqrt{2},\ \mathbf{x} = \tfrac{1}{2}\begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix}, \quad \lambda = 0,\ \mathbf{x} = \sqrt{\tfrac{1}{2}}\begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}, \quad \lambda = -\sqrt{2},\ \mathbf{x} = \tfrac{1}{2}\begin{pmatrix} -1 \\ \sqrt{2} \\ -1 \end{pmatrix}.$$

$(b)$

$$\lambda = -1,\ \mathbf{x} = \sqrt{\tfrac{1}{2}}\begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}, \qquad \lambda = 0,\ \mathbf{x} = \sqrt{\tfrac{1}{6}}\begin{pmatrix} 1 \\ 2 \\ 1 \end{pmatrix}, \qquad \lambda = 2,\ \mathbf{x} = \sqrt{\tfrac{1}{3}}\begin{pmatrix} 1 \\ -1 \\ 1 \end{pmatrix}.$$

**10.1**

$(a)$ $6!(49-6)!/49! = 6!/(49.48.47.46.45.44) = 1/13983816;$

$(b)$ $6!/\exp((49\ln 49 - 49) - (43\ln 43 - 43)) = 1/13102825.$

**10.2**

$$
\begin{aligned}
A &= -kT\ln(q^N/N!) \approx -kT(N\ln q - (N\ln N - N)) \\
&= -NkT(\ln\frac{q}{N}+1) = -NkT(\ln\frac{q\mathrm{e}}{N}),
\end{aligned}
$$

since $\ln \mathrm{e} = 1$.

**10.3** We have $N+Q-1$ objects (balls and partitions). The number of ways of choosing $Q$ of these to be balls is $(N+Q-1)!/(N-1)!Q!$.

**11.1** $(a)$ $LT^{-1}$ (velocity). $k_BT$ is an energy (dimensions $ML^2T^{-2}$) so $k_BT/m$ has dimensions $L^2T^{-2}$.
$(b)$ Dimensionless. $k_BT$ is an energy as before; the dimensions of $h$ are [energy] $\times$[time], *i.e.*, $ML^2T^{-1}$. Consequently the expression inside the parentheses has dimensions $L^{-2}$.
$(c)$ $ML^2T^{-2}$ (energy). It is simplest to note that $e^2/(4\pi\varepsilon_0)$ has dimensions of [energy]$\times$[length], while $\hbar$ has dimensions of [energy]$\times$[time]. Cancelling out the [energy] factors leaves $ML^2T^{-2}$.

**11.2** $(a)$ is invalid: the dimensions of $E$ are $ML^2T^{-2}N^{-1}$, and those of $k_B$ are $ML^2T^{-2}K^{-1}$, so the whole expression has dimensions of $N^{-1}$. (Probably the $k_B$ should be $R$, the gas constant — but note that the tabulated value is in $\mathrm{J\,mol^{-1}\,K^{-1}}$ while $E$ is in $\mathrm{kJ\,mol^{-1}}$, so a factor of 1000 must be included. Dimensional analysis doesn't help with numerical factors like this.)

$(b)$ and $(c)$ are dimensionally correct.

A.J.S. June 1997