Mathematical Methods for Chemistry

Why do you need to take this course?

Chemists today face an ever-increasing need for familiarity with a wide range of mathematical techniques. In addition to the mathematics needed for upper year courses, many of the techniques for chemical analysis used in industry involve the use of sophisticated mathematical methods. While modern computer software can take care of much of the detail, it is important for you to understand enough of the mathematics that you can follow what is going or tell if the results make sense. Because of the wide range of topics involved, it would require several disparate 'conventional' mathematics courses to address the relevant material. This course therefore brings together compact presentations of some of the most relevant aspects of a number of those topics, in order to provide you with appopriate preparation for situations when you encounter them in upper year courses and in the working world.

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1 Complex Numbers and their Functions

1.1 Types of Numbers, and their Arithmetic

Real numbers are the types of numbers we encounter in everyday life. There are three types:

integers are the ordinary positive or negative whole numbers, which are expressed without a decimal point

rational numbers are non-integers which may be expressed as a ratio of two integers; e.g., $r = m/n$ where m and n are integers. Integers are of course a special case of rational numbers,

When rational numbers are expressed in decimal form, it always involves a repeating decimal.

e.g. $22/7 =$

irrational numbers are non-integers which *may not* be expressed as a ratio of integers. We usually represent them by symbols, but when expressed in decimal form, they always become infinite non-repeating decimals

e.g.,

- Real numbers may be positive or negative.
- The sum or difference of two real numbers is a real number.
- The product or quotient of any two real numbers is a real number.

Imaginary numbers are numbers defined as the product:

$\{\text{real number}\}\times\sqrt{-1} = \{\text{real number}\}\, i$ where the symbol $i \equiv \sqrt{-1}$ represents the quantity whose square $i^2 = -1$.

e.g.

- The sum or difference of any two imaginary numbers is an imaginary number.

- The product or quotient of any two imaginary numbers is a *real* number.

- The product or quotient of an imaginary number and a real number is always an imaginary number.

A complex number is a number with with a real and an imaginary part.

$\{\text{complex no.}\}$ =

- real numbers are a special case of complex numbers for which the imaginary part is zero.

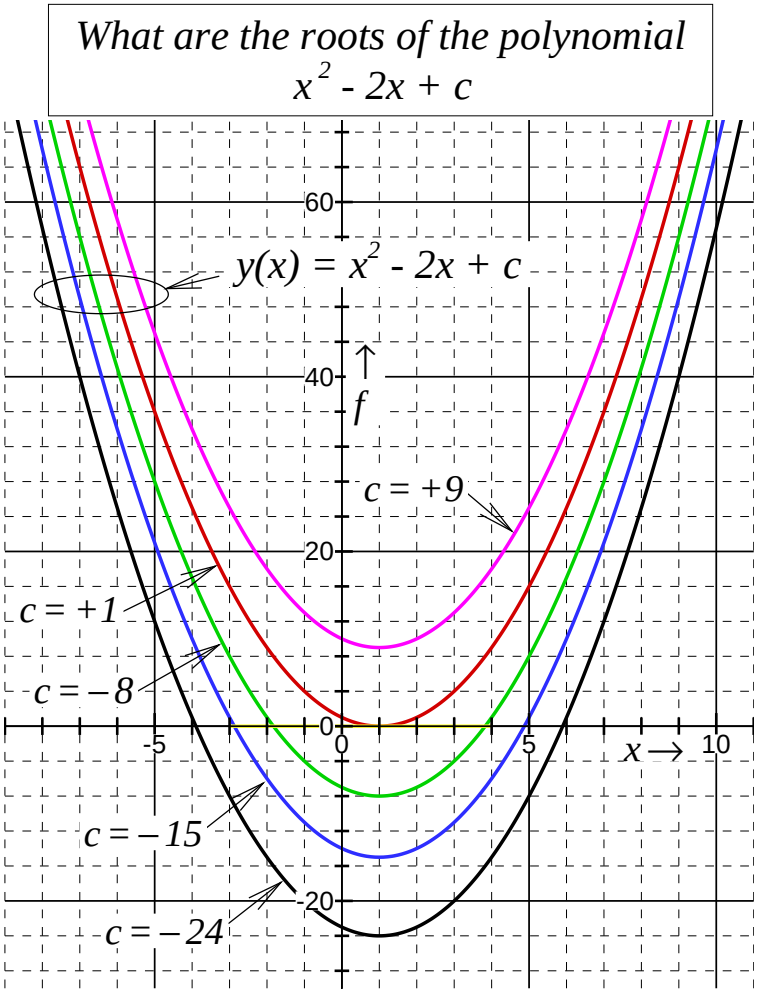
- imaginary numbers a special case of complex numbers for which the real part is zero.

Arithmetic with Complex Numbers

When determining the sum or difference of two complex numbers, simply add or subtract the real and imaginary parts separately.

Aside: ***Where do we encounter complex numbers ?***

Consider the polynomial: $y = x^2 - 2x + c$



To determine the product of two complex numbers, simply multiply them "algebraically" [the same way you would determine the product $(2x-3y)(x+4y)$], make use of the fact that $i^2=-1$, and collect the terms.

The "*complex conjugate*" of a given complex number is a complex number with the same real part, but with the sign changed on the imaginary part. It is identified by a superscript *

The product of a complex number and its complex conjugate is a non-negative real number.

The *magnitude* of a complex number is the square root of its product with its complex conjugate.

Fractions: the ratio or quotient of two complex numbers can always be reduced to an ordinary complex number by multiplying its numerator and denominator by the complex conjugate of the denominator.

Exercise 1.1: *What complex number equals:* (a) $\sqrt{i}$? (b) $(i)^{1/3}$? (c) $\sqrt{3+7i}$?

***Summary*:** although they have two parts, and there are special rules for their arithmetic, complex numbers are in fact simply ordinary scalar numerical factors, and may be used the same way you are accustomed to using real number factors. Complex number and complex values functions are encountered extensively in quantum mechanics, and other contexts.

1.2 The Euler Notation for Complex Numbers

Recall from Calculus the Taylor series representations for e^x, $\sin(x)$ and $\cos(x)$

Aside: *How do we get these series expansion expressions ?*

Apply the above expansion to the case e^{x} where $x = i\,\theta$ is a pure imaginary number !

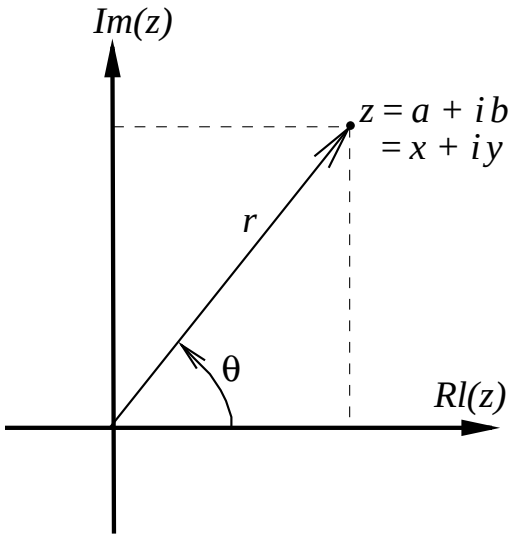
Now ... what about $e^{-x} = e^{-i\,\theta}$?

Combining these expressions for $e^{i\,\theta}$ and $e^{-i\,\theta}$ we can write:

We know that for any real argument $0 \leq |\sin\theta| \leq 1$ and $0 \leq |\cos\theta| \leq 1$, and of course that $\sin^2\theta + \cos^2\theta = 1$. This means that the magnitude of any complex number of the form $z = e^{i\,\theta}$, where θ is a purely real number, is

Geometric (or Polar) Representation of a Complex Number

It is often useful to think if the real and imaginary parts of a complex number $z = a + i\,b$ as being coordinates along orthogonal axes. We can readily describe the position associated with any such number in either Cartesian or polar coordinates.



Much arithmetic with complex numbers simplifies greatly if we use Euler's polar form but ... to exploit it you must become proficient in converting from one to the other !!

1.3 Functions of a Complex Variable

A function of a complex variable is in general a complex-values function, with distinct real and imaginary parts.

e.g., If $z = x + i\,y$, then $f(z) = z^2 - 2z =$

Other Properties of Complex Variables

1. If $z = r(\cos\theta + i\,\sin\theta)$ then $z^n = r^n\,\{\cos(n\theta) + i\,\sin(n\theta)\}$

   Proof:

2. If z_1 and z_2 are any two complex numbers, then $|z_1 + z_2| \le |z_1| + |z_2|$

   Proof:

Exercises. Use the Euler notation approach to determine the values of:
(i) $\sqrt{i}$ (ii) $(i)^{1/3}$ (iii) $\sqrt{3+7i}$ (iv) $(1-i)^{1/3}$, and express all your answers in algebraic form.

2 Some Topics from Calculus

(*Mostly things which you should know*)

2.1 Derivatives of Functions of a Single Variable

Recall the definition of the derivative of a function $f(x)$ at the position x:

$$\frac{d\,f(x)}{dx} \;=\; f'(x) \;=\; \lim_{\Delta x \to 0} \left\{ \frac{f(x+\Delta x) - f(x)}{\Delta x} \right\}$$

the sum, product and quotient rules

$$\begin{aligned}
\frac{d}{dx}\{f(x)+g(x)\} &= \frac{df(x)}{dx} + \frac{dg(x)}{dx} \\
\frac{d}{dx}\{f(x)\,g(x)\} &= f(x)\,\frac{dg(x)}{dx} + g(x)\,\frac{df(x)}{dx} \\
\frac{d}{dx}\left\{\frac{f(x)}{g(x)}\right\} &= \frac{g(x)\,\frac{df(x)}{dx} - f(x)\,\frac{dg(x)}{dx}}{g(x)^2}
\end{aligned}$$

and how to use the chain rule:

If $f = f(u)$ where $u = u(x)$, then: $\quad \dfrac{d\,f}{dx} \;=\; \dfrac{d\,f}{du} \times \dfrac{d\,u(x)}{dx}$

It is assumed that you can routinely evaluate derivatives of powers x^p, of exponentials e^{3x^2}, of sin and cos and other trigonometric functions, of logarithms $\log_e x^p$ or x^{5x}, and of arbitrary products or other combinations of such functions.

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e.g., Evaluate: $\quad \dfrac{d}{dx}\left\{e^{-3\sin(2x)}\right\} \quad$ and $\quad \dfrac{d^2}{dx^2}\left\{e^{-3\sin(2x)}\right\}$

Exercise 2.1. An expression for intermolecular potential energy functions proposed by Šurkus and co-workers [*Chemical Physics Letters* **105**, 291 (1984)] is

$$V(r) \;=\; c_0\, w^2 \left(1 + \sum_{k=1}^{N} c_k\, w^k \right)$$

where $w = w(r) = \left(r^3 - {r_e}^3\right) / \left(r^3 + {r_e}^3\right)$, and the equilibrium distance r_e and the constants c_i may be taken as known numerical constants.

(a) Determine an expression for $\dfrac{d\,V(r)}{dr}$.

(b) Given an expression for the value of $V(r)$ in the limit when $r \to \infty$.

(c) What is the limiting functional behaviour of $V(r)$ (as a power of $1/r$) as $r \to \infty$?

2.2 Integration

It is assumed that you can readily evaluate integrals of powers $\int x^p\,dx$, of exponentials $\int e^{3x}dx$, and of sine and cosine functions $\int \sin(7x)\,dx$, $\int \cos(7x)\,dx$, $\int \tan(7x)\,dx$.

It is assumed that you know and can work with the sine and cosine 'angle addition' formulae:

$$\begin{aligned} \sin(a+b) &= \sin(a)\,\cos(b)+\cos(a)\,\sin(b) \qquad \text{so} \quad \sin(2a) = \\ \sin(a-b) &= \sin(a)\,\cos(b)-\cos(a)\,\sin(b) \end{aligned}$$

$$\begin{aligned} \cos(a+b) &= \cos(a)\,\cos(b)-\sin(a)\,\sin(b) \qquad \text{so} \quad \cos(2a) = \\ \cos(a-b) &= \cos(a)\,\cos(b)+\sin(a)\,\sin(b) \end{aligned}$$

They allow us to evaluate integrals such as: $\int \sin^2(3x)\,dx$ and $\int \cos^2(2x)\,dx$

It is assumed that you know how to do integration by parts: $\int u\,dv = u\,v - \int v\,du$

e.g., evaluate: (a) $\int x^2\,e^{7x}\,dx$ and (b) $\int x^2\,\cos(3x)\,dx$

2.3 Partial Differentiation

If a function $f(x)$ depends on only the single variable x, then its derivative is called an *exact derivative*, and is written as $\dfrac{d\,f}{dx}$.

If a function depends on more than one independent variable, as in $g = g(x, y, z)$, its derivatives with respect to those variables are called *partial derivatives*, and are written as $\dfrac{\partial\, g}{\partial x}$ or $\dfrac{\partial\, g}{\partial y}$ or $\dfrac{\partial\, g}{\partial z}$, and are defined as:

$$\frac{\partial\, g}{\partial x} \equiv \lim_{\Delta x \to 0} \left\{ \frac{g(x + \Delta x, y, z) - g(x, y, z)}{\Delta x} \right\}$$

$$\frac{\partial\, g}{\partial y} \equiv \lim_{\Delta y \to 0} \left\{ \frac{g(x, y + \Delta y, z) - g(x, y, z)}{\Delta y} \right\}$$

$$\frac{\partial\, g}{\partial z} \equiv \lim_{\Delta z \to 0} \left\{ \frac{g(x, y, z + \Delta z) - g(x, y, z)}{\Delta z} \right\}$$

Partial derivatives are evaluated in exactly the same way as ordinary exact derivatives, with the one additional condition that when taking a partial derivative with respect to one particular variable, all other variables are assumed to be fixed constants.

e.g., If $u(x, y, z) = x^2 - 3xyz + (y - z)^2\, e^{3x}$, evaluate $\dfrac{\partial\, u}{\partial x}$, $\dfrac{\partial\, u}{\partial y}$ and $\dfrac{\partial\, u}{\partial z}$

For higher derivatives or mixed higher derivatives, we simply repeat the procedure.

For the above example, evaluate $\dfrac{\partial^2 u}{\partial x^2}$, $\dfrac{\partial}{\partial y}\left(\dfrac{\partial\, u}{\partial x}\right)$ and $\dfrac{\partial^2 u}{\partial x\, \partial y} \equiv \dfrac{\partial}{\partial x}\left(\dfrac{\partial\, u}{\partial y}\right)$

Theorem: For any function of more than one variable, the order of differentiation in mixed higher-order derivatives does not affect the result!

Proof: Consider the mixed second derivative of a function $u = u(x, y)$:

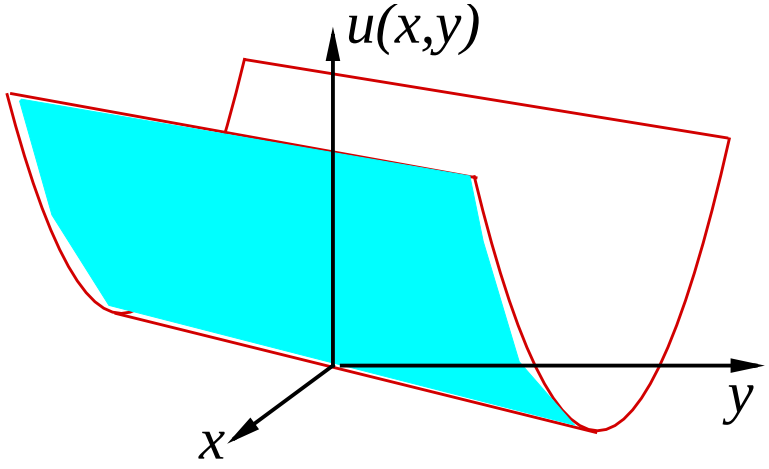
$$\frac{\partial^2 u}{\partial x\,\partial y} \equiv \frac{\partial}{\partial x}\left\{\frac{\partial u}{\partial y}\right\} = \frac{\partial}{\partial x}\left\{\lim_{\Delta y\to 0}\left(\frac{u(x,y+\Delta y)-u(x,y)}{\Delta y}\right)\right\}$$

$$= \lim_{\Delta x\to 0}\left[\lim_{\Delta y\to 0}\left\{\frac{\frac{u(x+\Delta x,y+\Delta y)\ -\ u(x+\Delta x,y)}{\Delta y}\ -\ \frac{u(x,y+\Delta y)\ -\ u(x,y)}{\Delta y}}{\Delta x}\right\}\right]$$

$$=$$

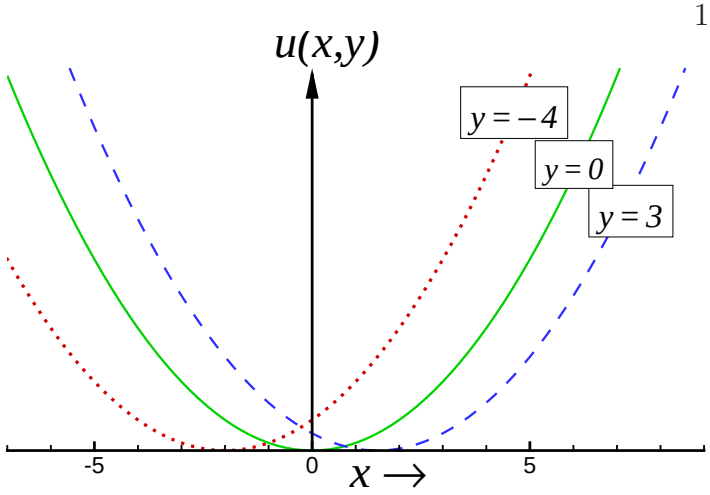
Geometric View of Partial Derivatives

Consider the function $u(x, y) = 4x^2 - 4xy + y^2$ which a 3D sketch shows to be shaped like a trough with its minimum on the line $y = 2x$ in the $x-y$ plane.



$y = 0$ and $y = 3$.

On each plane, the 2D surface $u(x, y)$ appears as a curve whose derivative w.r.t. x is defined in the usual way.



The partial derivative

$$\frac{\partial u}{\partial x} = \left.\frac{\partial u}{\partial x}\right|_y$$ is simply

the slope of that curve at the chosen x value in the chosen $y = \{constant\}$ plane.

The value of this slope at a given value of x clearly changes from one 'cut' (one value of y) to another, and the mixed second derivative

$$\frac{\partial^2 u}{\partial y\, \partial x} = \frac{\partial}{\partial y}\left(\frac{\partial u}{\partial x}\right)$$ is simply the rate of change of the slope of that x-tangent with increasing y.

Notation: *What is held constant?*

The partial derivative notation $\dfrac{\partial}{\partial x}$ tells us that all independent variables other than x are held constant. However, sometimes there is more than one way to choosing the other independent variable(s), and making an alternate choices will usually change the value of a given partial derivative.

In any case in which such ambiguity is possible, we supplement the notation $\dfrac{\partial u}{\partial x}$ by adding one (or more) subscripts which explicitly identify which other variables are held fixed, as in:

$$\left(\frac{\partial u}{\partial x}\right)_y \qquad \text{or} \qquad \left.\frac{\partial u}{\partial x}\right|_y$$

e.g., Consider the function $u(x, y) = 4x^2 - 4xy + y^2$.

Clearly $\left(\dfrac{\partial u}{\partial x}\right)_y =$ and at the point $(x, y) = (1, 1)$

it has the numerical value

Alternatively, we could introduce the new variable $w = x - y$, which may be used to replace the original variable y (since $y = x - w$). Using this new choice for the second independent variable, our (*exactly the same*) function becomes

$u(x,y) \;=\; u(x,w) \;=$

Using the new variables (x,w), the derivative $\dfrac{\partial u}{\partial x} = \left.\dfrac{\partial u}{\partial x}\right|_w =$

At the point $(x,y) = (1,1)$, clearly $(x,w) = (1,0)$, and at that point:

$\left(\dfrac{\partial u}{\partial x}\right)_y =$ while $\left(\dfrac{\partial u}{\partial x}\right)_w =$

even though we are dealing with *exactly* the same function in both cases!!

Note that by its definition, fixing $w = 0$ is equivalent to fixing $x = y$. Thus, the derivative $\left.\dfrac{\partial u}{\partial x}\right|_{w=0}$ is simply the slope of the tangent on the curve obtained if we cut through the surface

shown on the bottom of p. 12 with a plane aligned so that $y = x$.

The above example shows why, when there is any possible ambiguity, it is essential to use subscript(s) to identify the variables held fixed when taking a partial derivative.

e.g., In thermodynamics (e.g., in Chem 254) you will see that $\left(\dfrac{\partial H}{\partial T}\right)_P \neq \left(\dfrac{\partial H}{\partial T}\right)_V$

Exercise 2.2. A model for intermolecular potential energy functions proposed by Hajigeorgiou and Le Roy [*Journal of Chemical Physics* **119**, 3949 (2000)] has the form:

$$V(r) \;=\; \mathfrak{D}_e \left[1 - \left(\frac{r_e}{r}\right)^n \; e^{-\phi(r)\, y(r)}\right]^2 , \quad \text{where} \qquad \phi(r) = \sum_{k=0}^{N} \phi_k \, y(r)^k , \quad y(r) = \frac{r - r_e}{r + r_e}$$

$\mathfrak{D}_e$ is the potential energy well depth and r_e the equilibrium distance (bond length). In order to use a fit to experimental data to determine the values of the parameters ($\mathfrak{D}_e$, r_e and the ϕ_i coefficients) defining this potential energy function, it is necessary to have explicit expressions for the partial derivatives: $\partial V(r)/\partial \mathfrak{D}_e$, $\partial V(r)/\partial r_e$ and $\partial V(r)/\partial \phi_3$, Determine those expressions.

2.4 Total Differentials

The total differential of a function $u(x_1, x_2, x_3, ...)$ is the small change in that function caused by small changes dx_1, dx_2, dx_3, ... etc., in all of its independent variables

***Theorem*:** For a function $u(x_1, x_2, x_3, ...)$, the total differential is

$$du \;=\; \frac{\partial u}{\partial x_1}\, dx_1 + \frac{\partial u}{\partial x_2}\, dx_2 + \frac{\partial u}{\partial x_3}\, dx_3 + ...$$

Proof: for the simple case $u = u(x_1, x_2)$. For this case

$$du \;\equiv\; u(x_1 + dx_1,\, x_2 + dx_2) \;-\; u(x_x,\, x_2)$$

e.g., Recall the ideal gas law: $P = nRT/V$. Use the definition of the total differential to determine an expression for the effect on the pressure of small changes in the temperature, volume and amount (no. moles) of the gas.

$dP \;=$

Application of the definition of the total differential allows us to account for all sorts of changes of variables, and to determine expressions for partial derivatives involving otherwise not-obvious combinations of parameters.

e.g., If $u = u(x_1, x_2, x_3, ...)$, and each of those variables x_j depends on two other underlying variables, $x_j = x_j(s, t)$, what is the partial derivative $\left(\dfrac{\partial u}{\partial s}\right)_t$?

Ans. Begin as above: $du \;=\; \dfrac{\partial u}{\partial x_1}\quad dx_1 \quad + \quad \dfrac{\partial u}{\partial x_2}\quad dx_2 \quad + \quad \dfrac{\partial u}{\partial x_3}\quad dx_3 \quad +$

To get the desired derivative, simply divide both sides by ds while holding constant the other underlying parameter, t:

A problem in thermodynamics

For a fixed amount of matter in some state, the thermodynamic internal energy $U = U(V,T)$ is usually defined as being a function of temperature (T) and volume (V). This means, in effect, that we know the two partial derivatives: $\left(\frac{\partial U}{\partial V}\right)_T$ and $\left(\frac{\partial U}{\partial T}\right)_V$.

For the same system, the equation of state tells us how the volume is affected by the temperature

and pressure, $V = V(P,T)$; this means, in effect, that we know $\left(\frac{\partial V}{\partial P}\right)_T$ and $\left(\frac{\partial V}{\partial T}\right.$

[*Note* that this does not require that we can explicitly write out $V = V(n,T,P)$, as in the case of the Van der Waals equation of state: $\left(P + a\,\frac{n^2}{V^2}\right)(V - n\,b) = n\,RT$]

However, it is usually much more convenient in the laboratory to have P and T as the independent variables. Thus, we would like to be able to determine how small changes in P and T affect the value of U; in other words, we want to know $\left(\frac{\partial U}{\partial P}\right)_T$ and $\left(\frac{\partial U}{\partial T}\right)_P$.

Answer We can get our result in two ways.

(i) Write out the total differential of $U = U(V,T)$, and then in turn divide by dP at constant T, and by dT while holding P constant.

(ii) Alternatively ... treat it simply as a chain rule problem.

However, how would we determine expressions for $(\partial V/\partial P)_{n,T}$ and $(\partial V/\partial T)_{n,P}$ for the Van der Waals equation of state: $\left(P + a\,\frac{n^2}{V^2}\right)(V - n\,b) = n\,RT$?

Derivative of an Implicit Function

An *implicit function* is one in which the variables are related in a way which does not permit one to write one explicitly in terms of the other(s). For example, if $y = y(x)$ is defined by the equation: $x \sin(y) = y \cos(x)$, although we cannot solve to determine an explicit expression for $y = y(x)$, we still want to be able to determine $\dfrac{d\,y}{dx}$.

Consider the more general case of a set of variables x, y, z and w which are inter-related through some general equation which we choose to write as: $F = F(x, y, z, w) = 0$. In this case there clearly exist four *implicit* functions $x = f(y, z, w)$, $y = g(x, z, w)$, and $z = h(x, y, w)$, $w = u(x, y, z)$, and we would like to be able to determine derivatives such as:

$$\left(\frac{\partial\, x}{\partial y}\right)_{z,w}, \qquad \left(\frac{\partial\, x}{\partial z}\right)_{y,w}, \qquad \left(\frac{\partial\, y}{\partial x}\right)_{z,w}, \qquad \ldots \qquad \text{etc.}$$

To do so, begin by first writing down the total differential of $F(x, y, z, w)$, which will necessarily be equal to zero, since $F = \{constant\}$.

$$dF = \left(\frac{\partial\, F}{\partial x}\right)_{y,z,w} dx + \left(\frac{\partial\, F}{\partial y}\right)_{x,z,w} dy + \left(\frac{\partial\, F}{\partial z}\right)_{x,y,w} dz + \left(\frac{\partial\, F}{\partial w}\right)_{x,y,z} dw = 0$$

To get a particular derivative, we now simply divide both sides by the increment of the variable we want in the denominator and force all other variables to be constant (which makes their increments zero!).

e.g., to get an expression for $\left(\dfrac{\partial x}{\partial y}\right)_{z,w}$, divide both sides by dy holding y and z constant.

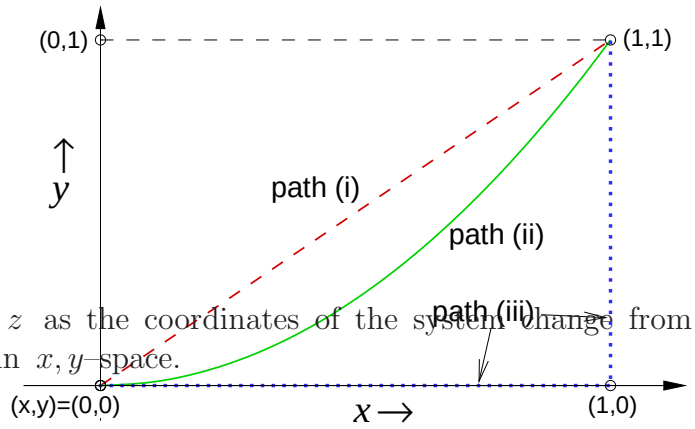
Exercise 2.3. If $F(x,y) = x\,\sin(y) - y\,\cos(x) = 0$, what is $\dfrac{d\,y}{dx}$?

Exercise 2.4. In Year-1 General Chemistry we discussed the Van der Waals equation of state which is sometimes used for non-ideal gases: $\left(P + a\,\dfrac{n^2}{V^2}\right)(V - nb) = nRT$. Although we cannot explicitly solve for $V = V(n,P,T)$, in describing the thermodynamics of non-ideal gases we still need to know its partial derivatives (e.g., see Notes p. 9).

Determine expressions for the derivatives $\left(\dfrac{\partial\,V}{\partial P}\right)_{n,T}$ and $\left(\dfrac{\partial\,V}{\partial T}\right)_{n,P}$

2.5 Exact and Inexact Differentials

In thermochemistry we often wish to calculate the change in a given quantity caused by particular changes in a given system; e.g., how much work W must be done to compress a given amount of gas while keeping the temperature constant? Such changes are special examples of line integrals, integrating the incremental changes of the quantity of interest dW along the specified path between the initial and final conditions: $\Delta W = \int_{P_1,V_1,T}^{P_2,V_2,T} dW$.



Consider an algebraic example of such a line integral for the overall change in the quantity z, where

$$dz = (xy^2 + 3y)\,dx + (2x^2\,y - 5x^4)\,dy$$

In particular case, what is the overall change in z as the coordinates of the system change from $(x, y) = (0, 0)$ to $(1, 1)$ along three different paths in x, y–space.

Path (i): $y = x$

Path (ii): $y = x^2$

Path (iii): **(a)** $y = 0$ **for** $x = 0$ **to 1** **and then** **(b)** $x = 1$ **for** $y = 0$ **to 1**

Clearly, the net change in z *depends on the particular path* between the fixed initial and final points.

If the quantity z (or the incremental changes dz) represented some property of a physical or chemical system, and the variables x and y were variables such as its temperature T and pressure P, such a property would not be useful for characterizing the state of the system. Rather, we would prefer to use properties whose values depend only on the actual conditions (coordinates) the system finds itself in, and *not* on its history (i.e., not on the path it took to get there).

Definition: For any given differential

$$dz = f_1(x_1, x_2, x_3, ..., x_n)\, dx_1 + f_2(x_1, x_2, ..., x_n)\, dx_2 \ ... \ + f_n(x_1, x_2, ..., x_n)\, dx_n$$

if changes in z *do not* depend on the path between initial and final points in $\{x_1, x_2, x_3, ...x_n\}$–space, then the quantity dz is an ***exact differential***, and there must exist some function $u = u(x_1, x_2, x_3, ...x_n)$ of which dz is the *total differential*, and $\dfrac{\partial\, u}{\partial x_1} = f_1(x_1, x_2, ..., x_n)$, $\dfrac{\partial\, u}{\partial x_2} = f_2(x_1, x_2, ..., x_n)$, $\dfrac{\partial\, u}{\partial x_3} = f_3(x_1, x_2, ..., x_n)$, etc.

Exercise 2.5. Test whether the differential $dz = (2xy^2 + 2y)\, dx + (2x^2\, y - 5x^4)\, dy$ is exact by determining the net changes Δz alone the same three paths from $(x, y) = (0, 0)$ to $(1, 1)$ considered above.

Euler's Criterion for the Exactness of a Differential

Given our definition of an *exact differential*, if $dz = f_1\,dx_1 + f_2\,dx_2 + f_3\,dx_3 + ...$ is exact, there must exist some function $u = u(x_1, x_2, x_3, ...)$ such that

$$\frac{\partial\, u}{\partial x_1} = f_1 \quad \text{and} \quad \frac{\partial\, u}{\partial x_2} = f_2 \quad \text{and} \quad \frac{\partial\, u}{\partial x_3} = f_3 \quad \text{and} \quad \frac{\partial\, u}{\partial x_4} = f_4 \quad ... \text{ etc.}$$

However, since the values of higher-order mixed second derivatives are *not dependent* on the order of differentiation, necessarily

$$\frac{\partial\, f_1}{\partial x_2} \;=$$

or more generally:

If this condition is satisfied for *all* possible pairs of independent variables appearing in the given differential, then it must be ***exact***, and the associated **"*function of state*"** u exists, and may (in principle) be determined!

[*Apply this test* to the two differentials considered on pp. 12 & 13.]

Summary: A given differential $dz = dz(x_1, x_2, x_3, \dots)$ is "*exact*", if and only if there exists some function $u = u(x_1, x_2, x_3, \dots)$ of which it is the *total differential*.

How do we determine the function $u(x_1, x_2, x_3, ...)$ associated with a given exact differential? It's quite straightforward, really!

- First, integrating f_1 with respect to x_1 (treating x_2, x_3, x_4 ... as constants!) yields

$$u_1 \;=\; \int f_1\, dx_1 \;=\; \int \frac{\partial\, u}{\partial x_1}\, dx_1 \;=$$

- Similarly, integrating f_2 with respect to x_2 (treating x_1, x_3, x_4 ... as constants!) yields

$$u_2 \;=\; \int f_2\, dx_2 \;=\; \int \frac{\partial\, u}{\partial x_2}\, dx_2 \;=$$

- Similarly, integrating f_3 with respect to x_3 (treating x_1, x_2, x_4 ... as constants!) yields

$$u_3 \;=\; \int f_3\, dx_3 \;=\; \int \frac{\partial\, u}{\partial x_3}\, dx_3 \;=$$

The total desired function $u = u(x_1, x_2, x_3, ...)$ is then readily determined as

$$\begin{aligned} u \;=\; u_1 \;&+\; \{\text{all terms in } u_2 \text{ which are independentof } x_1\,\} \\ &+\; \{\text{all terms in } u_3 \text{ which are independentof } x_1 \text{ and } x_2\,\} \\ &+\; \{\text{all terms in } u_4 \text{ which are independentof } x_1,\, x_2 \text{ and } x_3\,\} \\ &+\; \ldots \text{ etc.} \end{aligned}$$

or, $u = \{$ sum of all distinct (different) terms appearing in u_1, $u_{,2}$ u_3, ... etc. $\}$

Note that in this last version of the method, the words *distinct* or *different* are essential, since (for example) a contribution to u which depends on both x_1 and x_2 would appear in both u_1 and u_2, and we would not want to count it twice.

Apply this technitue to the example from Exercise 2.5 (p. 13).

Exercise 2.6 Consider the differential: $dz \;=\; (2xy^2 + y)\,dx \;+\; (x - y - 1)\,dy \;=\; f_x\,dx + f_y\,dy$

Is this differential is exact, and if so, what function it is the differential of?

Exercise 2.7 Consider: $dz \;=\; (2x + 3y)\,dx \;+\; (3x - 4y)\,dy \;=\; f_x\,dx \;+\; f_y\,dy$

Is this differential is exact, and if so, what function it is the differential of?

Exercise 2.8 We wish to solve the differential equation

$$\left(x^2 + 4xy + 4y^2\right) + \left(2y^2 + 8xy + 2x^2\right)\frac{d\,y}{dx} \;=\; 0$$

Multiplying through by dx clearly this equation to the form

$$\left(x^2 + 4xy + 4y^2\right)\,dx + \left(2y^2 + 8xy + 2x^2\right)\,dy \;=\; 0$$

Testing for exactness of the differential:

Exercise 2.9 Consider the differential $du = \left(3x - \dfrac{2x}{y}\right)\,dx + \left(\dfrac{x^2 - 2y}{y^2}\right)\,dy$.

(a) Is it exact ? (b) If so, what function is it the differential of ?

Integrating Factors

Sometimes an *inexact* differential may be made *exact* by multiplying it by an appropriate factor. If such a factor exists, it is called an ***integrating factor***.

e.g., Consider the differential $dz = xy^2\,dx + 2x^2\,y\,dy$ discussed on pp. 12 which was found to be *in*exact, since its integral depended on the path. It also fails the Euler criterion test.

Assume that there exists some function $g(x,y)$, such that the differential $dw = g(x,y)\,dz$ *is* exact.

Let us try to use the Euler criterion requirement to determine the function $g(x,y)$.

Since our original differential dz involves a sum of products of powers of x and y, let us assume that $g(x,y)$ has the form $g(x,y) = x^m\,y^n$ for some constants m and n. The resulting differential is then

$$dw \;=\; g(x,y)\,dz \;=\; \{g(x,y)\,xy^2\}dx + \{g(x,y)\,2x^2\,y\}dy \;=\; f_x\,dx + f_y\,dy$$

Applying the Euler criterion:

Note that In general, there exist an *infinite number* of integrating factors which can make a given *in*exact differential exact, and they often do not have the simple power form used in the above examples. However, in the context of real physical problems, usually only one of that infinite array of possible integrating factors defines a physically interesting and useful quantity.

Exercise 2.10 In thermochemistry, the change in the "heat content" of a system, the amount of heat energy which flows in/or out during some process, is denoted by the symbol q. In general, the change in total internal energy of a system during some process obeys the First Law of thermodynamics $\Delta U = q + w$. where w is the work done on (i.e., the amount of work energy put into) the the system during that process.

For one mole of an ideal gas (defined by $PV = RT$) undergoing some infinitesimal change, one can show that

$$dq \;=\; C_V\, dT \;+\; P\, dV$$

where $C_V = \frac{3}{2}\, R$ is a constant, and R is the familiar gas constant.

a) Verify that dq is not an exact differential.

b) Determine a general integrating factor for this case.

c) Give explicit expressions for: $\left(\frac{\partial\, q}{\partial T}\right)_V$, $\left(\frac{\partial\, q}{\partial V}\right)_T$, $\left(\frac{\partial\, q}{\partial T}\right)_P$, $\left(\frac{\partial\, q}{\partial V}\right)_P$, $\left(\frac{\partial\, q}{\partial P}\right)_V$.

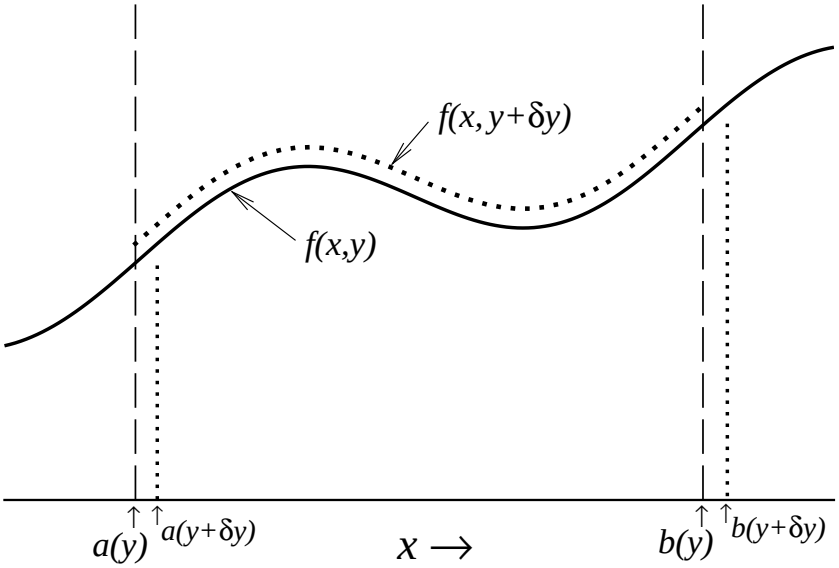
Note that the quantity $\dfrac{dq}{T} \equiv dS$, where the property S is called the *entropy*, is a quantitative measure of the degree of "molecular disorder" of the system. While the heat content itself q is not a "function of state", the entropy S is.

2.6 Derivative of an Integral (Leibnitz's Rule)

The value of a definite integral $I(y) = I(a, b; y) = \int_{a(y)}^{b(y)} f(x, y)\, dx$ depends in three things:

(i) the nature of the integrand $f(x, y)$ on the interval between the bounds $a(y)$ and $b(y)$

(ii) & (iii) the values of the two bounds $a(y)$ and $b(y)$.



The value of the integral depends only on y , but it is important to realize that part of this dependence is due to a dependence on the bounds $a(y)$ and $b(y)$.

By the chain rule: $\dfrac{d\,I}{dy} = \dfrac{\partial\, I}{\partial y} + \dfrac{\partial\, I}{\partial a}\,\dfrac{d\,a}{dy} + \dfrac{\partial\, I}{\partial b}\,\dfrac{d\,b}{dy}$, and clearly $\dfrac{\partial\, I}{\partial b} = f(b)$ & $\dfrac{\partial\, I}{\partial a} = -f(a)$.

Thus, the general expression for the derivative of an integral $I(y) = \int_a^b f(f, y)\, dy$ is

$$\frac{d\,I(y)}{dy} = \int_a^b \left(\frac{\partial\, f}{\partial y}\right) dx - f(a, y)\,\frac{d\,a}{dy} + f(b, y)\,\frac{d\,b}{dy} \tag{1}$$

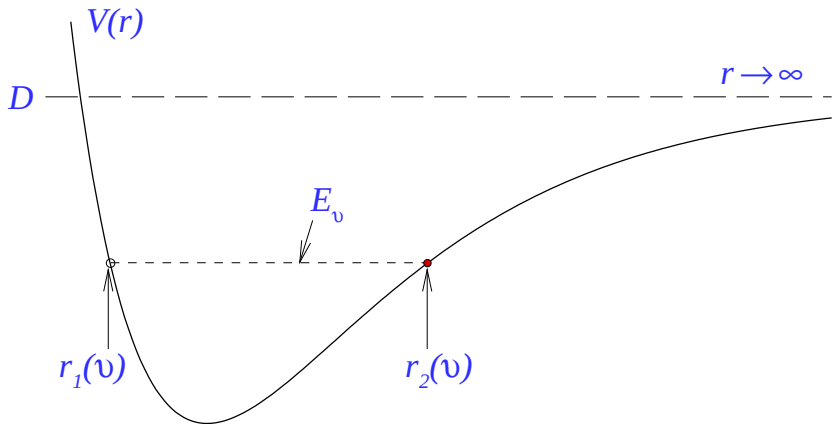
This is known as ***Leibnitz's rule***.

---

e.g., Find $\dfrac{d\,I(y)}{dy}$ for $I(y) = \int_{2y}^{4y} (x\, e^y + y\, e^x)\, dx$

Near-Dissociation Theory [a special topic; not on the exam]

Leibnitz's rule is central to the derivation of very important and widely used expressions for the the limiting near-dissociation behaviour of the vibrational level energies, rotational constants and other properties of diatomic molecules. This theory starts from a "semiclassical quantization condition" expression which defines the allowed energies E_v of the vibrational levels v of a molecular formed from atoms A and B with masses m_A and m_B, respectively, which are held together by a potential energy function $V(r)$.



where $r_1(v)$ and $r_2(v)$ are the classical "turning points", the distances at which the total energy of the system equals its potential energy $V(r_i) = E_v$.

According to the semiclassical quantization condition equation,

$$v + \tfrac{1}{2} \;=\; \frac{1}{\pi}\sqrt{\frac{2\mu}{\hbar^2}}\int_{r_1(v)}^{r_2(v)} [E_v - V(r)]^{1/2}\, dr \tag{2}$$

the allowed energy levels are the discrete energies E_v for which the right hand side of this equation [where $\mu = m_A\, m_B/(m_A + m_B)$] has *exactly* half-integer values: 1/2, 3/2, 5/2, 7/2, ... $(v + \frac{1}{2})$. This integral itself turns out to be difficult to use. However, its derivative with respect to E_v is much more useful!

In the above equation, the integer v is the vibrational quantum number, and it has the values 0, 1, 2, 3, 4, ... etc., for the allowed vibrational levels. It can also be thought of as a counter, showing how the number of vibrational levels increases with energy. Since we are interested in the *pattern* of vibrational energies, it is appropriate to consider the "density of states" at a given energy $d(v + \frac{1}{2})/dE_v$, which may also be thought of as the rate at which the number of vibrational levels increases with increasing energy.

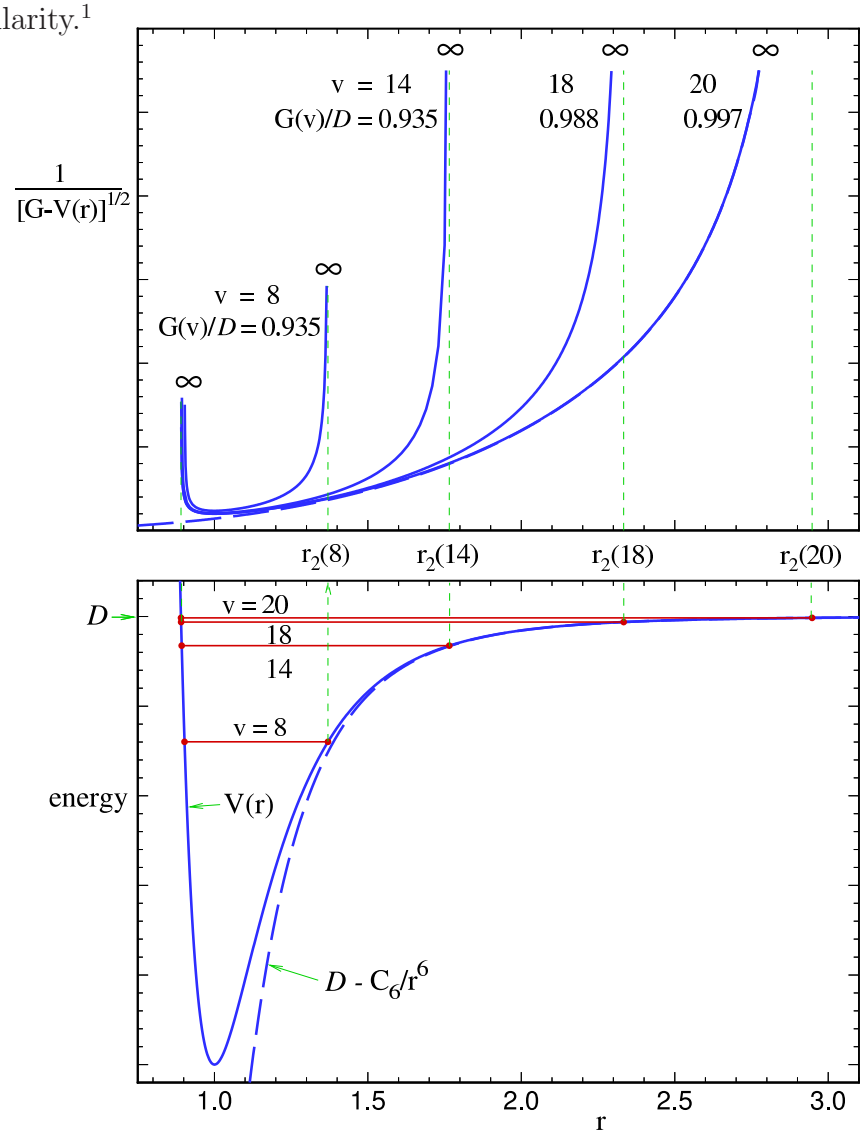
If we apply Leibnitz's rule in taking the derivative of the above integral, it turns out that only the term involving the 'integral of the derivative' remain, since by the *definition* of the classical turning points, the integrand itself it precisely zero at both the upper and lower bounds of integration:

$$\frac{dv}{dE_v} \;=\; \frac{1}{2\pi}\sqrt{\frac{2\mu}{\hbar^2}}\int_{r_1(v)}^{r_2(v)} \frac{dr}{[E_v - V(r)]^{1/2}} \tag{3}$$

Before we carry on with the derivation, it is necessary to first examine the nature of the integrand in this second integral. Consider the case of an analytic potential energy function form known as Lennard-Jones(12,6) potential,

$$V(r) \;=\; \mathfrak{D}_e\left[\left(\frac{r_e}{r}\right)^6 - 1\right]^2 \;=\; \mathfrak{D}_e\left[\left(\frac{r_e}{r}\right)^{12} - 2\left(\frac{r_e}{r}\right)^6 + 1\right] \;\rightarrow\; \{at\ very\ large\ r\} \;\simeq\; \mathfrak{D}_e - \frac{C_6}{r^6}$$

where $C_6 = 2\mathfrak{D}_e(r_e)^6$. The lower segment of the following figure shows this potential and a few of its allowed vibrational level energies, and the upper segment shows the nature of the integrand of this second equation for those levels. Note that while the integrand goes to infinity at the inner and outer turning points for each level, the area under the integrand is finite, because it is a simple square root singularity.[1]



It is immediately clear that the actuals *value* of these integrals, the areas under the curves in the upper segment of this figure, depend mainly on the shape of the integrand (i.e., of the potential function) in the neighbourhood of the outer turning points! The theory of intermolecular forces also tells us that at large distances all intermolecular potentials takes on the limiting analytic form $V(r) \simeq \mathfrak{D} - \dfrac{C_n}{r^n}$, where n is a known integer ($n = 6$ for many common cases). If we replace the full $V(r)$ function in the above integral by this simple single inverse-power term, apply a simple approximation and do a little manipulation, we obtain the limiting ***near-dissociation theory*** expression for the distribution of vibrational levels near the dissociation limit of a molecule:

$$E_v \;=\; \mathfrak{D} - X_0\,(v_{\mathfrak{D}} - v)^{2n/(n-2)} \tag{4}$$

where $X_0 = X_0(n, C_n, \mu)$ is a known numerical constant defined by the values of n, C_n and the molecule's "reduced mass" μ.

[1] And we know that $\displaystyle\int_0^a \frac{1}{\sqrt{x}}\,dx = 2\left[x^{1/2}\right]_0^a = 2\,a^{1/2}$ is finite.

Exercises

1. Determine an expression $\dfrac{d\,u}{dt}$ for each of the following cases, expressing your answer as much as possible in terms of the original variables $\{x, y, z\}$.
   [*Do not solve by simply substituting in*!]
   (a) $u = x^2 + 2xy + y^2$, where $x = (t+2)^2$ and $y = (2t-1)^2$.
   (b) $t^3 - 3t^2\,u^2 - 6t\,u^3 + 3tu + 1 = 0$.
   (c) $u = x\,\sin(y) + y\,\sin(x) + z\,cos(x+y)$ where $x = t^2$, $y = e^{2t}$ and $z = 1/t$

2. Evaluate the integrals: (i) $\int e^{2x}\sin(3x)\,dx$ (ii) $\int \sin(3x)\,\sin(2x)\,dx$

3. For each of the following cases, determine an expression for $\dfrac{\partial\,z}{\partial x}$ and $\dfrac{\partial\,z}{\partial y}$, expressing your answer as much as possible in terms of the initial variables.
   (a) $xy^2 - 2yz^2 + 3z^3 = 4 - x^3$.
   (b) $y = x\,e^z + z\,e^x$.
   (c) $z = u\,e^v + v\,e^u$ where $u = x\,\ln(y)$ and $v = x\,\ln(x)$.

4. For each of the following expression: (i) show whether or not it is an exact differential, and (ii) if it is, determine what function it is the differential of.
   (a) $dw = -\left(\dfrac{T}{P^2}\right)dP + \left(\dfrac{1}{P}\right)dT$.
   (b) $dw = \left(y\,e^{xy} + 3x^2\right)dx + \left(z^2 + x\,e^{xy}\right)dy + (yz+2)\,dz$.
   (c) $dw = (x^2 + 4xy + 4y^2)\,dx + (2y^2 + 8xy + 2x^2)\,dy$.
   (d) $dw = \left(3x - \dfrac{2x}{y}\right)dx + \left(\dfrac{x^2 - 2y}{y^2}\right)dy$.
   (e) $dw = z(xy - yz + 1)\,dx + (y\,z^2 - x\,z^2 - y)\,dy + [x + z(y-x)^2]^2 dz$.

5. Evaluate the following derivatives (performing all of the associated integration!).
   (a) $\dfrac{d}{d\theta}\displaystyle\int_{\sin\theta}^{\cos\theta} \ln(x+\theta)\,dx$.
   (b) $\dfrac{d}{du}\displaystyle\int_{0}^{\pi/2u} u\,\sin(ux)\,dx$.

6. For a rotating diatomic molecule with rotational quantum number J, the quantization condition of Eq. (2) remains valid, but the effective potential energy function now must include a centrifugal term, so $V(r)$ is replaced by $V_J(r) = V_0(r) + \left(\dfrac{\hbar^2}{2\,\mu\,r^2}\right)[J(J+1)]$. By the definition of the turning points $r_i(E)$ (as distances where the overall potential energy equals the total energy E) this means that they will also depend on J: $r_i(v) \to r_i(v, J)$. The resulting quantization condition equation makes the level energy E and implicit function of both v and J.

   In spectroscopy (e.g., Chem 209), the inertial rotational constant for a molecule is defined by the expression: $B_v = \left.\dfrac{\partial\,E_v(J)}{\partial[J(J+1)]}\right|_{v,J=0}$. Use this definition to determine an expression for B_v in terms of integrals over the potential (such as those of Eqs. (2) & (3)).

7. We saw in class that taking the derivative of Eq. (2) [on p. 20] w.r.t. energy gave us Eq. (3), and we saw in question #5 that the inertial rotation constant of a molecule, B_v, may be defined in terms of a ratio of integrals of this type.

   The leading "centrifugal distortion" rotational constant is defined as

$$D_v \;=\; \left.\frac{\partial^2 E_v}{\partial^2[J(J+1)]}\right|_{v,J=0} \;=\; \left.\frac{\partial\, B_v(J)}{\partial[J(J+1)]}\right|_{v,J=0}$$

   Determine an expression for D_v in terms of "phase integrals" such at those appearing above. Be sure the integrals you obtain *do not* have non-integral singularities at the end points!

   [Hint ... do you remember integration by parts?]

3. Differential Equations

A *differential equation* is simply any equation involving one or more derivatives or differentials, and solving a differential equation means that we want to determine the function involved in the differentiation. To begin, we must introduce and understand some of the related terminology.

3.1 Definitions and Terminology

An *ordinary* differential equation is one involving only one independent variable.

A *partial* differential equation is one involving more than one independent variable, so that all the derivatives are partial derivatives.

order of a differential equation is the order of the highest derivative (mixed of pure) appearing in it.

degree of a differential equation is the power with respect to the dependent variable and/or its derivatives, of the highest-power term in the equation.

A *linear* differential equation is one which is linear in the *dependent variable*and/or its derivatives (i.e., in $y(x)$ and any of its derivatives). This means that, e.g., if $y(x)$ is replaced everywhere by $2\,y(x)$, no term in the equation would change my more than a factor of 2.

A *homogeneous* differential equation is one in which every term contains one or more of $y(x)$ (the dependent variable) itself or one of its derivatives. If we set $y(x)=0$ in a homogeneous differential equation *all* terms disappear. If one or more terms in the equation do not depend at all on $y(x)$ or its derivatives, the equation is called ***inhomogeneous***.

The *solution* of a differential equation is any function which, when substituted for the dependent variable, satisfied the equation.

Exercise 3.1. Characterize each differential equation (below) with regard to the above criteria.

equation	order	degree	type
$\dfrac{d^2y}{dx^2} + 7\,x\,y = 0$			
$(x+y)\,dx + x^2\,y^2\,dy = 0$			
$\left(x + \dfrac{d\,y}{dx}\right)^7 + \left(\dfrac{d^3y}{dx^3}\right)^2 + y(x) = 0$			
$\dfrac{d^3y}{dx^3} = 0$			
$\dfrac{d\,y}{dx} + 7y = 4x^2$			
$\dfrac{d^2y}{dx^2} + x\left(y\,\dfrac{d\,y}{dx}\right)^2 = y$			
$\left(y\,\dfrac{\partial\,f}{\partial x} + x\,\dfrac{\partial\,f}{\partial y}\right)^3 + \left(2\,x\,y\,\dfrac{\partial^2 f}{\partial x\,\partial y}\right)^2 = 0$			

In practice, most of the differential equations encountered in physics and quantum chemistry are ***linear*** and ***homogeneous***, and most are also ***second order***, so we don't have to deal with too many types. However, since the real world is three-dimensional, and most physical systems consist of more than one particle, we often have to deal with ***partial*** and not ***ordinary*** differential equations. On the other hand, the *partial* differential equations which we *can* solve can usually be treated by breaking them up into multiple *ordinary* differential equations involving only one *in*dependent variable at a time.

Linear Dependence

A given set of functions $\{y_k(x)\}$ for $k = 1,\ 2,\ 3,\ ...\ N$ is said to be ***linearly dependent*** if there exists some set of numerical coefficients $\{c_k\}$ such that

$$\sum_{k=1}^{N} c_k\, y_k(x) \;=\; c_1\, y_1(x) + c_2\, y_2(x) + c_3\, y_3(x) + ... + c_N\, y_N(x) \;=\; 0 \qquad (5)$$

where at least two or more of the numerical coefficients c_k are non-zero. In other words, the set is *linearly dependent* if at least *one* of these functions may be expressed in terms of some of the others. e.g., any two functions y_1 and y_2 are *linearly dependent* iff $y_1 = A\, y_2$ where A is a non-zero numerical constant.[2]

Otherwise [if the only possible solution to Eq. (5) is $c_1 = c_2 = c_3 = ... = c_N = 0$], that set of functions is said to be ***linearly <u>in</u>dependent***.

Theorem (a): For any linear homogeneous differential equation of order n, there exist n linearly independent solutions.

(b): Any linear combination of those n solutions is also a valid solution of the given differential equation. This also means that if $y_1(x)$ is a solution, then so is $k\, y_1(x)$, where k is *any* numerical constant.

***Proof of (a)*:** We will merely illustrate the result. Consider the two differential equations $\dfrac{d^2y}{dx^2} = 0$ and $\dfrac{d^5y}{dx^5} = 0$. Integrate these equations and enumerate the various results.

[2] Mathematical notation: *iff* or "iff" means "if and only if".

Proof of (b): In general, *any* linear, homogeneous differential equation of order N may be written in the form

$$\sum_{n=0}^{N} c_n(x)\,\frac{d^n y(x)}{dx^n} \;=\; c_0(x)\,y(x) \;+\; c_1(x)\,\frac{dy(x)}{dx} \;+\; c_2(x)\,\frac{d^2 y(x)}{dx^2} \;+\; \ldots \;+\; c_N(x)\,\frac{d^N y(x)}{dx^N} \;=\; 0$$

where $c_n(x)$ are some functions of x, and $\dfrac{d^0 y(x)}{dx^0} \equiv y(x)$
{i.e., the function obtained on taking *no* derivatives w.r.t. x is the original function $y(x)$ itself.}

If $y_1(x)$ and $y_2(x)$ are solutions of this d.e., then *any* linear combination of them $y_3(x) = a\,y_1(x) + b\,y_2(x)$ will also be a solution of that same differential equation.

Exercise 3.2. Consider the linear, *in*homogeneous differential equation

$$\sum_{n=0}^{N} c_n(x)\,\frac{d^n y}{dx^n} = Q(x) \qquad \text{where} \qquad Q(x) \neq 0$$

Show that if $y_1(x)$ and $y_2(x)$ are solutions of this differential equation, their sum $y_3(x) = y_1(x) + y_2(x)$ ***is not*** a valid solution.

3.2 Simple Methods of Solving Some Simple Differential Equation

A. Solution by Integration

This approach is feasible for a few simple types of differential equations (e.g., see pp. 2-3).

Linear, Homogeneous First-Order Differential Equations

Consider the differential equation: $\dfrac{dy\,(x)}{dx} = y(x)\,[1 + 3x]$

Linear, Inhomogeneous Differential Equations Involving a Single Derivative

Consider the differential equation: $\dfrac{d^3\,y}{dx^3} = 3 + 5x - 7x^2$

To solve, simply integrate both sides w.r.t. x ... three times.

Note that in each step of a multiple integration of this sort, one must introduce an arbitrary integration constant. This yields the most general form of solution. However, the function obtained if we ignore the terms associated with these integration constants is also a solution, which is known as the ***particular solution*** of this inhomogeneous equation. For the above example it is:

The contributions to the *general solution* associated with these integration constants are known as ***complementary solutions*** of the original (inhomogeneous) differential equation. They are, in fact, the solutions of the *homogeneous* differential equation obtained if we ignore the *in*homogeneous part of the original equation.

For our example (above), the corresponding *homo*geneous differential equation is $\dfrac{d^3y}{dx^3} = 0$, which has the *linearly independent* solutions

$y(x)$ =

In summary ... the solution of *any* inhomogeneous differential equation of order N will consist of two parts: a *particular* solution, which is unique and has no arbitrary constants, and N *complementary* solutions, which are the linearly independent solutions of the corresponding homogeneous equation. The most general solution consists of the particular solution plus an *arbitrary* linear combination of the N complementary solutions.

B. The Auxiliary Equation Method

Linear, Homogeneous Differential Equations with Constant Coefficients

The auxiliary equation method is applicable to *linear, homogeneous* differential equations *with constant coefficients*. It is based on the fact that equations of this type have solutions which are exponential in nature. The procedure consists of simply *assuming* that the solution has the form $y(x) = e^{a\,x}$, where a is some constant, substituting this expression into the original equation, and solving the resulting equation (the *auxiliary* equation) for the value(s) of a .

e.g., consider the differential equation $\dfrac{d^2y}{dx^2} + A\,\dfrac{d\,y}{dx} + B\,y \;=\; 0$. If we assume $y(x) = e^{a\,x}$ and substitute it in, we obtain:

Exercise 3.3. Determine the solutions of the following equations.

(i) $\dfrac{d^2y}{dx^2} + 7\,\dfrac{d\,y}{dx} = 0$

(ii) $\dfrac{d^2y}{dx^2} + k^2\,y(x) = 0$

(iii) $\dfrac{d^2y}{dx^2} + 2\,\dfrac{d\,y}{dx} + 3\,y(x) = 0$

(iv) $\dfrac{d^2y}{dx^2} - k^2\,y(x) = 0$

Linear, Inhomogeneous, Differential Equations with a Polynomial Inhomogeneity

Exercise 3.4. Consider the following inhomogeneous differential equation:

$$2\,\frac{d^2y}{dx^2} \;+\; 3\,\frac{dy}{dx} - 2\,y \;=\; 8x + 3 \tag{6}$$

(a) It is easy to show that the *particular* solution of this differential equation must be a polynomial of order ≤ 2: $\quad y_p(x) = a + b\,x + c\,x^2$. *Determine* this solution by substituting this expression for $y_p(x)$ into the above equation and solving for a, b and c.

(b) By combining the above "particular solution" with the solution of the associated *homo*geneous differential equation, determine the *general* solution to Eq. (6).

3.3 Boundary Conditions and Eigenvalues

We have seen that for any *linear, homogeneous, n'th order* differential equation, there exist n linearly independent solutions. Hence, The general solution of that equation will contain n arbitrary constants. Similarly the general solution for and *linear, inhomogeneous, n'th order* differential equation will consist of the "particular solution" plus an arbitrary linear combination of the n complementary solutions of the corresponding *homo*geneous equation. Thus, the general solution of *any* linear, n'th order differential equation will contain n arbitrary constants.

Boundary conditions are restrictions applied to such general solutions which define the value(s) of those n constants appropriate for a particular case. Their particular form will usually be determined from the physical nature of the problem under consideration.

e.g. Consider the differential equation of Eq. (ii) in Exercise 3.3: $\dfrac{d^2y}{dx^2} + k^2\,y = 0$, where k is a real number. This equation describes the instantaneous displacement y of a vibrating string as a function of the distance x along its length. We saw above that its general solution is: $y(x) = b_1\,\cos(kx) + b_2\,\sin(kx)$.

(i) Consider a physical situation in which we know the value of the displacement $y(x)$ and the slope of the string $dy(x)/dx$ at some particular point along the string, say at $x = 0$.
e.g., assume we know that $y(x=0) = 3.0$ and $y'(x=0) = 2.0$. Applying these conditions to the general solution yields:

(ii) A second type of boundary condition for this system would correspond to having the string clamped (meaning that $y(x) = 0$) at two points, say at $x = 0$ and at $x = L$. Applying these conditions to the general solution then yields:

A differential equation problem for which application of boundary conditions gives rise to restrictions on one of the constants in the equation is called an ***eigenvalue problem***. The discrete allowed values of that constant (here parameter k) are called the ***eigenvalues*** of that differential equation, and the associated solutions [here $y = b\,\sin(n\pi v/L)$] are its ***eigenfunctions***.

In an eigenvalue problem, the boundary conditions are as important as the differential equation itself!

3.4 Method of Solution by Series

This method is applicable to linear, homogeneous differential equations whose coefficients are either constants, or functions of the independent variables. As the Schrödinger equation is a linear, homogeneous second-order differential equation, this approach will clearly be quite useful in quantum mechanics! We begin by considering the "ordinary" case of functions of a single independent variable.

The basic approach used is analogous to that of the *auxiliary equation method* of §3.2 B in that:

(i) The solution is assumed to have a particular functional form which involves unknown constants:

- in the auxiliary equation method of §3.2 B that form was $y(x) = e^{a\,x}$, where a was the unknown constant.
- in the present case, we assume that $y(x)$ is an infinite power series with unknown coefficients:

$$y(x) \;=\; \sum_{n=0}^{\infty} a_n\,x^n \;=\; a_0 + a_1\,x + a_2\,x^2 + a_3\,x^3 + a_4\,x^4 + a_5\,x^5 + ...$$

(ii) Substituting this assumed form into the differential equation and rearranging it, as appropriate, yields conditions which define the values of or relationships between the constants: ***there*** the value of the exponent coefficient a , and ***here*** the set of coefficients $\{a_0, a_1, a_2, a_3, ...\}$.

3.4.1 The Algebra of Summations

One key fact about summations is that the "running index", the integer n in the expression above, is a *dummy* variable with no significance other than that it must, in turn, take on all integer values between the lower and upper bound of the summation. Thus the name, and even the definition of that index can change, as long as it defines *exactly the same series*.

In particular, the function $y(x) = \sum_{m=0}^{\infty} a_m\,x^m$ is *not* a function of m , though it clearly does depend on the particular values of a_0, a_1, a_2, a_3, ... , etc.

Similarly, we can write

$$y(x) \;=\; a_0 + a_1\,x + a_2\,x^2 + a_3\,x^3 + a_4\,x^4 + ... \;=$$

All of these different ways of writing this series are subject to two conditions:

- the term corresponding to any particular power of x, say x^j, is combined with a coefficient a_j whose subscript index has exactly that same value as that power, and
- The series expression starts with the term $a_0\, x^0 = a_0$.

More generally, any summation is defined, not by the name or range of the running index, but rather by the relationships among the power, the subscript label(s), and any term-dependent numerical factors which appear there. For example, the sum

$$\sum_{m=1}^{9} (m+2)\, a_{m-1}\, x^{m+3} \;=\; 3\, a_0\, x^4 +$$

is defined by the properties:

So: $\displaystyle\sum_{m=1}^{9} (m+2)\, a_{m-1}\, x^{m+3} = \sum_{m'=4}$ $\qquad\qquad$ $= \displaystyle\sum_{m'=-2}$

Exercise 3.5. Express each of the following summation as a sum over powers of x^m.

(i) $\displaystyle\sum_{n=3}^{\infty} (n-2)\,(2n+1)\, a_n\, x^{n-2}$

(ii) $\displaystyle\sum_{k=4}^{9} k\,(2k-4)\,(a_k - 2k\, b_{k+2})\, x^{k+2}$

(iii) $\displaystyle\sum_{l=-5}^{\infty} \ell(\ell+1)(2\ell-1)\, b_{\ell+2}\, x^{\ell-1}$

Addition of Summations

Any given pair of summations of powers of a variable x may be added together to form a single summation *iff* they have the same numbers of terms and the terms can be combined so as to have the same power.

e.g., $\displaystyle\sum_{m=2}^{\infty} m(m-1)\,a_m\,x^{m-2} \;+\; \sum_{n=0}^{\infty} b_n\,x^n.$

Both sums start at x^0 and go to x^∞, but we cannot simply combine an x^{m-2} term with an x^n term, as there would be no common factor. Hence

- *first* we must express both series using the same index label (choose one of m or n, and use it for both), and
- then we must use using exactly the same form for the power exponent on both series.

We can achieve the latter by either

(a) changing the power of x appearing in the first sum to x^n, or

(b) changing the power of x appearing in the second sum to x^{m-2}.

Note that in either case:

(i) the subscript label on parameter b is the same as the associated power of x, and

(ii) the subscript label on parameter a is larger by 2 than that on the associated power of x (and hence also larger by 2 than the corresponding subscript label on b).

Series Equal to Zero for All x

We know that if a finite polynomial of order N is set equal to zero, there are exactly N distinct values of x for which that equation is satisfied.

e.g., $x^2 + 3x - 10 = 0$ is satisfied only if

However, if such a polynomial is required to be equal to zero for *all* possible values of x, necessarily *all of its coefficients must be zero*!

e.g., Consider $y(x) = a_0 + a_1\,x = 0$.

More generally, if $\sum_m a_m\, x^m = 0$ for all x, then necessarily $a_m = 0$ for all m.

Consider the example on the top of the preceding page. If that sum of summations is equal to zero:

$$\sum_{m=2}^{\infty} m(m-1)\, a_m\, x^{m-2} \;+\; \sum_{n=0}^{\infty} b_n\, x^n \;=\; 0 \quad , \quad \text{and since that sum may be rearranged as}$$

Derivatives of a Power Series $\dfrac{d^n}{dx^n}\left(\sum_n a_n\, x^n\right)$

We know that the derivative of a sum of terms is equal to the sum of the derivatives of the individual terms: $\dfrac{d}{dx}\{f(x)+g(x)\} \;=\; \dfrac{d\,f(x)}{dx} \;+\; \dfrac{d\,g(x)}{dx}$. This applies to general summations too:

$$\frac{d}{dx}\left\{\sum_{n=0}^{\infty} a_n\, x^n\right\} \;=$$

$$\frac{d^2}{dx^2}\left\{\sum_{n=0}^{\infty} a_n\, x^n\right\} \;=$$

We also note that in these two cases, the first one or two terms in the series may disappear because of being multiplied by a factor equal to zero. In particular, in both cases the $n=0$ term disappears because it is multiplied by the factor n, and in the second case the $n=1$ term disappears too, because of the factor $(n-1)$. When terms like this become zero, the limits of the summation may be varied to *include* or *exclude* them, as long as they do not affect the value of the result. For example

$$\frac{d^2}{dx^2}\left(\sum_n a_n\, x^n\right) \;=$$

3.4.2 "Recursion Relations" in Solution by Series – A Simple Example

Consider the simple differential equation $\dfrac{d^2y}{dy^2} + k^2\, y = 0$. In § 3.2.B we saw that it could be solved easily using the auxiliary equation method, yielding the general solution $y(x) = b_1\, \cos(kx) + b_2\, \sin(kx)$. We will now solve this same equation by the method of solution by series.

To begin, we assume that the solution can be expanded as a series: $y(x) \;=\; \sum_{m=0}^{\infty} a_m\, x^m.$

However, if this resulting polynomial truly equals zero for *all* values of x , then all of its coefficients must be identically zero, which means that:

$$a_{m+2} \;=\; \frac{-\,k^2}{(m+2)(m+1)}\;\; a_m$$

This type of expression, which interrelates various coefficients of a given power series, is called the ***recursion relation*** for that series. We will now use this relationship to determine an explicit expression for the *general solution* to our differential equation.

From its structure, it is immediately clear that this expression interrelates every second coefficient in the series. In particular, a_2 depends on a_0 , a_4 on a_2 , a_6 on a_4 , ... etc., so that the coefficients of all ever-power terms are interrelated. Similarly, a_3 depends on a_1 , a_5 on a_3 , a_7 on a_5 , ... etc., so the coefficients of all odd-power terms are also interrelated.

Consider the coefficients of the even-power terms.

- The first coefficient is not known, so simply leave it alone with the value a_0 .
- The next even coefficient a_2 depends on a_0 , and its value is obtained by setting $m = 0$ in the recursion relation.

- Similarly, a_4 depends on a_2 , and its value is obtained by first setting $m = 2.$ in the recursion relation, and then substituting in the above expression for a_2 .

- Similarly, $a_6 = \dfrac{-k^2}{(4+2)(4+1)}\, a_4 \;=\; ... \;=\; -\left(\dfrac{k^6}{6\cdot 5\cdot 4\cdot 3\cdot 2\cdot 1}\right) a_0$.

- Similarly, $a_8 =$ $\qquad\qquad$ $a_{10} =$

- and hence for *any* even term, we can write $a_{2m} =$

Similarly for the coefficients of odd-power terms:

- The first odd coefficient, a_1, is unknown, but .....
- The coefficient a_3 depends on a_1, and its value is obtained by setting $m=1$ in the recursion relation.

- Similarly, $a_5 =$

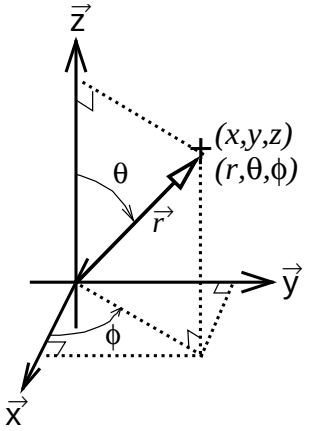
Thus ... the *general solution* has the form {collecting all of the odd and even terms separately}:

This general solution

clearly has exactly the same form as the one obtained by the auxiliary equation method! In any particular physical problem, we can then apply boundary conditions (see § 3.3) to determine values for the arbitrary constants on the solution and/or constraints on the allowed values of k.

3.4.3 A Series Solution with "Cut-Off" Boundary Conditions: the Legendre Equation

The quantum mechanical description of the vibration and rotation of a diatomic molecules or of the behaviour of an electron in a hydrogenic (one-electron) atom is always presented using polar coordinates $\{r, \theta, \phi\}$, where r is the interatomic bond distance and θ and ϕ are the usual polar angles which define the orientation of the bond axis in space. The form of the associated differential equation allows the resulting three-dimensional partial differential equation to be broken down into three separate differential equations, one for each coordinate. The one associated with the azimuthal angle ϕ we have solved already:



$x = r \sin\theta \cos\phi$
$y = r \sin\theta \sin\phi$
$z = r \cos\theta$

$\frac{d^2y(\phi)}{d\phi^2} = -k^2\, y(\phi)$, whose allowed solutions are $e^{\pm ik\phi}$ so that $y(\phi) =$

For the polar angle θ it turns out to be convenient to replace the variable θ by $x = \cos\theta$, and the resulting differential equation is

$$(1-x^2)\,\frac{d^2P(x)}{dx^2} \;-\; 2\,x\,\frac{dP(x)}{dx} \;+\; A\,P(x) \;=\; 0 \qquad (7)$$

where A is an unknown (at this point) numerical constant which appears when separating the angular and radial degrees of freedom. Note too that since the polar angle θ only has the physically meaningful range 0 to π (*think – why?*), the allowed range of values of x runs from $\cos(0) = 1$ to $\cos(\pi) = -1$, so that $-1 \le x \le 1$. Moreover, any acceptable solution must be continuous everywhere.

Applying the method of solution by series to the terms in our differential equation, we see that:

$$P(x) \;=\; \sum_{m=0}^{\infty} a_m\, x^m \qquad \text{implies that} \qquad A\,P(x) \;=\; \sum_{m=0}^{\infty} A\,a_m\, x^m$$

$$\frac{d\,P(x)}{dx} \;=\; \sum_{m=0}^{\infty} m\,a_m\, x^{m-1} \qquad \text{implies that} \qquad 2\,x\,\frac{d\,P(x)}{dx} \;=$$

$$\frac{d^2P(x)}{dx^2} \;=\; \sum_{m=0}^{\infty} m(m-1)\,a_m\, x^{m-2} \qquad \text{implies that}$$

$$(1-x^2)\,\frac{d^2P(x)}{dx^2} \;=$$

Substituting these expressions back into our differential equation then yields

As usual, if this summation is equal to zero for all possible values of x, then the coefficient of each and every power of x must equal zero:

As in the example considered in § 3.4.2, this ***recursion*** relation interrelates the coefficients of every second term in the series, so that the coefficients of all the even-power terms are interrelated, and that separately, the coefficients of all the off-power terms are related to one another.

Boundary Conditions

There are two key boundary conditions which define the physically allowed solutions of the differential equations encountered in quantum mechanics. The first is simply that the solution must be "well behaved", which means that it must be single-valued (at a single point in space, it cannot have more than one value) and continuous. The second is that allowed solutions must be "square integrable" or "normalizable". In the context of quantum mechanics, where we associate the square of the wave-function $|\psi(r,\theta,\phi)|^2 = \psi^*(r,\theta,\phi)\,\psi^*(r,\theta,\phi)$ with the probability of finding the system in a particular configuration $\{r,\theta,\phi\}$, this last condition simply implies that the integral of $|\psi(r,\theta,\phi)|^2$ over all space must be unity, since the system must be *somewhere* in configuration space! In practice, this usually means that the allowed solutions must be *finite* for all possible configurations.

For the polar coordinate θ [or $x=\cos(\theta)$], the polynomial form of the solution we have obtained means that the first conditions are automatically satisfied, and the remaining boundary condition is the second one – that the integral of $P^*(x)\,P(x)$ over the whole domain of x must be finite. Since the solution is a polynomial with no singular terms, this means that the function must be finite everywhere on the interval $-1 \le x \le 1$. In particular, this means that

$$P(x=1) \;=\; \sum_{m=0}^{\infty} a_m\,(1)^m \;=\; \sum_{m=0}^{\infty} a_m \;=\; a_0 + a_1 + a_2 + a_3 + ... + a_n + ... \qquad (8)$$

must be finite if the boundary condition is to be satisfied! This will certainly be true if the size of the a_m coefficients decreases sufficiently rapidly with increasing m. However, examination of the recursion relation shows that

$$\frac{a_{m+2}}{a_m} \;=$$

i.e., the values of the coefficient take on a constant value at sufficiently large m.

The above result means that the sum of Eq. (8) *will not* be finite if the series *does* include an infinite number of non-zero coefficients. In other words, our "square integrability" boundary condition will only be satisfied if

However, the series solution method requires that *all* coefficients a_m must satisfy the recursion relation derived above! Hence, that relation must *itself* cause the series to stop!

If $a_L\, x^L$ is the last term in the series with a non-zero coefficient, then on plugging $L = m$ into the recursion relation we obtain:

In other words, our polynomial series solutions of this differential equation will only satisfy the square integrability boundary condition if the numerical constant A in the original equation has values given by the condition $A = L(L+1)$, there the non-negative integer L it the power of the last non-zero term in the series. These discrete allowed values of the constant A are the ***eigenvalues*** of this differential equation.

It is clear that L can have an infinite number of possible values, since the series could cut off after *any* term a_0, $a_1\, x$, $a_2\, x^2$, $a_3\, x^3$, $a_4\, x^4$, ... etc. For each of these cases there exists a unique value of the 'eigenvalue' $A = A_L = L(L+1)$. Moreover, since the recursion relation depends on the value of $A = A_L$,

$$a_{m+2} \;=\; \left[\frac{m(m+1) - A_L}{(m+2)(m+1)}\right] a_m \;=\; \left[\frac{m(m+1) - L(L+1)}{(m+2)(m+1)}\right] a_m$$

there is a different distinct solution $P(x) = P_L(x)$ for each value of L.

Even vs. Odd Solutions $P_L(x)$

For a given value of L which is (say) even, the recursion relation will necessarily force $a_{L+2} = 0 = a_{L+4} = a_{L+6} = a_{L+8} = ...$ (and so on for the coefficients of all higher-power even terms). In other words, $a_{L+n} = 0$ for all (even or odd) $n \geq 1$.

Similarly, all coefficients of the form a_{L-2n} for $n = 1, 2, 3, ...$ etc., *must be non-zero*, since they are all

related to the non-zero coefficient a_L by some constant numerical factor, and $a_L \neq 0$ by definition.

Moreover, it is also clear that since x^L is the last non-zero term, necessarily
$a_{L+1} = 0 = a_{L+3} = a_{L+5} = a_{L+7} = ...$ (and so on for the coefficients of all higher-power odd terms).
In other words, $a_{L+2n+1} = 0$ for all $n \geq 0$.

However, in the latter case all of the coefficients a_{L-1}, a_{L-3}, a_{L-5}, a_{L-7}, ... etc., *must also equal zero*, since they are all related to a_{L+1} by some *non-zero* numerical factor (or product of factors).

It is clear that the above arguments could also be presented for the case of L being an odd, rather than an even integer. Thus (for this particular d.e.),

> the allowed solutions $P_L(x)$ of this differential equation consist either *only* of even-power terms, when L is even, *or only* of odd-power L is odd. No allowed solutions can include both even and odd-power terms!

Let us generate some specific solutions

If $L = 0$**.** In this case, $x^0 = 1$ is the highest-power appearing in the series, and $A = A_0 =$

If $L = 1$**.** In this case, x^1 is the highest-power in the series, $A = A_1 =$

If $L = 2$**.** The highest-power in the series is x^2, $A = A_2 =$

If $L = 3$**.** The highest-power in the series is x^3 , $A = A_3 =$

If $L = 4$**.** The highest-power in the series is x^4 , $A = A_4 =$

If $L = 5$**.** The highest-power in the series is x^5 , $A = A_5 =$

3.4.4 Overview/Review of Solution-by-Series Methodology

1. Substitute power series sum into d.e. and determine the recursion relation
2. Apply series cut-off criterion to determine eigenvalue condition

   (Note than for each eigenvalue, get a different version of the recursion relation!)
3. For each particular allowed eigenvalue, use the corresponding distinct recursion relation to get the solution.
4. Note than in the special cases of recursion relations involving adjacent coefficients:

   - if recursion relation involves every *second* coefficient ...

   - if recursion relation involves every *third* coefficient ...

Exercises

For each of the following differential equations

(i) Solve it, using the method of solution by series to determine the appropriate recursion relation.

(ii) Apply the boundary condition that the series must cut off after a finite number of terms, and determine the resulting eigenvalues of this equation.

(iii) Generate the eigenfunctions corresponding to the first few (smallest) eigenvalues of this equation.

3.6 $\dfrac{d^2H(x)}{dx^2} - 2x\dfrac{dH(x)}{dx} + (E-1)H(x) = 0$

3.7 $(x^2+2x)\dfrac{d^2y(x)}{dx^2} + 2(x+1)\dfrac{dy(x)}{dx} - By(x) = 0$

3.8 $x\dfrac{d^2y(x)}{dx^2} + 2x^3\dfrac{dy(x)}{dx} - Ax^2y(x) = 0$

3.9 $(1-x^2)\dfrac{d^2f(x)}{dx^2} - x\dfrac{df(x)}{dx} + Af(x) = 0$

3.10 $(1-x^2)\dfrac{d^2y(x)}{dx^2} - 3x\dfrac{dy(x)}{dx} + Ay(x) = 0$

3.11 $2x^2\dfrac{d^3f(x)}{dx^3} - 2x^2\dfrac{d^2f(x)}{dx^2} + (2-3x)\dfrac{df(x)}{dx} + Af(x) = 0$

3.5 Partial Differential Equations: Separation of Variables

Since the world is three dimensional, and molecular systems are made up of many particles, the differential equations which govern behaviour in the real world may be expected to be *partial* differential equations depending on several (or *many*!) variables. Whenever possible, we treat such problems by separating the overall differential equation into independent equations, each involving only a small number (preferably one!) of the independent variables. The common technique for doing this involves manipulating the differential equation into a form which consists of a sum of terms, each involving only a single independent variable.

Consider the case of the vibration of a stretched uniform string. At a particular location x along the string, the displacement from equilibrium $y(x,t)$ is a function of x and t is governed by the differential equation

$$u^2 \, \frac{\partial^2 y(x,t)}{\partial x^2} \;=\; \frac{\partial^2 y(x,t)}{\partial t^2}$$

where $u^2 = \kappa/\rho$ is the "phase velocity", the speed at which waves travel along the string, ρ is the density of the material in the string (in units: mass per unit length), and κ is the tension in the string. [When generalized to two dimensions, an analogous differential equation in the three independent variables $\{x, y, t\}$ describes waves in water.]

The method of ***separation of variables*** is based on the observation that this differential equation can be written as a sum of two terms, each [not counting the solution $y(x,t)$] depending on only one variable. The essential procedure is to simply assume, without initial justification (the real justification is that *it works*!), that the full solution is ***separable*** and can be written as a simple product of a function of x times a function of t:

$$y(x,t) \;=\; f(x)\, g(t)$$

Substituting this into the original differential equation then yields:

Next, dividing both sides of the equation by $y(x,t) = f(x)\, g(t)$ yields:

One side of this equation depends only on the time t while the other side depends only on the position coordinate x. The only way these two terms can be equal for all possible values of x and t is if both terms are equal to what we call a ***separation constant!*** While we have at this point no particular restrictions on the allowed value(s) of that constant, for convenience in later manipulations we will write it as $-\,\omega^2$. The net result is that we obtain two separate differential equations, one depending on each coordinate.

We have discussed differential equations with this form earlier. We know that their solutions may in general be written either in terms of sin and cos functions, or in terms of exponentials with purely imaginary exponents (such as $e^{\pm i\,\omega\,t}$). However, since the physical problem is a physical object (the string) moving in ordinary physical space, the displacement must be a *real number* quantity, so the appropriate general solutions are.

The Hydrogen(ic) Atom

The very simple approach outlined above is applicable to a number of problems, including the multidimensional vibrational motions of polyatomic molecules. However, it also works in case where the original differential equation is not so obviously separable. In particular, the Schrödinger equation for the internal energy of a one-electron (hydrogenic) atom system is, using spherical polar coordinates,

$$\begin{aligned} -\frac{\hbar^2}{2\,\mu}\left[\frac{\partial^2\Psi(r,\theta,\phi)}{\partial r^2}\;+\;\frac{2}{r}\,\frac{\partial\Psi(r,\theta,\phi)}{\partial r}\right] & \\ -\;\frac{\hbar^2}{2\,\mu\,r^2}\left[\frac{\partial^2\Psi(r,\theta,\phi)}{\partial\theta^2}\;+\;\cot(\theta)\,\frac{\partial\Psi(r,\theta,\phi)}{\partial\theta}\;+\;\frac{1}{\sin^2(\theta)}\,\frac{\partial^2\Psi(r,\theta,\phi)}{\partial\phi^2}\right] & \\ -\left(\frac{Z\,\mathrm{e}^2}{r}\right)\Psi(r,\theta,\phi)\;=\;E\;\Psi(r,\theta,\phi) & \end{aligned} \tag{9}$$

1: multiply through (from the left) by the factor: $\quad -\,\dfrac{2\mu\,r^2}{\hbar^2}$

2: Collect the terms depending on r and those depending on θ:

Note that we can also write this result in the language of "operators", where ***an "operator"*** is a 'set of instructions' which changes one function into another.

Aside. *Examples of operators.*

$$\left[r^2 \, \frac{\partial^2}{\partial r^2} + 2r \, \frac{\partial}{\partial r} + \frac{2\mu \, r^2}{\hbar^2} \left(E + \frac{Z\mathrm{e}^2}{r} \right) \right] \Psi(r,\theta,\phi) + \left[\frac{\partial^2}{\partial \theta^2} + \cot(\theta) \, \frac{\partial}{\partial \theta} + \frac{1}{\sin^2(\theta)} \, \frac{\partial^2}{\partial \phi^2} \right] \Psi(r,\theta,\phi) = 0 \tag{10}$$

The first term in Eq. (10) consists of an "*operator*" which only depends on and/or acts on the radial coordinate r, being applied to the wavefunction $\Psi(r,\theta,\phi)$, while in the second term the *operator* acting on Ψ only depends on and/or acts on the angular coordinates. If a partial differential equation can be written in this type of form, as a sum of operators depending and/or acting on different coordinates, means that its solution is "*separable*", and can be written as a *product* of functions depending on the different coordinates. In the present context, it means that we write

$$\Psi(r,\theta,\phi) = F(r) \, Y(\theta,\phi) \tag{11}$$

Substituting this product expression into Eq. (10) yields

If we then multiply from the left by the factor $\left\{ \dfrac{1}{F(r)\ Y(\theta,\phi)} \right\}$ we obtain

This expression consists of a term depending only on r plus a term depending only on θ & ϕ, whose sum is equal to zero for all possible values of the coordinates. This can only be possible if the first term is equal to some numerical constant (named, say) $+A$, and the second term is equal to $-A$. Hence:

Multiplying all terms in the *radial* equation (above) from the left by the factor $\left\{ \dfrac{F(r)}{r^2} \right\}$ yields

$$\frac{d^2\,F(r)}{dr^2} \ + \ \frac{2}{r}\,\frac{d\,F(r)}{dr} \ + \ \left[\ \frac{2\mu}{\hbar^2}\,\frac{Z\mathrm{e}^2}{r} \ + \ \frac{2\mu}{\hbar^2}\,E \ - \ \frac{A}{r^2} \right] F(r) \ = \ 0 \qquad (12)$$

If we define the collection of factors $\hbar^2/(\mu\,\mathrm{e}^2) \equiv a$ and recognize that the energy E appearing here is the negative of the binding energy $E_b = -E$ appearing there, we see that this equation is essentially identical to Eq. (1) of Problem Set $^{\#}3$! The only real difference is the fact that here we have not (yet!) determined any constraint to define the value of the *separation constant* A.

Let us now consider the angular variable differential equation appearing on the bottom of the preceding page. First of all, we multiply through (from the left) by the factor $Y(\theta,\phi)$, to obtain

Collecting all terms on the left hand side of the equal sign and multiplying through by the factor $\sin^2(\theta)$ then yields

$$\left[\sin^2(\theta)\,\frac{\partial^2}{\partial\theta^2} \ + \ \cos(\theta)\,\sin(\theta)\,\frac{\partial}{\partial\theta} \ + \ A\,\sin^2(\theta) \right] Y(\theta,\phi) \ + \ \frac{\partial^2}{\partial\phi^2}\,Y(\theta,\phi) \ = \ 0 \qquad (13)$$

This differential equation clearly has the same type of structure as did Eq. (10): the function $Y(\theta,\phi)$ is acted on by a sum of operators which depend on different coordinates. This indicates that in this case too the solution is *separable*, so we write $\quad Y(\theta,\phi) \;=\; S(\theta)\,T(\phi)\;.$

Substituting this product into Eq. (13) and pre-multiplying by the factor $\left\{\dfrac{1}{S(\theta)\,T(\phi)}\right\}$ yields

Once again, we have a sum of terms depending on different coordinates which must equal zero everywhere. This is only possible of those two terms are equal to equal and opposite values of some *separation constant*, which we choose to call B.

Multiplying the first of these angular equations (from the left) by $S(\theta)$ and collecting terms yields

$$\sin^2(\theta)\,\frac{d^2\,S(\theta)}{d\theta^2} \;+\; \cos(\theta)\,\sin(\theta)\,\frac{d\,S(\theta)}{d\theta} \;+\; \left[A\,\sin^2(\theta) - B\right]S(\theta) \;=\; 0 \qquad (14)$$

This differential equation in terms of θ itself turns out to rather difficult to solve. However, if we write it in terms of a different variable, it takes on a much more tractable (and familiar!) form. In particular, if we define $x = \cos(\theta)$ and write $S(\theta) = P(\cos(\theta)) = P(x)$, the chain rule shows us that:

$$\frac{dS}{d\theta} \;=\; \frac{dx}{d\theta}\,\frac{dS}{dx} \;=\; [-\sin(\theta)]\,\frac{dS}{dx} \;=\; -\left(1-x^2\right)^{1/2}\,\frac{dS}{dx}$$

Writing this result in the language of operators gives the relationship $\quad \dfrac{d}{d\theta} = -\left(1-x^2\right)^{1/2}\,\dfrac{d}{dx}\quad,$

and we obtain

$$\frac{d^2S}{d\theta^2} \;=\; \frac{d}{d\theta}\left\{\frac{dS}{d\theta}\right\} \;=\; -\left(1-x^2\right)^{1/2}\,\frac{d}{dx}\left\{-\left(1-x^2\right)^{1/2}\,\frac{dS}{dx}\right\} \;=$$

$$=\; \left(1-x^2\right)\,\frac{d^2S}{dx^2} - x\,\frac{dS}{dx} \;=\; \left\{\left(1-x^2\right)\,\frac{d^2}{dx^2} - x\,\frac{d}{dx}\right\}S$$

Substituting these derivative expressions into Eq. (14), replacing $S(\theta)$ by $P(x)$, and rearranging the result gives

$$\left(1-x^2\right)\,\frac{d^2P(x)}{dx^2}\;-\;2x\,\frac{dP(x)}{dx}\;+\;\left[A\;+\;\frac{B}{1-x^2}\right]P(x)\;=\;0 \qquad (15)$$

For the special case $B=0$ (which is allowed, see below), this becomes precisely the same the differential equation we first saw on p. 16, which served as our archetypical solution-by-series eigenvalue problem. For that case we found that the allowed eigenvalues were $A = 0,\ 2,\ 6,\ 12,\ \ldots\ ,\ L(L+1), \ldots$ for non-negative integer values of L. Analogous power-series solutions can be generated for the case $B \neq 0$, but their treatment is a little more complicated, and it will not be pursued here.

Azimuthal Part of the H-atom Differential Equation

Finally, multiplying the angular equation for $T(\phi)$ (middle of p. 26) from the left by the function $T(\phi)$ yields:

This has a *very* familiar form, and we recognize immediately that its solutions have the form

Recalling that ϕ is a real physical coordinate - the azimuthal angle - our normal requirement that acceptable solutions must be single-valued for every possible value of ϕ means that $T(\phi+2\pi) = T(\phi)$. The discussion of § 3.3 shows that this implies that:

which means in turn that our allowed solutions are

Requiring that the azimuthal wavefunction obtained above must be unit normalized then determines the amplitude factor A in the general solution. In particular, since the sum over all possible (unique) values of ϕ of the probability of funding the system configuration having any particular value of ϕ means that

$$\int_0^{2\pi} |T^*(\phi)\, T(\phi)|^2\, d\phi \;=\; 1 \;=$$

In conclusion, the above discussion shows the even for a *partial* differential equation in which the various terms appear to depend on multiple variables, it is sometimes possible to break it down into a set of *ordinary* differential equations which can be solved using relatively simple methods. This is an extremely important results, as it allows us to obtain exact solutions for some of the most important problems in quantum mechanics and statistical thermodynamics.

4. Vectors, Orthogonal Polynomials and Fourier Transforms

4.1 Geometric Vectors and their Arithmetic

In ordinary geometry in two or three dimensions, a ***vector*** is a line segment with two defining properties: (i) a magnitude or length, and (ii) a direction. In this context the notation used for a given vector is usually one of[3]

$$\vec{v} \;=\; (v_x, v_y, v_z) \qquad \text{or} \qquad \vec{v} \;=\; v_x\,\widehat{e}_1 \;+\; v_y\,\widehat{e}_2 \;+\; v_z\,\widehat{e}_3$$

where v_x, v_y and v_z are real numbers corresponding to the magnitude of the projection of the vector on the orthogonal x, y and z spatial axes, respectively, and $\widehat{e}_1$, $\widehat{e}_2$ and $\widehat{e}_3$ are mutually orthogonal vectors of unit length pointing along the x, y and z directions. It is a universal convention to define the relative orientation of the x, y and z axes according to a "right-hand rule" which gives the relative orientations seen in the figure on p. 15 of Chapter 2 of the Notes.

In order to identify a particular vector $\vec{v}$, it is clearly essential to specify the values of all its components, v_x, v_y and v_z, and any two vectors $\vec{v}$ and $\vec{u}$ can be said to be equal, if and only if all corresponding pairs of components are equal.

Vector Arithmetic

(a) *Addition*: Addition of two vectors gives a third vector, and this addition operation "commutes"

(b) *Multiplication by a Scalar*: Multiplication of a vector $\vec{v}$ by any real number 'scalar' k yields another vector $\vec{u} = k\,\vec{v}$ which point in exactly the same direction as the original vector, but is k time as long.

[3] While many texts use the convention of identifying a vector through the use of a bold font lettering $\vec{v} \equiv \mathbf{v}$, on a hand-written test or problem set the difference between bold and ordinary font can be difficult to recognize(!), so the $\vec{v}$ convention is used in these notes.

(c) *Multiplication of a pair of vectors*: The "product" of a pair of vectors may be defined in more than one way, and two different definitions are considered here. One of them is useful only in the discussion of geometric vectors in three dimensions, but the other turns out to be readily generalized to an arbitrary number of dimensions, and had much more general implications.

The Dot Product, or Scalar Product

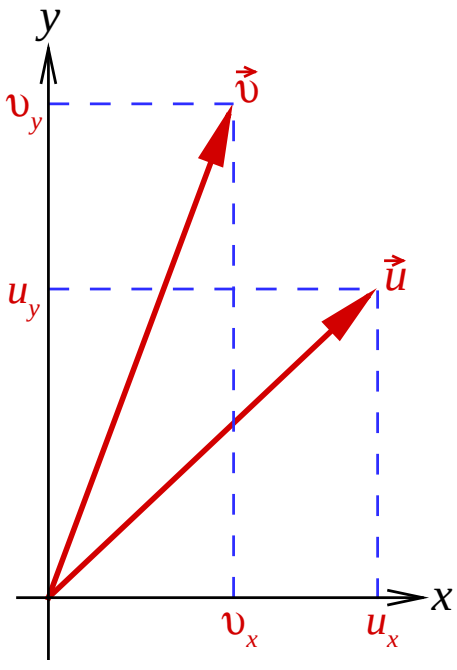
The "scalar product" of a pair or vectors $\vec{u} = (u_x, u_y, u_z)$ and $v = (v_x, v_y, v_z)$ is a *scalar* quantity and may be written in the form

The alternate notation $\langle \vec{u} | \vec{v} \rangle$ turns out to be more general, as its structure suggests that the order of multiplication may matter. However, for geometric vectors the 'dot' notation $\vec{u} \cdot \vec{v}$ is perfectly satisfactory , since the fact that the components u_x , u_y , u_z , v_x , v_y and v_z are all scalars (ordinary real numbers) means that

In other words for geometric vectors the scalar product operation *commutes*.

Theorem 4.1: $\vec{u} \cdot \vec{v} = |\vec{u}|\,|\vec{v}|\,\cos(\theta)$, where $|\vec{u}|$ is the magnitude of the length of vector $\vec{u}$, $|\vec{v}|$ is the magnitude of the length of vector $\vec{v}$, and θ is the angle between $\vec{u}$ and $\vec{v}$.

Proof: For simplicity, consider the case of two vectors lying in the $x - y$ plane (i.e., $u_z = v_z = 0$)



Corollary (1): $\vec{u} \cdot \vec{v} = \{$*magnitude of one vector*$\} \times \{$ projection of other along direction of first$\}$

Corollary (2): $\vec{u} \cdot \vec{v} = 0$ means the $\vec{u}$ and $\vec{v}$ are perpendicular or "orthogonal".

Corollary (3): $\vec{u} \cdot \vec{u} \geq 0$ for any geometric vector $\vec{u}$.

Exercise 4.1 Consider the vectors $\vec{u} = (1, 2, -3)$, $\vec{v} = (3, -2, -1)$ and $\vec{w} = (-3, 2, -1)$.

(i) Verify that $\vec{u} + \vec{v} = \vec{v} + \vec{u}$.

(ii) Evaluate the scalar products $\vec{u} \cdot \vec{v}$, $\vec{v} \cdot \vec{u}$, $\vec{u} \cdot \vec{w}$ and $\vec{w} \cdot \vec{v}$.

(iii) What is the angle (a) between the vectors $\vec{u}$ and $\vec{v}$?
(b) between the vectors $\vec{u}$ and $\vec{w}$?
(c) between the vectors $\vec{w}$ and $\vec{v}$?

The Cross Product, or Vector Product $\vec{A}\times\vec{B}$

This type of vector multiplication is only defined in a geometric three-dimensional vector space. However, because our normal physical world is three dimensional, it provides and extremely powerful shorthand notation for 'arithmetic' which would otherwise be very complicated to describe.

Consider two arbitrary vectors $\vec{A}$ and $\vec{B}$ in three-dimensional space based at a common origin. As long as they are not parallel [*Question: Precisely how do we define "parallel"?*], they will define a two-dimensional plane in our 3-D space. How would we determine a vector $\vec{C}$ which is perpendicular to that plane (i.e., which is perpendicular to both $\vec{A}$ and $\vec{B}$)?

If $\vec{C} = (C_x, C_y, C_z)$ is perpendicular to $\vec{A} = (A_x, A_y, A_z)$ and to $\vec{B} = (B_x, B_y, B_z)$

$$\vec{C}\cdot\vec{A} \;=\; C_x\,A_x \;+\; C_y\,A_y \;+\; C_z\,A_z \;=\; 0 \qquad (16)$$

$$\vec{C}\cdot\vec{B} \;=\; C_x\,B_x \;+\; C_y\,B_y \;+\; C_z\,B_z \;=\; 0 \qquad (17)$$

Now, take differences to eliminate one of C_x, C_y or C_z to determine realationshopw between the remaining coefficients:

$[\,B_z\times(1)] - [\,A_z\times(2)\,] \;=$

$[\,B_x\times(1)] - [\,A_x\times(2)\,] \;=$

$[\,B_y\times(1)] - [\,A_y\times(2)\,] \;=$

What is the length of the vector $\vec{C} = \vec{A} \times \vec{B}$?

$|\vec{C}|^2 \;=\; |\,\vec{C}\cdot\vec{C}\,|^2 \;=$

Final Result

$$\vec{A}\times\vec{B} \;=\; \vec{C} \;=\; (\,C_x\,,\,C_y\,,\,C_z\,) \;=\; (\,A_yB_z - A_zB_y\,,\,A_zB_x - A_xB_z\,,\,A_xB_y - A_yB_x\,)$$

is a vector which is *perpendicular* (or *orthogonal*) to both $\vec{A}$ and $\vec{B}$, and whose length (or magnitude) $|\vec{C}| = |\vec{A}||\vec{B}|\,\sin\theta$ is the area of the parallelogram defined by those two vectors. The direction of $\vec{C}$ relative to the plane defined by $\vec{A}$ and $\vec{B}$ is specified by the "right-hand rule".

Exercise 4.2 Consider the operation $\vec{A}\times\vec{B}\cdot\vec{D}=0$. Does it matter which operation is performed first ? If so which one goes first ? Is the result a vector or a scalar?

Exercise 4.3 If we have three vectors $\vec{A}$, $\vec{B}$ and $\vec{D}$ such that $\vec{A}\times\vec{B}\cdot\vec{D}=0$, what does it tell us about these three vectors ?

Exercise 4.4 Consider the quantity $\vec{A}\times\vec{B}\times\vec{D}$. Is this "triple product" a vector or a scalar ? If it is a vector whose length is non-zero, what can you say about where it points ? Do you expect $\vec{A}\times(\vec{B}\times\vec{C})$ to equal $(\vec{A}\times\vec{B})\times\vec{C}$?

Exercise 4.5 With vectors $\vec{u}=(1,2,1)$, $\vec{v}=(3,-2,-2)$ and $\vec{w}=(-3,2,-1)$, evaluate

(a) $\vec{u}\times\vec{v}$

(b) $\vec{v}\times\vec{u}$

(c) $\vec{u}\times(\vec{v}\times\vec{w})$

(d) $(\vec{u}\times\vec{v})\times\vec{w}$

Vector Differential Operators

Vector differential operators simply combine our familiar Cartesian differential operators $\frac{\partial}{\partial x}$, $\frac{\partial}{\partial y}$, $\frac{\partial}{\partial y}$, with vectors. We will consider three "operators" of this type.

(a) The gradient or "del" operator is written $\vec{\nabla} \equiv \widehat{e}_1 \frac{\partial}{\partial x} + \widehat{e}_2 \frac{\partial}{\partial y} + \hat{e}_2 \frac{\partial}{\partial z}$,

where $\widehat{e}_1$, $\widehat{e}_2$ and $\widehat{e}_3$ are vectors of unit length pointing along the orthogonal x , y and z axes. When it is applied to a scalar function of these coordinates $g(x, y, z)$, the result is a vector

$$\text{grad}\{g(x,y,z)\} = \vec{\nabla}\, g(x,y,z) \equiv \widehat{e}_1 \frac{\partial g(x,y,z)}{\partial x} + \widehat{e}_2 \frac{\partial g(x,y,z)}{\partial y} + \widehat{e}_3 \frac{\partial g(x,y,z)}{\partial z}$$

e.g., if $g(x, y, z) = 2x^2 \cos(3y)\, e^{-7z}$, evaluate $\vec{\nabla}\, g(x, y, z)$.

The components of the vector $\vec{\nabla}\, g(x, y, z)$ clearly represent the rates of change of the function in the three coordinate directions, and the resulting vector points in the direction in which the function is increasing most steeply.

(b) The divergence of a vector function is the *scalar* function obtained on taking the dot product of the gradient operator $\vec{\nabla}$ with that vector function.

In particular, if $\vec{A} = \widehat{e}_1\, A_x(x, y, z) + \widehat{e}_2\, A_y(x, y, z) + \widehat{e}_3\, A_z(x, y, z)$, the "divergence" of $\vec{A}$ is

$$\text{div}\{\vec{A}\} = \vec{\nabla} \cdot \vec{A} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right) \cdot (A_x, A_y, A_z) = \frac{\partial\, A_x}{\partial x} + \frac{\partial\, A_y}{\partial y} + \frac{\partial\, A_z}{\partial z}$$

e.g., What is the *divergence* of the vector function $\vec{A}(x, y, z) = (2xz^2,\, 3xy^2,\, -xyz^2)$?

(c) The curl of a vector function $\vec{A}(x, y, z)$ is the *vector product* of the gradient operator with that vector.

$$\begin{aligned} \text{curl}\{\vec{A}\} = \vec{\nabla} \times \vec{A} &= \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right) \times (A_x, A_y, A_z) \\ &= \left(\frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z}\,,\ \frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x}\,,\ \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}\right) \end{aligned}$$

e.g., What is the *curl* of the vector function $\vec{A}(x, y, z) = (2xz^2,\, 3xy^2,\, -xyz^2)$?

$\vec{\nabla} \times \vec{A}(x, y, z) =$

(d) The Laplacian or "del squared" operator, usually denoted ∇^2, is the scalar function which is defined as the *divergence* of the *gradient* of a given scalar function. In particular, for a given scalar function $g(x,y,z)$,

$$\begin{aligned}
\text{div}\,(\text{grad}\,\{g(x,y,z)\}) &= \vec{\nabla}\cdot\left\{\vec{\nabla}\,g(x,y,z)\right\} = \vec{\nabla}\cdot\left(\frac{\partial g(x,y,z)}{\partial x}\,,\,\frac{\partial g(x,y,z)}{\partial y}\,,\,\frac{\partial g(x,y,z)}{\partial z}\right) \\
&= \frac{\partial^2 g(x,y,z)}{\partial x^2}+\frac{\partial^2 g(x,y,z)}{\partial y^2}+\frac{\partial^2 g(x,y,z)}{\partial z^2} \equiv \nabla^2\,g(x,y,z) \\
&= \left\{\vec{\nabla}\cdot\vec{\nabla}\right\}g(x,y,z)
\end{aligned}$$

e.g., What is the Laplacian of the scalar function $g(x,y,z)=2x^2\,\cos(3y)\,e^{-7z}$?

4.2 Generalized Vector Spaces

The formal definition of a *vector space* is much more general than the special three-dimensional geometric case discussed in § 4.1. This formal language is very powerful, as it provides us with a common language for discussing many different types of quantities, such as (i) geometric vectors (see § 4.1), (ii) the algebra of multiple angular momenta, (iii) the solutions of differential equations, (iv) wavefunctions for electronic orbitals in atoms and molecules, (v) matrix eigenvalue problems (see Chapter 5), and (vi) Fourier analysis. We start with some definitions.

A ***set*** is any collection of elements which all satisfy the rules or rules which provide the defining property of the "set". For example, we can speak of

- the set of even integers
- the set of imaginary numbers
- the set of red-haired, Swedish, co-op Earth Science students

A ***vector space*** is any set of elements which obeys the following rules.

(i) The set is *closed* under addition.

i.e., if $\vec{u}$ and $\vec{v}$ are elements of the set, then so is $\vec{u}+\vec{v}$, and

(a) this operation of "addition" *commutes*: $\vec{u}+\vec{v}=\vec{v}+\vec{u}$.

(b) this operation of "addition" is *associative*: $\vec{u}+(\vec{v}+\vec{w})=(\vec{v}+\vec{u})+\vec{w}$.

(ii) The set contains a *zero vector* $\vec{0}$, which is defined by the property that $\vec{0}+\vec{v}=\vec{v}$ for any vector $\vec{v}$ in the set.

(iii) For every element $\vec{u}$ of the set, its additive inverse $-\vec{u}$ [defined by the fact that $\vec{u}+(-\vec{u})=\vec{0}$] is also a member of that set.

(iv) The set is closed under multiplication by scalars.

i.e., if k is any (real or complex) scalar and $\vec{u}$ is any element of the set, then $k\,\vec{u}$ is also a member of that set.

Corollaries: (a) scalar multiplication is *associative*: $k_1(k_2\,\vec{u})=(k_1\,k_2)\,\vec{u}$.

(b) scalar multiplication is *distributive*: $(k_1+k_2)\,\vec{u}=k_1\,\vec{u}+k_2\,\vec{u}$ and $k_1(\vec{u}+\vec{v})=k_1\,\vec{u}+k_1\,\vec{v}$.

Note: In this most general definition of a *vector space*, there exists no operation which one might associate with the "multiplication" of a pair of vectors!

Examples of Vector Spaces

(i) Geometric vectors in 2- or 3-dimensional space — directed line segments, as discussed above.

(ii) The set of all ordered "n–tuples" (n-components) of the form $\vec{v}=(v_1,v_2,v_3,\cdots,v_n)$, where the n individual components v_1 , v_2 , v_3 , $\ldots v_n$, are complex numbers.

This type of vector space is clearly just a generalization of our familiar 3-dimensional vector space to n–dimensions, with the additional property that the *scalar* components *need not be real numbers*.

For this type of vector space, the operation of "addition" of two vectors is defined as consisting of the addition of corresponding (scalar) components:

the operation of "multiplication by a scalar" means that every one of those components is multiplied by that same scalar.

and the *zero vector* is defined as the particular n–tuple

Particular examples of such ordered n–tuples are:

What about the set of ordered 4-tuples over the field of imaginary numbers?

(iii) The set of all 4×3 matrices (objects with four rows and three columns) with complex elements is a vector space over 'the field of complex numbers' (i.e., the components are complex numbers, and scalar multiplication includes multiplication by complex numbers).

(iv) The set of all polynomials whose coefficients are elements of some field $\mathfrak{F}$ (e.g., the 'field' of real numbers, or the field of complex numbers).

(v) The set of all polynomials of order less than or equal to some particular integer m (say, $m=4$), whose coefficients are elements of a particular field $\mathfrak{F}$ (i.e., of a particular class of scalars).

(vi) The set of all functions which are solutions of a particular linear, homogeneous differential equation such as

$$(2x-1)\,\frac{d^2y(x)}{dx^2} \;+\; x^2\,\frac{d\,y(x)}{dx} \;+\; 3\,x^3\,y(x) \;=\; 0$$

Exercise 4.6 If the above example was made into a *non*-linear homogeneous differential equation by (say) multiplying last two terms together to yield $3x^5\;y(x)\;\frac{d\,y(x)}{dx}$, do its solutions comprise a vector space?

Exercise 4.7 If the above example was made into an *in*homogeneous differential equation by (say) replacing the 0 on the right hand side by the function $2\,x^2$, do its solutions comprise a vector space?

Linear Dependence

A finite set of vectors $\{\vec{X}_1\,,\,\vec{X}_2\,,\,\vec{X}_3\,,\,\cdots\,,\,\vec{X}_n\}$ is said to be *linearly dependent* if those vectors are related by some non-trivial[4] relationship of the form

$$c_1\,\vec{X}_1\;+\;c_2\,\vec{X}_2\;+\;c_3\,\vec{X}_3\;+\;\ldots\;+\;c_n\,\vec{X}_n\;=\;\vec{0}$$

in which at least two of the coefficients c_i are non-zero.

Another wording: a set of vectors is *linearly dependent* if at least one of them may be expressed as a linear combination of one or more of the others.

A give set of vectors $\{\vec{X}_1\,,\,\vec{X}_2\,,\,\vec{X}_3\,,\,\cdots\,,\,\vec{X}_n\}$ is said to ***generate*** or ***span*** a given vector space if *every* vector in that space may be expressed as a linear combination of those n vectors.

e.g.,

Any set of vectors which spans a given vector space is called a ***generating system*** for that space. If the members of such a *generating system* are *linearly independent*, they are said to form a ***basis*** for that space.

The ***dimension*** of a given vector space is the *minimum* number or vectors required to span it,

or ... it is the *maximum* number of linearly *in*dependent vectors in that space.

Example (i). The set of "ordered 4–tuple" vectors $\vec{S}=(1,2,0,4)\,,\;\vec{T}=(-1,0,5,1)$ and $\vec{U}=(1,6,10,14)$ is linearly dependent, since

$$3\,\vec{S}\;+\;2\,\vec{T}\;-\;\vec{U}\;=\;\vec{0}$$

Example (ii). Are the three vectors $\vec{S}=(2,-1,7)\,,\;\vec{T}=(-4,6,-5)$ and $\vec{U}=(6,-7,12)$ linearly dependent ?

[4] The "trivial" solution would be the one for which $c_1=c_2=c_3=\cdots\;=c_n=0\,.$

Example (iii). Determine the *dimension* of the vector space spanned by the polynomials

$$\begin{aligned}\vec{v}_1 &= 3\,x \;-\; 7\,x^3 \;+\; 5\,x^5\\ \vec{v}_2 &= \;-\; x \;+\; 3\,x^2 - x^3 \;+\; 6\,x^4\\ \vec{v}_3 &= 2\,x^2 \;+\; 3\,x^4\\ \vec{v}_4 &= x \;+ x^2 \;+\; x^3\end{aligned}$$

and give a *basis* for this space.

Ans. If these vectors are linearly *de*pendent, then there exists a non-trivial solution of the equation:

$$c_1\;\vec{v}_1 \;+\; c_2\;\vec{v}_2 \;+\; c_3\;\vec{v}_3 \;+\; c_4\;\vec{v}_4 \;=\; 0$$

Hence, let us attempt to determine coefficients c_1, c_2. c_3 and c_4 such that:

$$c_1\left(3\,x - 7\,x^3 + 5\,x^5\right) \;+\; c_2\left(-\,x + 3\,x^2 - x^3 + 6\,x^4\right) \;+\; c_3\left(2\,x^2 + 3\,x^4\right) \;+\; c_4\left(x + x^2 + x^3\right) \;=\; 0$$

4.3 Inner-Product Vector Spaces

An *inner product* is a straightforward generalization of the *dot product* or *scalar product* operation encountered in geometric vector spaces.

A given vector space is called an ***inner-product space*** if every pair of vectors $\vec{u}$ and $\vec{v}$ in that space is associated with a unique *scalar* quantity denoted $\langle \vec{u} \,|\, \vec{v} \rangle$, called the *inner product* of $\vec{u}$ and $\vec{v}$, which satisfies the following requirements:

(i) For every vector $\vec{v}$ in that space, $|\vec{v}|^2 \equiv \langle \vec{v} \,|\, \vec{v} \rangle$ is a *real* and non-negative number, and $\langle \vec{v} \,|\, \vec{v} \rangle = 0$ if and only if $\vec{v}=0$.

(ii) $\langle \vec{u} \,|\, \vec{v} \rangle = \langle \vec{v} \,|\, \vec{u} \rangle^*$

(iii) For any scalar k, $\langle \vec{u} \,|\, k\,\vec{v} \rangle = k \langle \vec{u} \,|\, \vec{v} \rangle$

(iv) $\langle \vec{u} \,|\, \vec{v} + \vec{w} \rangle = \langle \vec{u} \,|\, \vec{u} \rangle + \langle \vec{u} \,|\, \vec{w} \rangle$ i.e., the inner product operation is *distributive*.

One can also show that

Theorem 4.2 $|\langle \vec{u} \,|\, \vec{v} \rangle| \leq |\,\vec{u}\,|\,|\,\vec{v}\,|$. {This is the same as saying that $|\langle \vec{u} \,|\, \vec{v} \rangle|^2 \leq \langle \vec{u} \,|\, \vec{u} \rangle \langle \vec{v} \,|\, \vec{v} \rangle$}

This inequality is used in the formal derivation of the Heisenberg uncertainty principle of quantum mechanics.

Theorem 4.3 $|\,\vec{u}+\vec{v}\,| \equiv \sqrt{\langle \vec{u}+\vec{v} \,|\, \vec{u}+\vec{v} \rangle} \leq |\,\vec{u}\,| + |\,\vec{v}\,|$

Note: (a) Many vector spaces *are not* inner-product spaces!

(b) The precise operational definition of the *inner product*
[i.e., the procedure for evaluating $\langle \vec{u} \,|\, \vec{v} \rangle$ for a given pair of vectors $\vec{u}$ and $\vec{v}$]
is a property of the particular type of inner-product space being considered. Thus, a description of this procedure is an essential part of the identification of a particular vector space.

Example (i). The set of geometric 3-component vectors in real 3-dimensional space, with the inner product $\langle \vec{u} \,|\, \vec{v} \rangle$ defined as the dot product (scalar product) $\vec{u} \cdot \vec{v}$.

Because all components of these vectors are real, $\vec{u}^{\,*} = (u_1^*, u_2^*, u_3^*) = (u_1, u_2, u_3) = \vec{u}$, and hence

Example (ii). A set of ordered n–tuples over the field of *complex* numbers, with the inner product defined by the operation $\langle \vec{u} \,|\, \vec{v} \,\rangle = u_1^* \, v_1 + u_2^* \, v_2 + u_3^* \, v_3 + u_4^* \, v_4 + ... + u_n^* \, v_n$.

This definition of an inner product is clearly a simple generalization of the inner product for geometric vectors with real-number components; the added twist is that the components of the vector appearing *first* in the inner product all appear as complex conjugates of the corresponding vector components.

It is simple to show that this set of objects satisfies all the requirements of an inner product vector space.

e.g., Consider the vector space generated from all possible linear combinations of the three vectors $\vec{v}_1 = (1\,,\, i\,,\, -1)\,,\ \vec{v}_2 = (2i\,,\, 3i\,,\, -4)$ and $\vec{v}_3 = (1+i\,,\, 1-i\,,\, 2i)$. Determine numerical values of the inner products $\langle \vec{v}_1 \,|\, \vec{v}_2 \,\rangle\,,\ \langle \vec{v}_2 \,|\, \vec{v}_1 \,\rangle\,,\ \langle \vec{v}_1 \,|\, \vec{v}_3 \,\rangle\,,\ \langle \vec{v}_3 \,|\, \vec{v}_1 \,\rangle\,,\ \langle \vec{v}_1 \,|\, \vec{v}_1 \,\rangle$ and $\langle \vec{v}_2 \,|\, \vec{v}_2 \,\rangle$.

Function Vector Spaces

A vector space of *functions* consists of a set of functions characterized by some defining properties, such as the set of all polynomials with real coefficients, or the set of functions $\{\sin(mx)\}$ for $m = 1, 2, 3, \ldots$. In a vector space of functions, the *inner product* is defined as a *definite integral* with specified upper and lower bounds, and a particular "weight function" $w(x)$:

$$\langle\, \vec{f}(x) \,|\, \vec{g}(x) \,\rangle \;\equiv\; \int_a^b \vec{f}^{\,*}(x)\, \vec{g}(x)\, w(x)\, dx$$

If the functions are *real*, the *weight function* $w(x)$ must also be real since the requirement $\langle\, \vec{g}(x) \,|\, \vec{f}(x) \,\rangle = \langle\, \vec{f}(x) \,|\, \vec{g}(x) \,\rangle^*$ must be satisfied. [In many cases of interest, $w(x) = 1$.]

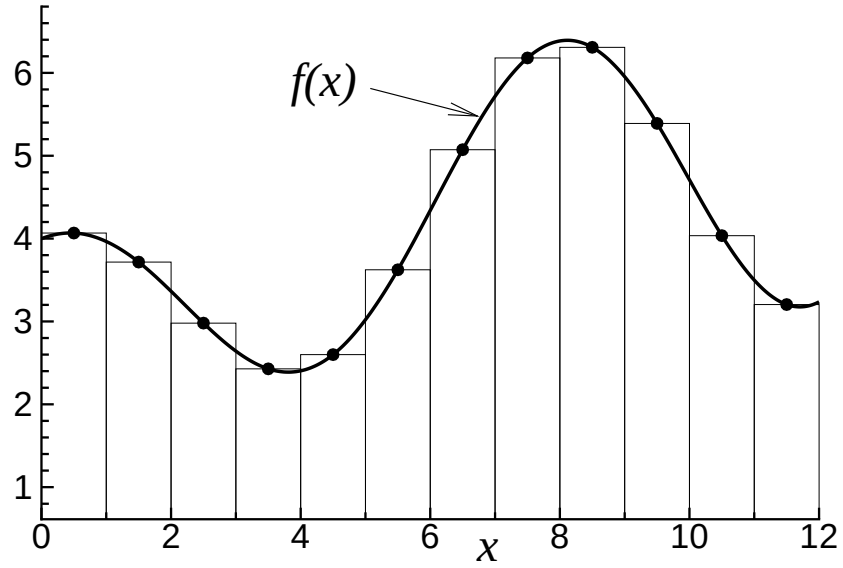
Example 1: Consider the inner-product vector space generated by the four vectors: $\vec{v}_1 = (1+i) + (1-i)\,x$, $\vec{v}_2 = 2i\,x^2$, $\vec{v}_3 = x + x^2$ and $\vec{v}_4 = (1-2i)\,x^3$, where the inner product integration interval is $[a, b] = [0, 1]$ and the weight function is $w(x) = 1$.

Evaluate the inner products of all possible various combinations of these vectors.

Exercise 4.8 For the same interval and vectors given above, evaluate these inner products for the case in which the weight function is $w(x) = x$.

Analogy between Ordered n–tuples and Functions as Vectors

Consider some smooth function $f(x)$. It is clearly possible to approximate its behaviour in terms of a series of steps of some fixed width (say, width = 1) so that its actual behaviour over the interval $0 \leq x \leq 12$ is reasonably well mimicked by listing the values of the function in the middle of each of those intervals.



For example, in the above figure, we approximate the behaviour of the function $f(x)$ by the set of function values $f(x=0.5)$, $f(x=1.5)$, $f(2.5)$, $f(3.5)$, $f(4.5)$ $\ldots$, $f(11.5)$. If this $f(x)$ is a member of a function vector space, we can approximately represent it by the ordered 12–tuple:

$$\vec{f}(x) \;\approx\; (\, f(0.5),\, f(1.5),\, f(2.5),\, f(3.5), \ldots\,,\, f(11.5)\,)$$

If we make the step width narrower, we will clearly have a better representation of the real function $f(x)$, although it will of course requires use of a higher-order n–tuple. In general, any function vector may be thought of as being an ordered n–tuple in the limit when the step length goes to zero.

Consider the nature of the inner product of two such n–tuples, representing functions $\vec{f}(x)$ and $\vec{g}(x)$:

$$\begin{aligned}
\langle\, \vec{f}(x)\,|\,\vec{g}(x)\,\rangle \;&=\; \langle\, (f(x_1), f(x_2), f(x_3), \ldots\,, f(x_n)) \;|\; (g(x_1), g(x_2), g(x_3), \ldots\,, g(x_n))\,\rangle \\
&=\; f^*(x_1)\, g(x_1) + f^*(x_2)\, g(x_2) + f^*(x_3)\, g(x_3) + \ldots\; + f^*(x_n)\, g(x_n)
\end{aligned}$$

Of course, if this approach is to provide a meaningful approximation to the true inner product function, its value must become independent of the number of steps used. This occurs if the sum in the last row of the above equation is multiplied by the width of the interval $\delta x = |x_2 - x_1|$. In the limit when the number of steps $\to \infty$ (and hence the step width $\delta x \to 0$), this ordered n-tuple sum becomes our integral definition of the inner produce of a pair of functions.

Thus, function vectors in an inner-product vector space may be thought of as simple ordinary ordered n–tuples with an *infinite* number of components corresponding to values of the function at equally-spaced points with an *infinitesimal* nearest-neighbour separation. Just as with ordinary ordered n–tuples, the number of components does not determine the dimension of the space.

Notes

(a) There exist other commonly used notations for the definition of an "inner product" or "scalar product" in inner-product vector spaces. In particular, what we write as $\langle\, \vec{u}\,|\,\vec{v}\,\rangle$ is sometimes written as $(\,\vec{u}\,,\,\vec{v}\,)$. Our choice of notation is based on the fact that this "bra–ket" notation, in which $\langle\, \vec{u}\,|$ is called a "bra" vector and $|\,\vec{u}\,\rangle$ is called a "ket" vector, is almost universally used in quantum mechanics.

(b) What we have introduced here is usually called a "Hermitian" inner product, where the Hermitianness is based on the property that

$$\langle\, \vec{u}\,|\,\vec{v}\,\rangle \;=\; \langle\, \vec{v}\,|\,\vec{u}\,\rangle^*$$

Of course, in an inner-product space in which all components of all vectors are real, and we only allow multiplication by real scalars, clearly

$$\langle\, \vec{u}\,|\,\vec{v}\,\rangle \;=\; \langle\, \vec{v}\,|\,\vec{u}\,\rangle^* \;=\; \langle\, \vec{v}\,|\,\vec{u}\,\rangle$$

This would be what we call a "Euclidean" vector space; a familiar example is our conventional 3-dimensional geometric space with the inner product defined as the vector scalar product. However, such Euclidean vector spaces are clearly just *subspaces* of some corresponding more general Hermitian vector space, in which the vector components (functions) can have complex values.

(c) In Hermitian vector spaces there exist two "modes" in which a given vector can be represented:

$$\text{as a "ket" vector } |\,\vec{v}\,\rangle \quad \text{or} \quad \text{as a "bra" vector } \langle\, \vec{v}\,|\,,$$

each being known as the "dual" of the other. Taking a linear combination of *ket* vectors always yields another *ket* vector, and taking a linear combination of *bra* vectors always yields another *bra* vector. However, one *cannot* combine *bra* and *ket* vectors in a single linear combination: such an object is not allowed!

Vectors in different modes can only be coupled through taking the inner product $\langle\, \vec{u}\,|\,\vec{v}\,\rangle$.

e.g., In a Hermitian vector space of *column* matrices, the *dual* of a given vector is a *row* matrix whose elements are the complex conjugates if corresponding row elements in the original vector.

(d) Orthogonality and Normalization

- A pair of vectors in a given *inner-product vector space* is said to be "orthogonal" if and only if their inner product is zero.

- A given vector $\vec{u}$ in an inner-product vector space is said to be "normalized" if and only if $\langle \vec{u} \,|\, \vec{u} \rangle = 1$.

- A given set of vectors $\{ \vec{v}_1 , \vec{v}_2 , \vec{v}_3 , \ldots , v_n \}$ is said to be "orthonormal" if they are all mutually orthogonal, and they are all normalized.

(e) Generalized Geometric Significance of the Inner Product

In our discussion of scalar products in geometric vector spaces on pp. 2 of this Chapter, we saw that

$$\begin{aligned} \vec{u} \cdot \vec{v} &= \{\text{length of one vector}\} \times \{\text{component of the other } \parallel \text{ to the first}\} \\ &= \{\text{length of } \vec{u}\} \times \{\text{length of the projection of } \vec{v} \text{ in direction parallel to } \vec{u}\} \\ &= \{\text{length of } \vec{v}\} \times \{\text{length of the projection of } \vec{u} \text{ in direction parallel to } \vec{v}\} \end{aligned}$$

This verbal description is valid for any Euclidean (real) inner-product vector space.

However, for a *Hermitian* vector space, only one of those definitions is correct:

$$\langle \vec{u} \,|\, \vec{v} \rangle \;=\; \{\text{length of } \vec{u}\} \times \{\text{length of projection of } \vec{v} \text{ in direction parallel to } \vec{u}\}$$

Note that the value of the inner product has built into it the information about whether the projection of the *ket* vector in the direction of the *bra* vector is parallel or anti-parallel. In Euclidean spaces this information is simply given by the algebraic sign ($\pm$) of the inner product.

4.4 Orthogonal Bases: the Gram-Schmidt Orthogonalization Process

In a given vector space, it is possible to express any particular vector in terms of *any* basis, independent of whether of not the basis vectors are orthogonal. However, in general it is much easier to determine the coefficients defining the vector in terms of the basis if that basis is orthogonal.

***For Example*:** In a 2-D Euclidean vector space, it is trivially straightforward to describe the vector $\vec{v} = (7, 3) = 7\,\widehat{e}_1 + 3\,\widehat{e}_2$ in terms of unit vectors $\widehat{e}_1$ and $\widehat{e}_2$ pointing along the x and y axes.

However, how do we determine how to express this same vector $\vec{v}$ in terms of the equally valid pair of basis vectors $\vec{b}_1 = (1, 2)$ and $\vec{b}_2 = (1, -2)$?

This problem becomes even more complicated for function vector spaces, so let's find a better way!

Question: If a given set of vectors $\{\vec{v}_1, \vec{v}_2, \vec{v}_3, \ldots, \vec{v}_n\}$ spans a given vector space, *how do we determine an orthonormal basis for this space ?*

<u>*Solution:*</u> use the ***Gram-Schmidt*** orthogonalization procedure.

1. We must first choose some vector as a starting point. We arbitrarily select $\vec{v}_1$, and then label it with a prime $'$ to identify it as a member of our new orthogonal basis: $\vec{v}_1{}' = \vec{v}_1$.

2. We know that if we consider the subspace formed by $\vec{v}_1{}'$ and any one of the other vectors, say $\vec{v}_2$, we can find some other vector in that space which is orthogonal to $\vec{v}_1{}'$, which together with $\vec{v}_1{}'$ can form an alternate basis for that subspace. Since it lies in the subspace, this orthogonal second vector may be written as
$$\vec{v}_2{}' \;=\; a\,\vec{v}_2 + b\,\vec{v}_1{}' \;=\; a\left\{\,\vec{v}_2 + \left(\frac{b}{a}\right)\,\vec{v}_1{}'\,\right\}$$
where a and b are scalar constants which we wish to determine.

   Since this second vector is defined by the fact that is is orthogonal to $\vec{v}_1{}'$, necessarily:

This yields the result: $\vec{v}_2\,' \;=\; a\left\{\;\vec{v}_2 \;-\; \dfrac{\langle\,\vec{v}_1\,'\,|\,\vec{v}_2\,\rangle}{\langle\,\vec{v}_1\,'\,|\,\vec{v}_1\,'\,\rangle}\;\vec{v}_1\,'\;\right\}$

Clearly, the scalar constant a may be selected arbitrarily, since if $\vec{v}_2\,'$ is orthogonal to $\vec{v}_1\,'$, then so is $k\,\vec{v}_2\,'$, for any (non-zero) scalar k.

---

3. If we now consider the 3-dimensional subspace generated by the vectors $\vec{v}_1\,'$, $\vec{v}_2\,'$ and (say) $\vec{v}_3$, we can define a new third basis vector in that space, $\vec{v}_3\,'$, by the requirement that it must be orthogonal to both $\vec{v}_1\,'$ and $\vec{v}_2\,'$. In particular,

$$\vec{v}_3\,' \;=\; a\,\vec{v}_3 + b\,\vec{v}_1\,' + c\,\vec{v}_2\,' \;=\; a\left\{\,\vec{v}_3 + \left(\frac{b}{a}\right)\,\vec{v}_1\,' + \left(\frac{c}{a}\right)\,\vec{v}_2\,'\,\right\}$$

where a, b and c are scalar constants which we wish to determine.

Since $\vec{v}_3\,'$ is *defined by* the fact that is is orthogonal to both $\vec{v}_1\,'$ and $\vec{v}_2\,'$, necessarily

This yields the result: $\vec{v}_3\,' \;=\; a\left\{\;\vec{v}_3 \;-\; \dfrac{\langle\,\vec{v}_1\,'\,|\,\vec{v}_3\,\rangle}{\langle\,\vec{v}_1\,'\,|\,\vec{v}_1\,'\,\rangle}\;\vec{v}_1\,' \;-\; \dfrac{\langle\,\vec{v}_2\,'\,|\,\vec{v}_3\,\rangle}{\langle\,\vec{v}_2\,'\,|\,\vec{v}_2\,'\,\rangle}\;\vec{v}_2\,'\;\right\}$

This new vector is clearly the original $\vec{v}_3$ *minus* {the portion of $\vec{v}_3$ pointing in direction $\vec{v}_1\,'$} *minus* {the portion of $\vec{v}_3$ pointing in direction $\vec{v}_2\,'$}.

Once again, the constant a is an arbitrary scaling factor.

---

4. Similarly, we can determine a fourth vector which is orthogonal to the first three using the expression

$$\vec{v}_4\,' \;=\; a\left\{\;\vec{v}_4 \;-\; \frac{\langle\,\vec{v}_1\,'\,|\,\vec{v}_4\,\rangle}{\langle\,\vec{v}_1\,'\,|\,\vec{v}_1\,'\,\rangle}\;\vec{v}_1\,' \;-\; \frac{\langle\,\vec{v}_2\,'\,|\,\vec{v}_4\,\rangle}{\langle\,\vec{v}_2\,'\,|\,\vec{v}_2\,'\,\rangle}\;\vec{v}_2\,' \;-\; \frac{\langle\,\vec{v}_3\,'\,|\,\vec{v}_4\,\rangle}{\langle\,\vec{v}_3\,'\,|\,\vec{v}_3\,'\,\rangle}\;\vec{v}_3\,'\;\right\}$$

Generalizing, for the n^{th} orthogonal vector in this space, the Gram-Schmidt formula gives:

$$\vec{v}_n\,' \;=\; a\left\{\;\vec{v}_n \;-\; \sum_{m=1}^{n-1}\;\frac{\langle\,\vec{v}_m\,'\,|\,\vec{v}_n\,\rangle}{\langle\,\vec{v}_m\,'\,|\,\vec{v}_m\,'\,\rangle}\;\vec{v}_m\,'\;\right\}$$

While it is certainly convenient to represent arbitrary vectors (functions) in terms of an *orthogonal* basis, it is even more convenient to work with an *orthonormal basis*, an *orthogonal* basis of unit-normalized vectors. We can clearly normalize any vector $\vec{v}_n\,'$ using the following expression:

$$\widehat{v}_n\,' \;=\; \frac{1}{\sqrt{\langle\, \vec{v}_n\,' \,|\, \vec{v}_n\,' \,\rangle}}\; \vec{v}_n\,'$$

If we normalize each member of our new orthogonal basis set as it is produced, our general Gram-Schmidt expression becomes:

$$\vec{v}_n\,' \;=\; a \left\{ \vec{v}_n \;-\; \sum_{m=1}^{n-1} \langle\, \widehat{v}_m\,' \,|\, \vec{v}_n \,\rangle\; \widehat{v}_m\,' \right\}$$

Exercise 4.9 Starting with the three Euclidean vectors $\vec{v}_1 = (0, -1, 0)$, $\vec{v}_2 = (1, 1, 2)$ and $\vec{v}_3 = (-1, 0, 3)$, determine an orthogonal basis using the Gram-Schmidt procedure.

Exercise 4.10 Starting with the same three Euclidean vectors considered in Exercise 3.9, but with the order of the first two vectors interchanged, $\vec{v}_1 = (1, 1, 2)$, $\vec{v}_2 = (0, -1, 0)$, and $\vec{v}_3 = (-1, 0, 3)$, determine an orthogonal basis using the Gram-Schmidt procedure.

Exercise 4.11 Starting with the three vectors $\vec{v}_1 = (1, i, 2)$, $\vec{v}_2 = (i, -1, 2i)$ and $\vec{v}_3 = (i, 1, -1)$ in a Hermitian vector space, determine an orthogonal basis using the Gram-Schmidt procedure.

Exercise 4.12 Consider the vector space generated by all possible linear combinations of the function vectors $1, x, x^2, x^3, x^4, \ldots$ etc., with the inner product defined on the interval $[a, b] = [-1, 1]$ and the weight function $w(x) = 1$. Determine an orthonormal basis for this space.
[Compare your results with the differential equation solutions determined on pp. 19−21 of Chapter 3 of the Notes.]

We have just obtained the following set of "orthogonal polynomials" by applying the Gram-Schmidt procedure on the interval $[-1,\,1]$ with weight function $w(x)=1$.

$$\begin{aligned}
\vec{v}_1\,' &= 1 \\
\vec{v}_2\,' &= x \\
\vec{v}_3\,' &= 1 - 3\,x^3 \\
\vec{v}_4\,' &= x - \tfrac{5}{3}\,x^3 \\
\vec{v}_5\,' &= 1 - 10\,x^2 + \tfrac{35}{3}\,x^4 \\
\vec{v}_6\,' &= x - \tfrac{14}{3}\,x^3 + \tfrac{21}{5}\,x^5 \\
\vec{v}_7\,' &= \ldots
\end{aligned}$$

This turns out to be exactly the same set of polynomials we determined on pp. 16 − 21 of Chapter 3 when we used the method of solution-by-series to solve the differential equation

$$(1-x^2)\,\frac{d^2P(x)}{dx^2} - 2\,x\,\frac{dP(x)}{dx} + A\,P(x) \;=\; 0$$

and applied the "boundary condition" that the solution must have finite values everywhere on the range $-1 \le x \le +1$.

This illustrates a general property of linear, homogeneous, second-order differential equations with "eigenvalue" boundary conditions: their solutions are a set of *orthogonal polynomials* associated with a weight function and interval $[a,b]$ which are peculiar to that particular differential equation. Other important examples are the *Hermite polynomials* obtained on solving the Schrödinger equation for vibrational motion subject to a harmonic potential function, and the *Laguerre polynomials* which you encountered in Problem Set #3 as solutions to the Schrödinger equation for radial motion in a hydrogenic atom.

Recurrence Relations

It may be shown formally that solutions of a linear, homogeneous differential such as the "Legendre" equation are related by what we call *recurrence relations* which allow solutions of different order to be defined in terms of one another.

For a set of such orthogonal polynomials $\{\,f_n(x)\,\}$, the general form of a *recurrence relation* is

$$a_{1,n}\,f_{n+1}(x) \;=\; (\,a_{2,n} + a_{3,n}\,x)\,f_n(x) - a_{4,n}\,f_{n-1}(x)$$

For the ordinary Legendre functions, those coefficients are

$$\begin{aligned}
a_{1,n} &= n+1 \\
a_{2,n} &= 0 \\
a_{3,n} &= 2n+1 \\
a_{4,n} &= n
\end{aligned}$$

which yields: $\qquad (n+1)\,P_{n+1}(x) \;=\; (2n+1)\,x\;P_n(x) - n\,P_{n-1}(x)$

Let us use this *recurrence relation* to generate the Legendre polynomials, starting with: $\quad P_0(x) = 1$

Sets of recurrence-relation coefficients $\{a_{1,n}\,,\,a_{2,n}\,,\,a_{3,n}\,,\,a_{4,n}\}$ for generating the orthogonal polynomial solutions of a number of differential equations may be found in Table 22.7 (p. 782) of *Handbook of Mathematical Functions*, by M. Abramowitz and I.A. Stegun
(http://www.knovel.com/knovel2/Toc.jsp?BookID=528 from any UWaterloo IP address).

Components of a Vector Relative to Some Orthogonal Basis

Given an orthogonal basis $\{\vec{\phi}_i\}$ for a given vector space, then any vector $\vec{v}$ in that space may be expressed as a linear combination of those basis vectors:

$$\vec{v} \;=\; \sum_{i=1} a_i\,\vec{\phi}_i \;=\; a_1\,\vec{\phi}_1 + a_2\,\vec{\phi}_2 + a_3\,\vec{\phi}_3 + a_4\,\vec{\phi}_4 + ...$$

We want to be able to find the values of the expansion coefficients a_i.

This turns out to be a very straightforward thing to do!

Choose any one of the basis vectors $\vec{\phi}_j$ and take its inner product with $\vec{v}$:

$$\langle\,\vec{\phi}_j\,|\,\vec{v}\,\rangle \;=$$

What is the Error in a Given Finite-Basis Approximation?

or

What is the error in approximating a function by a finite set of basis functions?

Consider a vector $\vec{u}$ which lies partially inside a vector subspace generated by the first $\boldsymbol{n}$ of our basis vectors $\{\vec{\phi}_i\}$, and partially outside of it. To find the part of $\vec{u}$ which lies *outside* that subspace, we simply subtract from $\vec{u}$ its components in the "directions" of the first n of our basis vectors. This yields:

where $\quad \vec{u}\,' =$

is an approximation to the full vector $\vec{u}$. Moreover, as n increases, this approximation will become an ever better approximation to the full $\vec{u}$. For any particular value of n, it is therefore reasonable to speak of the "error" in our approximation as being the difference $\Delta\vec{u} = \vec{u} - \vec{u}\,'$. The magnitude of this error is clearly

$$|\,\Delta\vec{u}\,| \;\equiv\; \sqrt{\langle\,\Delta\vec{u}\,|\,\vec{\Delta}u\,\rangle} \;=\; \sqrt{\langle\,\vec{u}-\vec{u}\,'\,|\,\vec{u}-\vec{u}\,'\,\rangle}$$

and since the basis vectors $\vec{\phi}_i$ form an orthogonal set

$$|\,\Delta\vec{u}\,|^2 \;=\; \langle\,(\vec{u}-\vec{u}\,')\,|\,(\vec{u}-\vec{u}\,')\,\rangle \;=\; \left\langle\, \vec{u}-\sum_{i=1}^{n}\frac{\langle\,\vec{\phi}_i\,|\,\vec{u}\,\rangle}{\langle\,\vec{\phi}_i\,|\,\vec{\phi}_i\,\rangle}\,\vec{\phi}_i \;\right|\; \vec{u}-\sum_{j=1}^{n}\frac{\langle\,\vec{\phi}_j\,|\,\vec{u}\,\rangle}{\langle\,\vec{\phi}_j\,|\,\vec{\phi}_j\,\rangle}\,\vec{\phi}_j \,\right\rangle$$

$$= \;\langle\,\vec{u}\,|\,\vec{u}\,\rangle \;-\; \sum_{j=1}^{n}\frac{\langle\,\vec{\phi}_j\,|\,\vec{u}\,\rangle}{\langle\,\vec{\phi}_j\,|\,\vec{\phi}_j\,\rangle}\,\langle\,\vec{u}\,|\,\vec{\phi}_j\,\rangle \;-\; \sum_{i=1}^{n}\left(\frac{\langle\,\vec{\phi}_i\,|\,\vec{u}\,\rangle}{\langle\,\vec{\phi}_i\,|\,\vec{\phi}_i\,\rangle}\right)^{*}\langle\,\vec{\phi}_i\,|\,\vec{u}\,\rangle$$

$$+\;\sum_{i=1}^{n}\sum_{j=1}^{n}\left(\frac{\langle\,\vec{\phi}_i\,|\,\vec{u}\,\rangle}{\langle\,\vec{\phi}_i\,|\,\vec{\phi}_i\,\rangle}\right)^{*}\left(\frac{\langle\,\vec{\phi}_j\,|\,\vec{u}\,\rangle}{\langle\,\vec{\phi}_j\,|\,\vec{\phi}_j\,\rangle}\right)\left\langle\,\vec{\phi}_i\,|\,\vec{\phi}_j\,\right\rangle$$

$$= \;\langle\,\vec{u}\,|\,\vec{u}\,\rangle \;-\; \sum_{j=1}^{n}\frac{\langle\,\vec{u}\,|\,\vec{\phi}_j\,\rangle\langle\,\vec{\phi}_j\,|\,\vec{u}\,\rangle}{\langle\,\vec{\phi}_j\,|\,\vec{\phi}_j\,\rangle} \;-\; \sum_{i=1}^{n}\frac{\langle\,\vec{u}\,|\,\phi_i\,\rangle\langle\vec{\phi}_i\,|\,\vec{u}\,\rangle}{\langle\,\vec{\phi}_i\,|\,\vec{\phi}_i\,\rangle}$$

$$+\;\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{\langle\,\vec{u}\,|\,\phi_i\,\rangle}{\langle\,\vec{\phi}_i\,|\,\vec{\phi}_i\,\rangle}\frac{\langle\,\vec{\phi}_j\,|\,\vec{u}\,\rangle}{\langle\,\vec{\phi}_j\,|\,\vec{\phi}_j\,\rangle}\left\langle\,\vec{\phi}_j\,|\,\vec{\phi}_j\,\right\rangle\,\delta_{ij}$$

$$= \;\langle\,\vec{u}\,|\,\vec{u}\,\rangle \;-\; \sum_{j=1}^{n}\frac{\left|\langle\vec{\phi}_j\,|\,\vec{u}\,\rangle\right|^2}{\langle\,\vec{\phi}_j\,|\,\vec{\phi}_j\,\rangle} \;=\; \langle\,\vec{u}\,|\,\vec{u}\,\rangle \;-\; \sum_{j=1}^{n}|a_j|^2\,\langle\vec{\phi}_j|\vec{\phi}_j\rangle$$

4.5 An Illustrative Application of Orthogonality & Recurrence Relations

We have seen that we can solve a differential equation by the method of solution by series and determine a set of polynomial eigenfunction solutions, and that that same set of functions can also be determined by the Gram-Schmidt procedure for some appropriate weight function $w(x)$ and interval $[a,\, b]$. It was also mentioned that (within scalar factors) we can generate the same set of orthogonal functions using a ***recurrence*** relation, which interrelates polynomial solutions of different order.

In particular, for the Legendre differential equation

$$(1-x^2)\,\frac{d^2P(x)}{dx^2} \;-\; 2x\,\frac{d\,P(x)}{dx} \;+\; A\,P(x) \;=\; 0$$

we found [class notes, § 3.4.3] that the method of solution by series yielded eigenfunctions $P_n(x)$ corresponding to eigenvalues $A = n(n+1)$, where $n = 0,\ 1,\ 2,\ 3,\ \ldots$. We later saw [pp. 21-24 in § 4.4] that these same functions could be obtained by applying the Gram-Schmidt procedure to the set of generating functions $\{\,1,\, x,\, x^2,\, x^3,\, \ldots\,\}$ on the interval $[-1,\, +1]$ with weight function $w(x) = 1$. We also discussed the fact (p. 24 in § 4.4) out that these same functions (within scalar factors) can be generated by the *recurrence* relation

$$(n+1)\;P_{n+1}(x) \;=\; (2n+1)\,x\,P_n(x) \;-\; n\,P_{n-1}(x)$$

Note that when the functions are obtained using this recurrence relation, their normalization factors are determined by the inner product result:

$$\langle\, P_n(x) | P_m(x)\,\rangle \;=\; \left(\frac{2}{2n+1}\right)\delta_{n,m} \tag{18}$$

In quantum mechanics, the "expectation value" or average value of a property $f(x)$ of the system when it is in the state with (unit normalized) eigenfunction $\widehat{P_n}(x)$ associated with quantum number n is defined as

$$\overline{f} \;=\; \langle f(x)\rangle \;\equiv\; \langle\, \widehat{P_n}(x) | f(x) | \widehat{P_n}(x)\,\rangle \;=\; \langle\, \widehat{P_n}(x) | \{\, f(x)\,\widehat{P_n}(x)\,\}\,\rangle \;=\; \left(\frac{2n+1}{2}\right)\langle\, P_n(x) | \{\, f(x)\,P_n(x)\,\}\,\rangle$$

$$=\; \left(\frac{2n+1}{2}\right)\int_a^b P_n(x)^*\; f(x)\; P_n(x)\; w(x)\; dx$$

where as usual, $\widehat{P_n}(x) = P_n(x)/\langle\, P_n(x)\,|\,P_n(x)\,\rangle^{1/2}$.

Exercise 4.13 Using our recurrence relation, *without* explicitly evaluating any integrals, determine expressions for the expectation values:

(i) $\langle\, \widehat{P_n}(x) | x | \widehat{P_n}(x)\,\rangle$ (ii) $\langle\, \widehat{P_n}(x) | x^2 | \widehat{P_n}(x)\,\rangle$

Ans. To begin, rearrange our recurrence relation to yield an expression for $x\,P_n(x)$ in terms of Legendre functions of higher and lower order.

Next, substitute this into the expression for the first of our expectation values:

$$\overline{x} \;=\; \langle x\rangle \;=\; \langle \widehat{P}_n(x)\,|\,x\,|\,\widehat{P}_n(x)\rangle \;=$$

Similarly, repeated application of our recurrence relation shows that

$$x^2\,\widehat{P}_n(x) = x\left\{x\,\widehat{P}_n(x)\right\} \;=$$

This then yields the result:

$$\overline{x^2} \;=\; \langle x^2 \rangle \;=\; \langle \widehat{P}_n(x)\,|\,x^2\,|\,\widehat{P}_n(x) \rangle \;=$$

In quantum mechanics, the functions $P_n(x)$ arise as solutions of the Legendre differential equation which governs the dependence on the polar angle θ (recall, $x = \cos\theta$) of the wavefunction for the rotation of a linear molecule, or for the angular motion of an electron in a hydrogenic atom. If light whose frequency $\nu_{m,n}$ corresponds to the level energy spacing ($\Delta E = |E_m - E_n| = h\,\nu_{m,n}$) shines on such a system, the probability that it will excite a transitions between states n and m is proportional to the factor

$$p_{\rm d}(m \leftarrow n) \;=\; \left| \left\langle \, \widehat{P_m}(x) \,|\, x \,|\, \widehat{P_n}(x) \, \right\rangle \right|^2$$

where the subscript d on the transition probability $p_{\rm d}(m \leftarrow n)$ reflects the fact that this is the expression associated with the "electric dipole" transition mechanism.

Exercise 4.14 Using only the recurrence and normalization relations given above, determine the relationship between m and n for which $p(m \leftarrow n)$ is non-zero (this relation is called a spectroscopic "selection rule"), and determine an expression for the value of $p(m \leftarrow n)$ for this case.

Exercise 4.15 In Raman spectroscopy, the transition intensities are proportional to the factor

$$p_{\rm R}(m \leftarrow n) \;=\; \left| \left\langle \, \widehat{P_m}(x) \,|\, x^2 \,|\, \widehat{P_n}(x) \, \right\rangle \right|^2$$

Determine the analogous "selection rule" and intensity factor $p_{\rm R}(m \leftarrow n)$ for Raman-allowed rotational transitions.

4.6 Fourier Series

Fourier series are a special application of our understanding of orthogonal bases and of how to determine the components or "projections" of an arbitrary given vector (or function) in terms of a finite number of those known orthogonal basis vectors (or functions). The error discussion above implies that we can in principle make our approximation achieve any chosen level of accuracy. One of the reasons for wanting to be able to do this is that the properties of the basis functions (e.g., their derivatives and integrals) may be very well known and very easy to evaluate.

Fourier series consist of expansions in term of basis functions of the form

$e^{\pm imx}$ or of the form $\sin(mx)$ and $\cos(mx)$, for $m = 0, 1, 2, 3, ...$

on the interval $[-\pi, +\pi]$ with weight function $w(x) = 1$.

$$f(x) \;=\; a_0 \cdot 1 \;+\; a_1^s \sin(x) \;+\; a_1^c \cos(x) \;+\; a_2^s \sin(2x) \;+\; a_2^c \cos(2x) \;+\; a_3^s \sin(3x) \;+\; \cdots$$

or

$$f(x) \;=\; c_0 \;+\; c_1\, e^{i\,x} + \; c_{-1}\, e^{-i\,x} + \; c_2\, e^{i\,2x} + \; c_{-2}\, e^{-i\,2x} \;+\; \cdots \;=\; \sum_{m=-\infty}^{\infty} c_m\, e^{i\,mx}$$

Exercise 4.16 For the real-value Fourier basis functions $\{\sin(mx), \cos(mx)\}$ on the interval $-\pi \le x \le +\pi$, show that all possible combinations of different functions are orthogonal, and determine the normalization factor for each basis function.

Recalling that since

$$\begin{cases} \sin(a+b) \;=\; \sin(a)\,\cos(b) \;+\; \cos(a)\,\sin(b) \\ \sin(a-b) \;=\; \sin(a)\,\cos(b) \;-\; \cos(a)\,\sin(b) \\ \cos(a+b) \;=\; \cos(a)\,\cos(b) \;-\; \sin(a)\,\sin(b) \\ \cos(a-b) \;=\; \cos(a)\,\cos(b) \;+\; \cos(a)\,\cos(b) \end{cases}$$

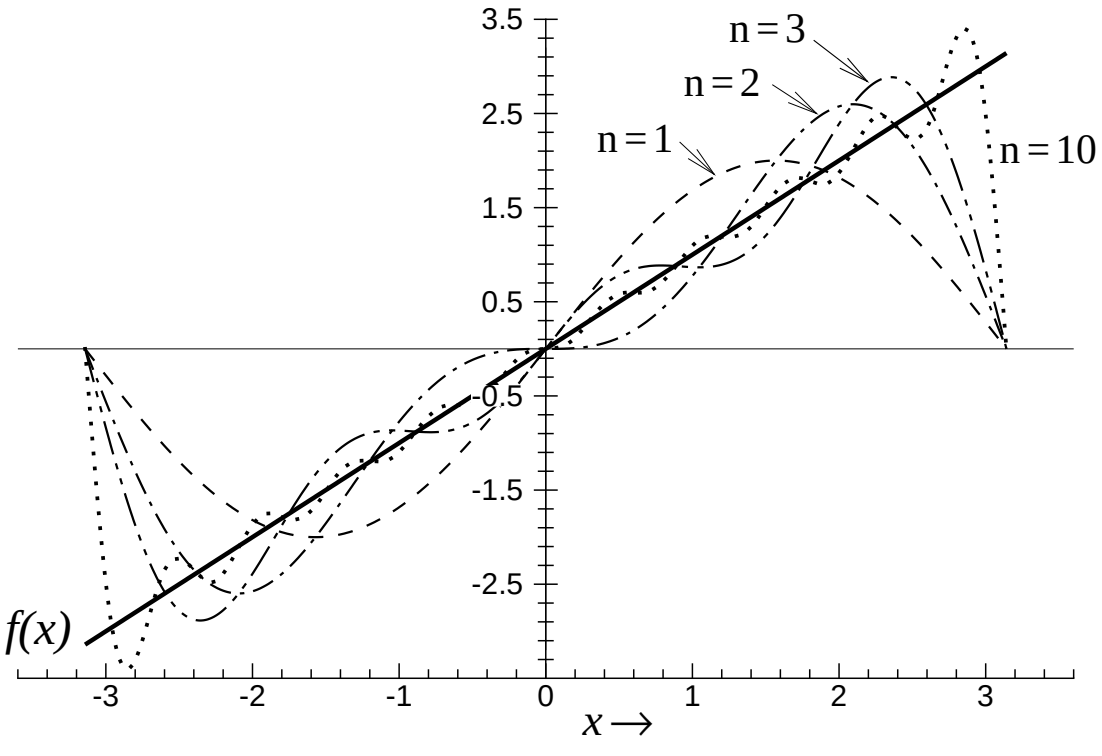
taking sums and differences yields

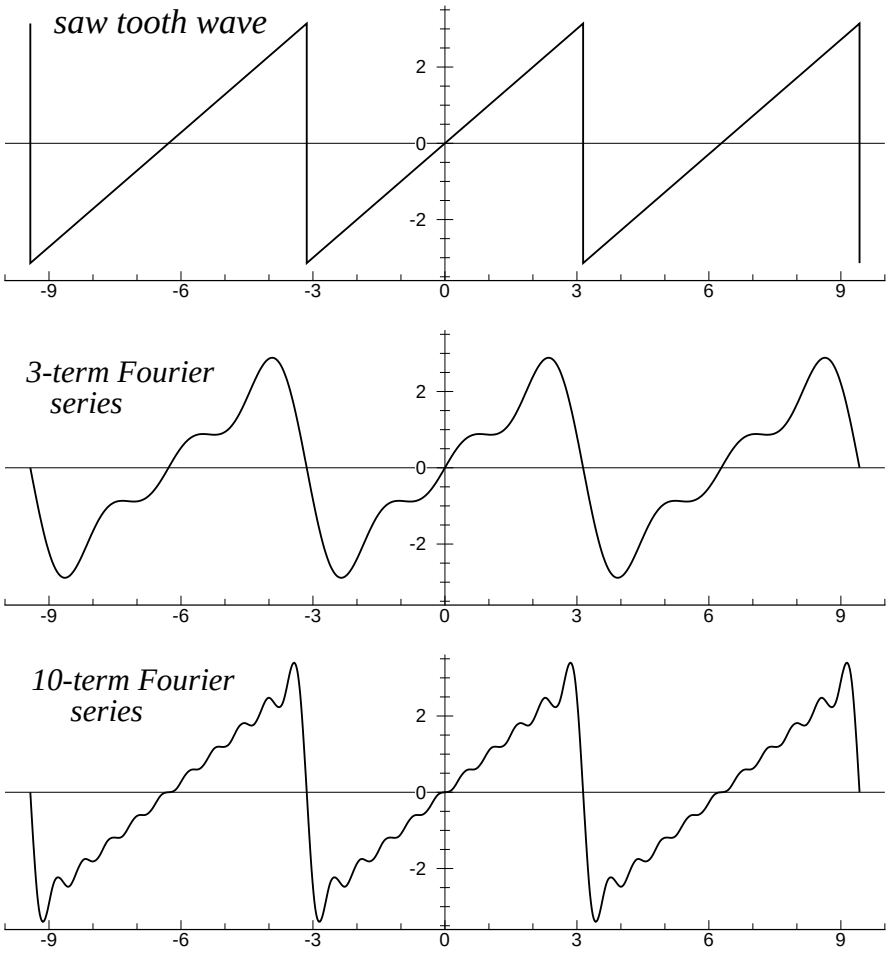
$$\begin{cases} \sin(a)\,\cos(b) \;=\; [\sin(a+b) \;+\; \sin(a-b)]/2 \\ \cos(a)\,\cos(b) \;=\; [\cos(a+b) \;+\; \cos(a-b)]/2 \\ \sin(a)\,\sin(b) \;=\; [\cos(a+b) \;-\; \cos(a-b)]/2 \end{cases}$$

One of the reasons that Fourier series are important is the fact that sinusoidal (or cosine) oscillations of electric and magnetic fields are relatively easy to generate with electronic devices, while other wave shapes such as square wave or sawtooth waves, are not. This problem may be resolved if a sufficiently accurate approximation to the desired wave shape may be constructed using a Fourier series approximation to the true shape.

Exercise 4.17 How accurately can we approximately the "sawtooth function" which has the shape $f(x) = x$ on the interval $-\pi \leq x \leq +\pi$, and repeats itself indefinitely with a period of length 2π, by a finite number of terms in a Fourier series?

Ans.




saw tooth wave
2
0
-2
-9
-6
-3
0
3
6
9
3-term Fourier series
2
0
-2
-9
-6
-3
0
3
6
9
10-term Fourier series
2
0
-2
-9
-6
-3
0
3
6
9

Note !

In general, a Fourier series consists of the set of all functions $\{\sin(mx) \quad \text{and} \quad \cos(mx)\}$ for $m=0$, 1, 2, 3, ... etc.

$$f(x) \;=\; a_0 \;+\; a_1^s \sin(x) \;+\; a_1^c \cos(x) \;+\; a_2^s \sin(2x) \;+\; a_2^c \cos(2x) \;+\; \cdots$$

Why did we consider only the $\sin(mx)$ in the above example ?

Exercise 4.18 For the function $f(x) = e^{ix/2}$, determine the expansion coefficients a_0 , a_1 , a_2 , b_1 and b_2 for the leading terms in its trigonometric Fourier series expansion:

$$f_p(x) \;=\; a_0 + \sum_{m=1}^{2} [\, a_m \cos(mx) + b_m \sin(mx) \,]$$

• What is the squared error $|\, f(x) - f_p(x) \,|^2$ associated with the approximation of representing $f(x)$ by $f_p(x)$?

Ans. $a_0 = 4/2\pi$, $a_1 = 4/3\pi$, $b_2 = -16i/15\pi$.

Exercise 4.19 Consider the square wave function

$$\begin{aligned} f(x) \;&=\; +1 \qquad \text{for} \qquad 0 \le x \le +L \\ &=\; -1 \qquad \text{for} \qquad -\,L \le x < 0 \end{aligned}$$

Determine the error $|\Delta f|$ in the approximation to this function provided by the first 10 non-zero terms in a Fourier series representation of it.

4.7 Fourier Transforms

Generalizing the Interval for Fourier Series

Because of the periodic nature of sine and cosine functions, it might appear that our initial definition of Fourier series restricts us to consideration of either

- functions which are only defined on the interval $[-\pi, +\pi]$ or
- functions defined on the infinite range $-\infty < x < \infty$ which are periodic with period 2π .

However, a simple change of variable in the sin/cos (or exponential) function argument allows Fourier series to be used either for

- any function defined on any finite interval $a \le x \le b$.

Moreover, making the simple change of variable $x \longrightarrow \dfrac{\pi x}{L}$ in the sin/cos function argument allows Fourier series to be used for

- any function which is defined on any symmetric interval of $-L \le x \le +L$ of length $2L$, or
- any function defined on an indefinite interval $-\infty < x < \infty$ which is periodic with 'wavelength' (i.e., period of repetition) $2L$.

In particular, for a function $f(x)$ defined on the symmetric interval $[-L, +L]$, we can write:

$$f(x) \;=\; \sum_m a_n^s \;\sin\Big(\frac{m\,\pi\,x}{L}\Big) \;+\; \sum_m a_n^c \;\cos\Big(\frac{m\,\pi\,x}{L}\Big)$$

where now

$$a_m^s \;=\; \frac{1}{L}\int_{-L}^{+L} f(x)\;\sin\Big(\frac{m\,\pi\,x}{L}\Big)\,dx \qquad \text{and} \qquad a_m^c \;=$$

Summarizing: In general, the effect of determining the Fourier expansion representation of a given function is to summarize our knowledge of the nature of that function $f(x)$ in terms of our knowledge of the values of the sets of coefficients $\{a_m\}$ and $\{b_m\}$. *The same information is available*, but instead of being stored as an (in general infinite) number of function values $f(x)$, it is stored as (in general) infinite sets of m–dependent expansion coefficients.

Making use of the Euler relation, for any function $f(x)$ defined on the interval $[-L, +L]$, we can replace our sin/cosine basis functions be exponentials, and write

$$f(x) \;=\; \sum_{m=-\infty}^{+\infty} c_m\; e^{\,i\,m(\pi\,x/L)} \qquad \text{where as usual} \qquad c_m = \frac{1}{L}\int_{-L}^{+L} f(x)\; e^{-im\pi\,x/L}\,dx$$

Since the step length from one term to another is $\Delta m = 1$, we can also write this as

$$f(x) \;=\; \sum_{m=-\infty}^{+\infty} c_m \; e^{i\,m\pi\,x/L} \; \Delta m$$

Now, consider what happens to this expression if we make the change of variable $k = m\pi/L$, so that $\Delta k = (\pi/L)\,\Delta m$, or $\Delta m = (L/\pi)\Delta k$. If we wish to make k our summation variable, $c_m \leftrightarrow c(k)$ and our expansion becomes

$$f(x) \;=\; \sum_{k=-\infty}^{+\infty} \left\{ \frac{L}{\pi}\, c(k) \right\} \; e^{i\,k\,x} \; \Delta k$$

Finally, if we want to use this expansion for virtually *any* function, then we will want to let the interval $[-L,\, +L]$ expand to $[-\infty,\, +\infty]$ by taking the limit as $L \to \infty$. Before we do this, however, it is convenient to replace our generalized coefficient $c(k)$ by the function $g(k) = \sqrt{2\pi}\,(L/\pi)\,c(k)$, where the factor of $\sqrt{2\pi}$ is introduced simply because it turns our to be convenient later.

After making this substitution, taking the limit as $L \to \infty$ means that:

$$f(x) \;=\; \frac{1}{\sqrt{2\pi}} \lim_{L\to\infty} \left\{ \sum_{k=-\infty}^{+\infty} g(k)\; e^{i\,k\,x} \; \Delta k \right\} \;=\; \frac{1}{\sqrt{2\pi}} \lim_{\Delta k\to 0} \left\{ \sum_{k=-\infty}^{+\infty} g(k)\; e^{i\,k\,x} \; \Delta k \right\}$$

$$\;=\; \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} g(k)\; e^{ikx} \; dk$$

Of course, application of the usual expression for determining the coefficients of a Fourier series on a general interval yields

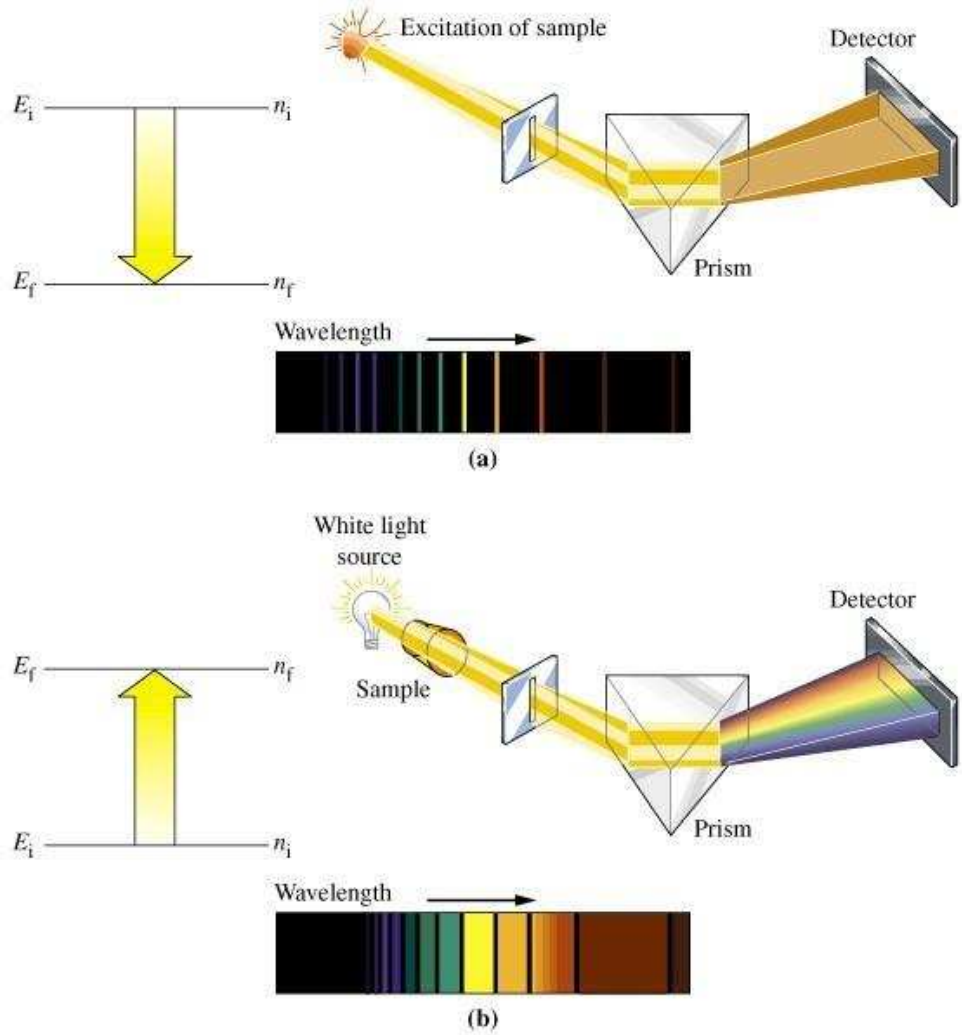
$$g(k) \;=\; \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(x)\; e^{-ikx} \; dx$$

These functions $f(x)$ and $g(k)$ are called *continuous Fourier transforms* of one another. As this final result suggests, the reason for introducing the the factor of $\sqrt{2\pi}$ into our definition of $g(k)$ was to achieve the symmetry we see between the forms of the forward and reverse Fourier transforms.

But why is this Fourier Trnasform stuff important?

Fourier Transforms in Experimental Spectroscopy

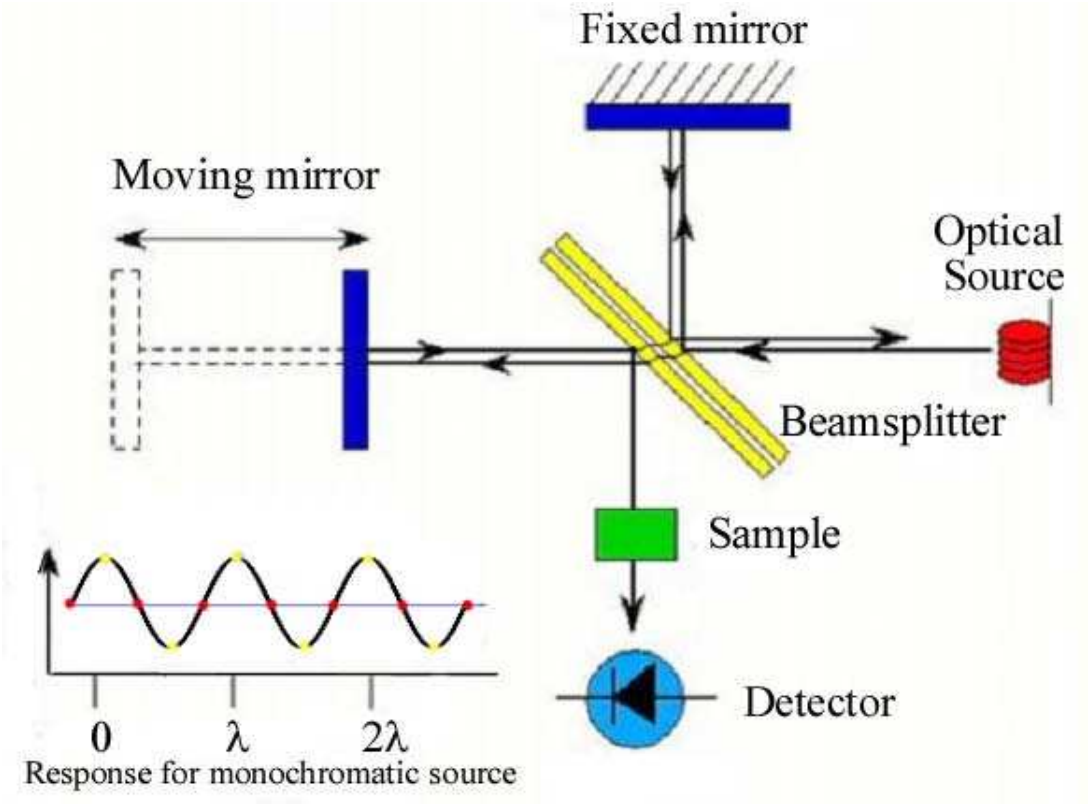
Fourier transforms are an essential tool in much modern scientific instrumentation. Consider the problem of measuring the positions and intensities of absorption of emission lines on molecular spectra. A traditional 'dispersive' spectroscopic experiment is schematically illustrated below.



In this type of experiment, one physically moves the detector across the dispersed light beam while measuring the light intensity, and attempts to locate the positions where there is an intensity maximum (in an emission experiment) or minimum (in an absorption experiment). In some cases, however, the lines are may orders of magnitude narrower than the spacing between them, so the search is very tedious. In others, the lines are sufficiently close together that they partially overlap, and it can be very difficult to physically locate the precise line centre positions.

A very successful modern approach is the technique of Fourier Transform spectroscopy which is based on the type of instrumentation schematically illustrated in the following figure (top of next page). In this approach, clever tricks of physical optics are used to take the light beam coming from the optical source and split it into two parts, one of which travels to a ***Fixed Mirror*** and them bounces back on itself, while the other goes to a ***Moving Mirror*** and is then reflected back the way it came. Those two components of the original light beam are then recombined at the ***Beamsplitter*** and sent to the detector. In emission spectroscopy the experimental sample of interest is itself the ***Optical Source***, while in absorption spectroscopy the sample is placed in the beam as shown in the figure.

We know that light is a wave phenomenon, consisting of oscillating electric and magnetic waves travelling with the speed $c = 2.99782458 \times 10^{10}$ cm/s, and that light of a particular 'colour' is characterized

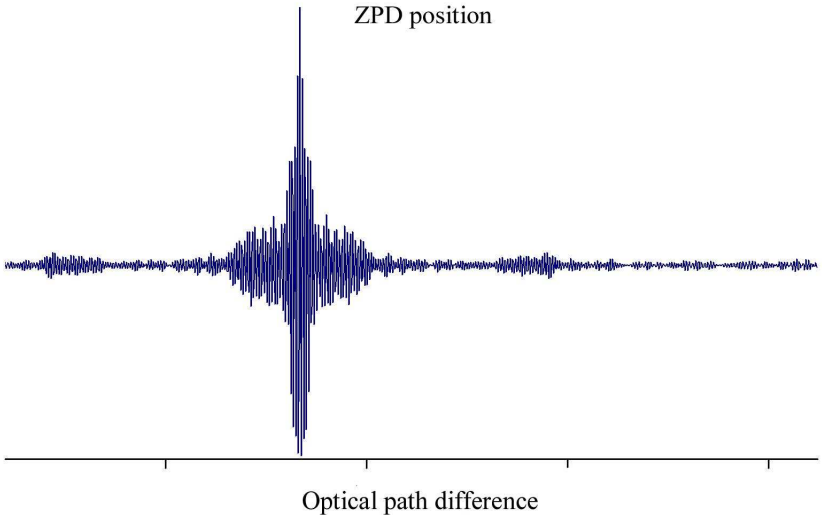


by a wavelength λ and frequency ν, where $c = \lambda\,\nu$. We also know that energy of a beam of light is carried by tiny 'quanta' of magnitude $\delta E_\nu = h\,\nu = c/\lambda$, where h is Planck's constant.

Let us consider the case of an emission spectrum consisting of only a single frequency (or wavelength) of light. If the total distance from the light source to the detector for the two parts of the beam is precisely zero, there will be *constructive interference* and the detector will see high intensity. However, if the path-length difference is precisely *half* a wavelength, there will be *destructive interference*, and the observed intensity will be zero. Hence, as the ***moving mirror*** travels back and forth, the intensity at the detector will oscillate in a simple sinusoidal fashion, as shown in the botom left of this figure.

If instead of being a single frequency, the emission consists of light of several different frequencies, an oscillating intensity pattern of this type will occur for each distinct frequency (wavelength). However, each component will have a different periodic dependence on the path length difference x, and the total intensity seen at the detector will be a *sum* of the oscillating intensities of all those individual components.

An illustration of the type of resulting intensity vs. path-length-difference is provided by the figure at the top of the next page, and an expanded version of an narrow segment from the middle of this spectrum was provided in the handout distributed in class.



5. Operators, Matrices, Determinants and the Matrix Eigenvalue Problem

A *matrix* is any rectangular array of elements arranged in rows and columns. The elements may be scalars, functions or operators.

The *order* of a matrix is the specification of the number of rows and number of columns. An $m \times n$ (or 'm by n') matrix is one which has $\begin{cases} m \text{ rows} \\ n \text{ columns} \end{cases}$

e.g.,

$$\begin{pmatrix} 1 & 3-i & 2i \\ 3+2i & -7 & 4i \end{pmatrix} \qquad \begin{pmatrix} \sin(x) & \cos(x) \\ \sin(2x) & \cos(2x) \\ \sin(3x) & \cos(3x) \\ \sin(4x) & \cos(4x) \end{pmatrix} \qquad \begin{pmatrix} \frac{\partial^2}{\partial x^2} & \frac{\partial^2}{\partial x\,\partial y} \\ \frac{\partial^2}{\partial y\,\partial x} & \frac{\partial^2}{\partial y^2} \end{pmatrix}$$

5.1 Matrix Algebra

Two matrices $\mathbb{A}$ and $\mathbb{B}$ are *equal* if and only if they are of the same order and all corresponding elements are equal.

(a) Addition and Subtraction. These operations are defined only between matrices of the same order, and the result is always a matrix of that same order. The operation is defined such that if a_{ij}, b_{ij} and c_{ij} are the elements in the i'th row and j'th column of $\mathbb{A}$, $\mathbb{B}$ and $\mathbb{C}$, respectively, then

$$\mathbb{A} + \mathbb{B} = \mathbb{C} \qquad \text{means that} \qquad c_{ij} = a_{ij} + b_{ij} \qquad \text{for all } i \text{ and } j$$

e.g.,

Matrix addition *commutes*:

Matrix addition *is associative*:

(b) Scalar Multiplication. The result of multiplying a matrix $\mathbb{A}$ by a scalar k is a matrix $k\,\mathbb{A}$ of the same order whose elements are each k times the corresponding element of $\mathbb{A}$.

i.e., $\quad (k\,\mathbb{A})_{ij} = k\,(\mathbb{A})_{ij}$

e.g.,

(c) Matrix Multiplication. Two matrices $\mathbb{A}$ and $\mathbb{B}$ may be multiplied together to give the product matrix $\mathbb{C} = \mathbb{A}\,\mathbb{B}$ if and only if

$$\{\text{No. rows of first } (\textit{on the left})\} = \{\text{No. columns of second } (\textit{on the right})\}$$

More explicitly ... if $\mathbb{A}$ is an $m_1 \times n_1$ matrix and $\mathbb{B}$ is an $m_2 \times n_2$ matrix:

- $\mathbb{A}\,\mathbb{B}$ only exists of $n_1 = m_2$, in which case it has order $m_1 \times n_2$
- $\mathbb{B}\,\mathbb{A}$ only exists of $n_2 = m_1$, in which case it has order $m_2 \times n_1$

Note that except for some special cases, $\mathbb{A}\,\mathbb{B} \neq \mathbb{B}\,\mathbb{A}$

Operational Definition of Matrix Multiplication

If $\mathbb{A}\,\mathbb{B} = \mathbb{C}$, then the element $c_{ij} = (\mathbb{C})_{ij}$ of the product matrix is obtained by taking

$\left\{ \begin{array}{l} \bullet \text{ the elements in the } j^{th} \text{ column of } \mathbb{B} \\ \bullet \text{ and the elements in the } i^{th} \text{ row of } \mathbb{A} \end{array} \right\}$

$$\begin{pmatrix} \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ a_{i,1} & a_{i,2} & a_{i,3} & a_{i,4} \\ \cdots & \cdots & \cdots & \cdots \end{pmatrix} \begin{pmatrix} \cdots & \cdots & b_{1,j} & \cdots \\ \cdots & \cdots & b_{1,j} & \cdots \\ \cdots & \cdots & b_{1,j} & \cdots \\ \cdots & \cdots & b_{1,j} & \cdots \end{pmatrix} = \begin{pmatrix} & & c_{ij} & \\ & & & \end{pmatrix}$$

$$\text{i.e.,} \qquad c_{i,j} = a_{i,1}\,b_{1,j} + a_{i,2}\,b_{2,j} + a_{i,3}\,b_{3,j} + a_{i,4}\,b_{4,j} + a_{i,5}\,b_{5,j} + \ldots$$

$$= \sum_k a_{i,k}\,b_{k,j}$$

$$\text{e.g.,} \quad \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \\ a_{31} & a_{32} \end{pmatrix} \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} =$$

But,

$$\begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \\ a_{31} & a_{32} \end{pmatrix} =$$

Exercise 5.1 If $\mathbb{A} = \begin{pmatrix} 3 & 1 & 2 \\ 2 & 1 & 3 \end{pmatrix}$, $\mathbb{B} = \begin{pmatrix} 1 & 2 \\ 3 & 1 \\ 2 & 3 \end{pmatrix}$, $\mathbb{C} = \begin{pmatrix} 0 & 1 \\ 1 & 1 \end{pmatrix}$, $\mathbb{D} = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$,

evaluate all possible products of these four matrices.

Which of these products do not exist ?

Matrix Multiplication is Associative. i.e., $(\mathbb{A}\,\mathbb{B})\,\mathbb{C} = \mathbb{A}\,(\mathbb{B}\,\mathbb{C})$.

In a product of 3 matrices, it doesn't matter which pair is considered first.

This result follows trivially from the summation algebra of the formal definition of matrix multiplication:

$$((\mathbb{A}\,\mathbb{B})\,\mathbb{C})_{ij} = \sum_k (\mathbb{A}\,\mathbb{B})_{ik}\,(\mathbb{C})_{kj} = \sum_k \left\{ \sum_m (\mathbb{A})_{im}\,(\mathbb{B})_{mk} \right\} (\mathbb{C})_{kj} = \sum_k \sum_m (\mathbb{A})_{im}\,(\mathbb{B})_{mk}\,(\mathbb{C})_{kj}$$

$$= \sum_m (\mathbb{A})_{im} \left\{ \sum_k (\mathbb{B})_{mk}\,(\mathbb{C})_{kj} \right\} = \sum_m (\mathbb{A})_{im}\,(\mathbb{B}\,\mathbb{C})_{mj} = (\mathbb{A}\,(\mathbb{B}\,\mathbb{C}))_{ij}$$

e.g., considering $\mathbb{A}$, $\mathbb{B}$ & $\mathbb{C}$ from the previous page:

$(\mathbb{A}\,\mathbb{B})\,\mathbb{C} =$

$\mathbb{A}\,(\mathbb{B}\,\mathbb{C}) =$

Matrix Multiplication is Distributive. i.e., $\mathbb{A}\,(\mathbb{B} + \mathbb{C}) = \mathbb{A}\,\mathbb{B} + \mathbb{A}\,\mathbb{C}$

Commuting Matrices. Any particular pair of matrices $\mathbb{A}$ and $\mathbb{B}$ for which $\mathbb{A}\,\mathbb{B} = \mathbb{B}\,\mathbb{A}$ are called *commuting matrices*, since they commute under matrix multiplication. For this to occur, at the very least the two matrices must be *square matrices* of the same order, since otherwise either the resulting product matrices will be of different order (e.g., compare $\mathbb{A}\,\mathbb{B}$ with $\mathbb{B}\,\mathbb{A}$ on preceding page) or at least one of those products will not exist. Note that this is a *necessary* condition, but not a *sufficient* condition, and most pairs of square matrices of the same order *do not* commute.

5.2 Types of Matrices

(a) A *row matrix* is any $1 \times n$ matrix: e.g., $(\,a_1,\, a_2,\, a_3,\, a_4,\, a_5,\, \cdots\,)$

(b) A *column matrix* is any $m \times 1$ matrix: e.g., ... $\begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \\ \vdots \end{pmatrix}$

(c) A *zero* or *null matrix* is any matrix in which all of the elements are *zero*.

(d) A *square matrix* is a matrix in which $\{\text{number of rows}\} = \{\text{number of columns}\}$.

(i) A *diagonal matrix* is a square matrix in which all off-diagonal elements are zero.

e.g., $\mathbb{D} = \begin{pmatrix} d_{11} & 0 & 0 & 0 & 0 & \cdots \\ 0 & d_{22} & 0 & 0 & 0 & \cdots \\ 0 & 0 & d_{33} & 0 & 0 & \cdots \\ 0 & 0 & 0 & d_{44} & 0 & \cdots \\ 0 & 0 & 0 & 0 & d_{55} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \cdots \end{pmatrix} = \begin{pmatrix} d_{11} & & & & & \\ & d_{22} & & & & \\ & & d_{33} & & & \\ & & & d_{44} & & \\ & & & & d_{55} & \\ & & & & & \cdots \end{pmatrix}$

On multiplying some other matrix $\mathbb{A}$ by a diagonal matrix $\mathbb{D}$

- after multiplying from the left, row i of $\mathbb{D}\mathbb{A}$ is the same as row i of $\mathbb{A}$, but with each element being multiplied by the diagonal term d_{ii}.
- on multiplying from the right, each column j of $\mathbb{A}\mathbb{D}$ is the same as column j of $\mathbb{A}$, but with each element being multiplied by the diagonal term d_{jj}.

e.g. $$\begin{pmatrix} d_{11} & 0 & 0 \\ 0 & d_{22} & 0 \\ 0 & 0 & d_{33} \end{pmatrix} \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} =$$

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} d_{11} & 0 & 0 \\ 0 & d_{22} & 0 \\ 0 & 0 & d_{33} \end{pmatrix} =$$

(ii) A *Unit Matrix or Identity Matrix*, usually denoted $\mathbb{I}$ or $\mathbb{E}$, is a diagonal matrix in which all diagonal elements are 1.

i.e., $$\mathbb{I} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & \cdots \\ 0 & 1 & 0 & 0 & 0 & \cdots \\ 0 & 0 & 1 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 1 & 0 & \cdots \\ 0 & 0 & 0 & 0 & 1 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \cdots \end{pmatrix} = \begin{pmatrix} 1 & & & & & \\ & 1 & & & & \\ & & 1 & & & \\ & & & 1 & & \\ & & & & 1 & \\ & & & & & \cdots \end{pmatrix}$$

It's special structure means that for any other square matrix $\mathbb{A}$ whose product with $\mathbb{I}$ exists (i.e., they are of the same order), $\mathbb{I}\mathbb{A} = \mathbb{A} = \mathbb{A}\mathbb{I}$.

(iii) An *upper triangular matrix* is a square matrix $\mathbb{A}$ for which $a_{ij} = 0$ for all $i > j$; i.e., all elements "below" the diagonal are zero.

e.g., $$\mathbb{A} = \begin{pmatrix} a_{11} & a_{12} & a_{13} & a_{14} & a_{15} & \cdots \\ 0 & a_{22} & a_{23} & a_{24} & a_{25} & \cdots \\ 0 & 0 & a_{33} & a_{34} & a_{35} & \cdots \\ 0 & 0 & 0 & a_{44} & a_{45} & \cdots \\ 0 & 0 & 0 & 0 & a_{55} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \cdots \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} & a_{13} & a_{14} & a_{15} & \cdots \\ & a_{22} & a_{23} & a_{24} & a_{25} & \cdots \\ & & a_{33} & a_{34} & a_{35} & \cdots \\ & & & a_{44} & a_{45} & \cdots \\ & & & & a_{55} & \cdots \\ & & & & & \cdots \end{pmatrix}$$

(iv) A *lower triangular matrix* is a square matrix $\mathbb{A}$ for which $a_{ij} = 0$ for all $i < j$; i.e., all elements "above" the diagonal are zero.

e.g., $$\mathbb{B} = \begin{pmatrix} b_{11} & 0 & 0 & 0 & 0 & \cdots \\ b_{21} & b_{22} & 0 & 0 & 0 & \cdots \\ b_{31} & b_{32} & b_{33} & 0 & 0 & \cdots \\ b_{41} & b_{42} & b_{43} & b_{44} & 0 & \cdots \\ b_{51} & b_{52} & b_{53} & b_{54} & b_{55} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \cdots \end{pmatrix} = \begin{pmatrix} b_{11} & & & & & \\ b_{21} & b_{22} & & & & \\ b_{31} & b_{32} & b_{33} & & & \\ b_{41} & b_{42} & b_{43} & b_{44} & & \\ b_{51} & b_{52} & b_{53} & b_{54} & b_{55} & \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{pmatrix}$$

(v) The ***inverse*** of a square matrix $\mathbb{A}$ is a matrix, denoted $\mathbb{A}^{-1}$, which is defined by the property that

$$\mathbb{A}^{-1}\mathbb{A} \;=\; \mathbb{I} \;=\; \mathbb{A}\mathbb{A}^{-1}$$

* A matrix always commutes with its inverse.
* If the inverse of a particular matrix exists, it is unique!

(e) The *transpose* of an $m \times n$ matrix $\mathbb{A} = (a_{ij})$ is the matrix, usually denoted $\widetilde{\mathbb{A}}$, which is obtained from $\mathbb{A}$ by interchanging all of its rows and columns.

$$\left(\widetilde{\mathbb{A}}\right)_{ij} \;=\; (\mathbb{A})_{ji}$$

e.g., if $\mathbb{A} = \begin{pmatrix} 1 & 4 \\ 1 & 5 \\ 3 & -6 \end{pmatrix}$, then $\widetilde{\mathbb{A}} =$

Clearly: $\widetilde{\left(\widetilde{\mathbb{A}}\right)} \;=\; \mathbb{A}$

Product Theorem: If $\mathbb{A}\mathbb{B} = \mathbb{C}$, then $\widetilde{\mathbb{C}} \equiv \widetilde{(\mathbb{A}\mathbb{B})} = \widetilde{\mathbb{B}}\,\widetilde{\mathbb{A}}$.

More generally $\widetilde{(\mathbb{A}\mathbb{B}\mathbb{C}\mathbb{F}\mathbb{G})} =$

The proof of this theorem is a trivial application of the definition of matrix multiplication:

$\left(\widetilde{\mathbb{B}}\,\widetilde{\mathbb{A}}\right)_{ij} =$

e.g., If $\mathbb{A} = \begin{pmatrix} 1 & 6 \\ 2 & 5 \\ 3 & 4 \end{pmatrix}$, $\mathbb{B} = \begin{pmatrix} 1 \\ -1 \end{pmatrix}$,

then $\mathbb{A}\mathbb{B} =$

(f) A *Symmetric Matrix* is a square matrix which is equal to its own transposed matrix.

i.e., if $\mathbb{A}$ is a symmetric matrix, then $\widetilde{\mathbb{A}} = \mathbb{A}$, which means that for any row and column labels, $a_{ij} = a_{ji}$.

Similarly, a "*skew-symmetric*" or *anti-symmetric* matrix is one for which $\widetilde{\mathbb{A}} = -\mathbb{A}$;
i.e., for which $(\mathbb{A})_{ij} = -(\mathbb{A})_{ji}$.

Any square matrix may be written as a sum od a symmetric matrix and a skew-symmetric matrix.

(g) The ***hermitian conjugate*** of a matrix $\mathbb{A}$ is the transpose of the matrix obtained on converting every element to its complex conjugate. The *hermitian conjugate* of $\mathbb{A}$ is denoted $\mathbb{A}^\dagger \equiv \widetilde{(A^*)}$, so that $\left(\mathbb{A}^\dagger\right)_{ij} = (\mathbb{A})^*_{ji}$.

e.g. If $\mathbb{A} = \begin{pmatrix} 1+i & 2 & -i \\ 3 & 2-i & 1+2i \end{pmatrix}$, then $\mathbb{A}^\dagger =$

A ***hermitian matrix*** is a square matrix which is its own *hermitian conjugate*.

i.e., if $\mathbb{A}$ is a hermitian matrix, then:

5.3 Determinants

There are two different unique scalar numbers associated with any square matrix:
The ***trace*** (or *spur*) of a square matrix is the sum of its diagonal elements:

$$\mathrm{Tr}(\mathbb{A}) \;=\; \sum_i a_{ii} \;=\; \sum_i (\mathbb{A})_{ii}$$

In *group theory* (see § 6) the *trace* is know as the *character* of the matrix representation of the group.

The ***determinant*** of a square matrix $\mathbb{A}$ of order n is formally defined as the scalar

$$\det(\mathbb{A}) \;=\; |\,\mathbb{A}\,| \;\equiv\; \sum_{\hat{P}} \left\{ \mathrm{sgn}(\hat{P})\; a_{1,\hat{P}(1)}\; a_{2,\hat{P}(2)}\; a_{3,\hat{P}(3)}\; a_{4,\hat{P}(4)}\; \cdots\; a_{n,\hat{P}(n)} \right\}$$

in which $\hat{P}$ is a particular permutation of all of the set of column indices $\{\,1,\,2,\,3,\,4,\,\ldots\,\mathrm{n}\,\}$.

Note that while the formal definition given above is expressed in terms of a sum over all possible *distinct* permutations of the column indices, with the row labels appearing in increasing order, it would be equally valid to define the determinant in terms of all possible distinct permutations of the row indices.

$$\det(\mathbb{A}) \;=\; |\,\mathbb{A}\,| \;\equiv\; \sum_{\hat{P}} \left\{ \mathrm{sgn}(\hat{P})\; a_{\hat{P}(1),1}\; a_{\hat{P}(2),2}\; a_{\hat{P}(3),3}\; a_{\hat{P}(4),4}\; \cdots\; a_{\hat{P}(n),n} \right\}$$

Aside about *Permutations*

A ***permutation*** is any change in the order of a discrete set of ordered elements.

A ***permutation operator*** is a set of instructions for performing some specific change in the order of a discrete set of ordered elements. It is usually denoted by a symbol with a 'hat', such as $\hat{P}_{3,7}$, for which the instructions are "*interchange the 3rd and 7th elements of the set*".

- We write permutation operators as being applied from the left.

- For a set of sequential permutation operations, the operators are applied in order, starting from the one on the *right*.

- Every overall permutation may be expressed in terms of a number of elementary pairwise permutations.

  e.g., the interchange $(a, b, c, d) \rightarrow (b, c, d, a)$ may be represented by

- A permutation is *even* or *odd* depending on whether it is expressible as an even or odd number of distinct pairwise interchanges.

- If there are a set of N distinguishable elements in a set, there are $N!$ possible distinct permutations of them.

Illustrative Applications of the Formal Definition of a Determinant

Consider the 2×2 matrix

$$|\,\mathbb{A}\,| = \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}$$

column labels		$\hat{P}$	$\text{sgn}(\hat{P})$	term
1	2	$\mathbb{I}$	$+1$	$+\,a_{11}\ a_{22}$

Consider the 3×3 matrix

$$|\,\mathbb{B}\,| = \begin{vmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{vmatrix}$$

column labels			$\hat{P}$	$\text{sgn}(\hat{P})$	term
1	2	3	$\mathbb{I}$	$+1$	$+\,b_{11}\ b_{22}\ b_{33}$
					$b_1\ \ b_2\ \ b_3$
					$b_1\ \ b_2\ \ b_3$
					$b_1\ \ b_2\ \ b_3$
					$b_1\ \ b_2\ \ b_3$
					$b_1\ \ b_2\ \ b_3$

Evaluating Determinants *in practise!* There are a number of possible methods.

1. Use the formal definition ..... as per the examples on the previous page.

   This formal definition is essential for deriving the formal properties of determinants (see below), but it is not very convenient to use in practice.

2. Special method for 2×2 determinants. Use the "cross-cross" rule.

3. Special method for 3×3 determinants. Use the "extended cross-cross" rule.

   For $\mathbb{A} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix}$ write out the elements as ... $\begin{matrix} a_{11} & a_{12} & a_{13} & a_{11} & a_{12} \\ a_{21} & a_{22} & a_{23} & a_{21} & a_{22} \\ a_{31} & a_{32} & a_{33} & a_{31} & a_{32} \end{matrix}$

   and sum products of terms on diagonals,
   - with $+$ signs for those with negative slopes and
   - with $-$ signs for those with positive slopes to give

$$|\,\mathbb{A}\,| \;=\; a_{11}\ a_{22}\ a_{33} \;+\; a_{12}\ a_{23}\ a_{31} \;+\; a_{13}\ a_{32}\ a_{21} \;-\; a_{31}\ a_{22}\ a_{13} \;-\; a_{32}\ a_{23}\ a_{11} \;-\; a_{33}\ a_{23}\ a_{12}$$

An alternate diagrammatic scheme is: $|\mathbb{A}| = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix}$

Note that diagrammatic approaches of this type *do not work* for larger matrices!

4. Expansion by "cofactors" or "minors". If $\mathbb{A}$ is a square matrix with elements a_{ij} then
   - the ***minor*** of element a_{ij}, written as $\mathbf{M}(a_{ij})$, is the determinant of the submatrix of $\mathbb{A}$ obtained on *deleting* its i^{th} row and j^{th} column, and
   - the ***cofactor*** of element a_{ij}, written $\mathbf{C}(a_{ij})$, is $(-1)^{i+j}\,\mathbf{M}(a_{ij})$.

e.g. For $\mathbb{A} = \begin{pmatrix} a_{11} & a_{12} & a_{13} & a_{1,4} \\ a_{21} & a_{22} & a_{23} & a_{24} \\ a_{31} & a_{32} & a_{33} & a_{34} \\ a_{41} & a_{42} & a_{43} & a_{44} \end{pmatrix}$ the minor of a_{32} is $\begin{vmatrix} a_{11} & a_{23} & a_{2,4} \\ a_{21} & a_{23} & a_{24} \\ a_{41} & a_{43} & a_{44} \end{vmatrix}$

the cofactor of a_{13} is $(-1)^{1+3}\begin{vmatrix} a_{21} & a_{22} & a_{2,4} \\ a_{31} & a_{32} & a_{34} \\ a_{41} & a_{42} & a_{44} \end{vmatrix}$; the cofactor of a_{32} is $(-1)^{3+2}\begin{vmatrix} a_{11} & a_{23} & a_{2,4} \\ a_{21} & a_{23} & a_{24} \\ a_{41} & a_{43} & a_{44} \end{vmatrix}$

Theorem 5.1: For any column j of a square matrix $\mathbb{A}$ of order n,
$$\det(\mathbb{A}) = \sum_{i=1}^{n} a_{ij}\,\mathbf{C}(a_{ij}) = a_{1j}\,\mathbf{C}(a_{1j}) + a_{2j}\,\mathbf{C}(a_{2j}) + a_{4j}\,\mathbf{C}(a_{3j}) + \ldots a_{nj}\,\mathbf{C}(a_{nj})$$

Theorem 5.2: For any row i of a square matrix $\mathbb{A}$ of order n,
$$\det(\mathbb{A}) = \sum_{j=1}^{n} a_{ij}\,\mathbf{C}(a_{ij}) = a_{i1}\,\mathbf{C}(a_{i1}) + a_{i2}\,\mathbf{C}(a_{i2}) + a_{i4}\,\mathbf{C}(a_{i3}) + \ldots a_{in}\,\mathbf{C}(a_{in})$$

---

e.g. (i) $\mathbb{A} = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} =$

e.g. (ii) $\mathbb{B} = \begin{vmatrix} -2 & 4 & -4 & 3 \\ 4 & 3 & -1 & 2 \\ 1 & 4 & 3 & -2 \\ 3 & 2 & 1 & 4 \end{vmatrix} =$

Properties of Determinants

While the formal definition of a determinant (see p. 7) is not very useful for the practical evaluation of determinants, it is essential for deriving their general properties.

1. If $\mathbb{A}'$ is the matrix obtained on multiplying every element of one particular row (or one particular column) by a constant k, then

$$\det(\mathbb{A}') = k\det(\mathbb{A})$$

and similarly, if $\mathbb{A}'' = k\,\mathbb{A}$, then $\det(\mathbb{A}'') = k^n \det(\mathbb{A})$, where n is the order of $\mathbb{A}$.

2. If $\mathbb{A}'$ is the matrix obtained on interchanging any two columns (or interchanging any two rows) of matrix $\mathbb{A}$, then $\det(\mathbb{A}') = -\det(\mathbb{A})$.

3. If any two columns of $\mathbb{A}$ are identical, then $\det(\mathbb{A}) = 0$.

   If any two rows of $\mathbb{A}$ are identical, then $\det(\mathbb{A}) = 0$.

4. Addition of a scalar multiple of any given column to another column *doesn't change the value of the determinant*!

   Addition of a scalar multiple of any given row to another row *doesn't change the value of the determinant*!

5. $\det(\,\widetilde{\mathbb{A}}\,) = \det(\,\mathbb{A}\,)$
$\det(\,\mathbb{A}^\dagger\,) = [\det(\,\mathbb{A}\,)]^*$

6. If $\mathbb{A}$ is a triangular matrix (either upper or lower triangular), then its determinant is equal to the product of the elements on the diagonal.

e.g., $|\mathbb{A}| = \begin{vmatrix} a_{11} & a_{12} & a_{13} & a_{14} & a_{15} & \cdots \\ 0 & a_{22} & a_{23} & a_{24} & a_{25} & \cdots \\ 0 & 0 & a_{33} & a_{34} & a_{35} & \cdots \\ 0 & 0 & 0 & a_{44} & a_{45} & \cdots \\ 0 & 0 & 0 & 0 & a_{55} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \cdots \end{vmatrix} =$

7. If $\mathbb{A}$ and $\mathbb{B}$ are square matrices of the same order, then

$$\det(\,\mathbb{A}\,\mathbb{B}\,) \;=\; \det(\,\mathbb{A}\,)\,\det(\,\mathbb{B}\,)$$

Some practical implications of the above properties.

Property 4 above has great practical implication w.r.t. minimizing the amount of work involved in evaluating determinants by the cofactor method, since we can use addition/subtraction of multiples of other rows/columns to produce zeros!

e.g. (ii) from p. 10:

$$|\mathbb{B}| = \begin{vmatrix} -2 & 4 & -4 & 3 \\ 4 & 3 & -1 & 2 \\ 1 & 4 & 3 & -2 \\ 3 & 2 & 1 & 4 \end{vmatrix}$$

***Note*:** One has to be careful about where the 'final' row is placed. Compare the following two changes:

$$\left\{ \begin{array}{lcl} \text{row}(i) & \longrightarrow & \text{row}(i) \\ \text{row}(j) & \longrightarrow & \text{row}(j) + k\ \text{row}(i) \end{array} \right\}$$

$$\left\{ \begin{array}{lcl} \text{row}(i) & \longrightarrow & \text{row}(i) \\ \text{row}(j) & \longrightarrow & k\ \text{row}(j) + \text{row}(i) \end{array} \right\}$$

Exercise 5.2 Compare the determinants $\begin{vmatrix} a & c \\ b & d \end{vmatrix}$

$$\begin{vmatrix} a & c+k\,a \\ b & d+k\,b \end{vmatrix}$$

$$\begin{vmatrix} a & k\,c+a \\ b & k\,d+b \end{vmatrix}$$

5.4 Inverse of a Matrix

As was mentioned on p. 6, the ***inverse*** of a square matrix $\mathbb{A}$ is a matrix, denoted $\mathbb{A}^{-1}$, which is defined by the property that $\mathbb{A}^{-1}\mathbb{A} = \mathbb{I} = \mathbb{A}\mathbb{A}^{-1}$

Theorem 5.3: $\mathbb{A}^{-1} = \dfrac{1}{|\mathbb{A}|}\,\text{adj}(\mathbb{A})$, where $\text{adj}(\mathbb{A})$ denotes the ***adjoint*** of matrix $\mathbb{A}$,

which is defined as the *transpose* of the matrix made up of the cofactors of $\mathbb{A}$; i.e.,

$$\text{if} \quad \mathbb{A} = \begin{pmatrix} a_{11} & a_{12} & a_{13} & a_{14} & \ldots\ldots \\ a_{21} & a_{22} & a_{23} & a_{24} & \ldots\ldots \\ a_{31} & a_{32} & a_{33} & a_{34} & \ldots\ldots \\ a_{41} & a_{42} & a_{43} & a_{44} & \ldots\ldots \\ \ldots & \ldots & \ldots & \ldots & \ldots\ldots \\ a_{n1} & a_{n2} & a_{n3} & a_{n4} & \ldots\ldots \end{pmatrix} \quad \text{then} \quad \text{adj}(\mathbb{A}) = \begin{pmatrix} \mathbf{C}(a_{11}) & \mathbf{C}(a_{21}) & \mathbf{C}(a_{31}) & \ldots\ldots \\ \mathbf{C}(a_{12}) & \mathbf{C}(a_{22}) & \mathbf{C}(a_{32}) & \ldots\ldots \\ \mathbf{C}(a_{13}) & \mathbf{C}(a_{23}) & \mathbf{C}(a_{33}) & \ldots\ldots \\ \mathbf{C}(a_{14}) & \mathbf{C}(a_{24}) & \mathbf{C}(a_{34}) & \ldots\ldots \\ \ldots & \ldots & \ldots & \ldots\ldots \\ \mathbf{C}(a_{1n}) & \mathbf{C}(a_{2n}) & \mathbf{C}(a_{3n}) & \ldots\ldots \end{pmatrix}$$

E.g., if $\mathbb{A} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}$, then $\mathbf{C}(a_{11}) = (-1)^{1+1}\, a_{22} = a_{22}$, $\mathbf{C}(a_{12}) = (-1)^{1+2}\, a_{21} = -\, a_{21}$,

$\mathbf{C}(a_{21}) = (-1)^{2+1}\, a_{12} = -\, a_{12}$ and $\mathbf{C}(a_{22}) = (-1)^{2+2}\, a_{11} = a_{11}$.

Combining this with the result that $|\,\mathbb{A}\,| = a_{11}\, a_{22} - a_{21}\, a_{12}$ then yields

$$\mathbb{A}^{-1} \;=\; \frac{1}{|\mathbb{A}|} \begin{pmatrix} a_{22} & -\, a_{12} \\ -\, a_{21} & a_{11} \end{pmatrix} \;=\; \frac{1}{[a_{11}\, a_{22} - a_{21}\, a_{12}]} \begin{pmatrix} a_{22} & -\, a_{12} \\ -\, a_{21} & a_{11} \end{pmatrix}$$

Test this inverse by evaluating $\mathbb{A}^{-1}\, \mathbb{A}$.

Why does this work ? Consider the case of a general $n \times n$ matrix:

$$\mathbb{A}^{-1}\, \mathbb{A} \;=\; \frac{1}{|\mathbb{A}|} \begin{pmatrix} \mathbf{C}(a_{11}) & \mathbf{C}(a_{21}) & \mathbf{C}(a_{31}) & \ldots\ldots \\ \mathbf{C}(a_{12}) & \mathbf{C}(a_{22}) & \mathbf{C}(a_{32}) & \ldots\ldots \\ \mathbf{C}(a_{13}) & \mathbf{C}(a_{23}) & \mathbf{C}(a_{33}) & \ldots\ldots \\ \mathbf{C}(a_{14}) & \mathbf{C}(a_{24}) & \mathbf{C}(a_{34}) & \ldots\ldots \\ \ldots & \ldots & \ldots & \ldots\ldots \\ \mathbf{C}(a_{1n}) & \mathbf{C}(a_{2n}) & \mathbf{C}(a_{3n}) & \ldots\ldots \end{pmatrix} \begin{pmatrix} a_{11} & a_{12} & a_{13} & a_{14} & \ldots\ldots \\ a_{21} & a_{22} & a_{23} & a_{24} & \ldots\ldots \\ a_{31} & a_{32} & a_{33} & a_{34} & \ldots\ldots \\ a_{41} & a_{42} & a_{43} & a_{44} & \ldots\ldots \\ \ldots & \ldots & \ldots & \ldots & \ldots\ldots \\ a_{n1} & a_{n2} & a_{n3} & a_{n4} & \ldots\ldots \end{pmatrix}$$

(a) Consider (say) the $\{2,\, 2\}$ element of the product matrix.

(b) Consider (say) the $\{2,\, 3\}$ element of the product matrix.

$$\begin{pmatrix} a_{11} & a_{12} & a_{12} & a_{14} & \ldots\ldots \\ a_{21} & a_{22} & a_{22} & a_{24} & \ldots\ldots \\ a_{31} & a_{32} & a_{32} & a_{34} & \ldots\ldots \\ a_{41} & a_{42} & a_{42} & a_{44} & \ldots\ldots \\ \ldots & \ldots & \ldots & \ldots & \ldots\ldots \\ a_{n1} & a_{n2} & a_{n2} & a_{n4} & \ldots\ldots \end{pmatrix}$$

Some Properties of the Inverse Matrix

(i) $\mathbb{A}^{-1}$ only exists if $\mathbb{A}$ is a square matrix for which all rows (or all columns) are *linearly independent.*

A ***singular*** matrix is a square matrix whose determinant equals zero; i.e., is square matrix whose columns/rows are linearly dependent.

(ii) $\mathbb{A}^{-1}$ commutes with $\mathbb{A}$: $\quad \mathbb{A}\,\mathbb{A}^{-1} \;=\; \mathbb{I} \;=\; \mathbb{A}^{-1}\,\mathbb{A}$

(iii) The inverse of a given matrix is unique.

(iv) The inverse of a product of matrices is equal to the product of the inverses of those matrices, *taken in the opposite order.*

i.e., $\quad (\,\mathbb{A}\,\mathbb{B}\,\mathbb{C})^{-1} \;=\; \mathbb{C}^{-1}\,\mathbb{B}^{-1}\,\mathbb{A}^{-1}$

Exercise 5.3 Determine the inverse of the matrix $\begin{pmatrix} 1 & 2 & 1 \\ 2 & 1 & 2 \\ 3 & -1 & 1 \end{pmatrix}$

5.5 Solving Sets of Linear Equations

A particularly important application of the inverse matrix is its use to solve sets of linear equations.

Consider the following set of n linear equations in the n unknowns $\{ x_1, x_2, x_3, \ldots, x_n \}$, in which the factors a_{ij} and b_j are known scalars.

$$\begin{array}{rcl}
a_{11}\,x_1 + a_{12}\,x_2 + a_{13}\,x_3 + \ldots + a_{1n}\,x_n &=& b_1 \\
a_{21}\,x_1 + a_{22}\,x_2 + a_{23}\,x_3 + \ldots + a_{2n}\,x_n &=& b_2 \\
a_{31}\,x_1 + a_{32}\,x_2 + a_{33}\,x_3 + \ldots + a_{3n}\,x_n &=& b_3 \\
a_{41}\,x_1 + a_{42}\,x_2 + a_{43}\,x_3 + \ldots + a_{4n}\,x_n &=& b_4 \\
\ldots\ldots & = & \ldots \\
a_{n1}\,x_1 + a_{n2}\,x_2 + a_{n3}\,x_3 + \ldots + a_{nn}\,x_n &=& b_n
\end{array}$$

A set of linear equations of this type is called ***homogeneous*** if $b_j = 0$ for all j.

A set of linear equations of this type is called ***inhomogeneous*** if one or more of the b_j coefficients are non-zero.

This set of n linear equations is clearly equivalent to the single *matrix equation*

$$\mathbb{A}\,\mathbb{X} = \begin{pmatrix} a_{11} & a_{12} & a_{13} & \ldots & a_{1n} \\ a_{21} & a_{22} & a_{23} & \ldots & a_{2n} \\ a_{31} & a_{32} & a_{33} & \ldots & a_{3n} \\ a_{41} & a_{42} & a_{43} & \ldots & a_{4n} \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ a_{n1} & a_{n2} & a_{n3} & \ldots & a_{nn} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_2 \\ x_4 \\ \ldots \\ x_n \end{pmatrix} = \begin{pmatrix} b_1 \\ b_2 \\ b_2 \\ b_4 \\ \ldots \\ b_n \end{pmatrix} = \mathbb{B}$$

We need to consider two cases: *non-homogeneous* set of equations *vs.* *homogeneous* set of equations.

A. For Non-Homogeneous Linear Equations

If the inverse of $\mathbb{A}$ exists (i.e., if $\mathbb{A}$ is *non*-singular), then simply multiplying both sides of the matrix equation (from the left) by $\mathbb{A}^{-1}$ yields the desired solution.

i.e., starting from $\mathbb{A}\,\mathbb{X} = \mathbb{B}$ and multiplying from the left by $\mathbb{A}^{-1}$ yields:

$$\mathbb{A}^{-1}\,(\mathbb{A}\,\mathbb{X}) = (\mathbb{A}^{-1}\,\mathbb{A})\,\mathbb{X} = \mathbb{I}\,\mathbb{X} = \mathbb{X} = \mathbb{A}^{-1}\,\mathbb{B}$$

E.g., $\left.\begin{array}{rcl} x + 2y + z &=& 1 \\ 2x + y + 2z &=& 2 \\ 3x - y + z &=& -1 \end{array}\right\}$ is equivalent to $\begin{pmatrix} 1 & 2 & 1 \\ 2 & 1 & 2 \\ 3 & -1 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 1 \\ 2 \\ -1 \end{pmatrix}$

However, $\begin{pmatrix} 1 & 2 & 1 \\ 2 & 1 & 2 \\ 3 & -1 & 1 \end{pmatrix}^{-1} =$

Cramer's Rule

For the matrix equation $\mathbb{A}\,\mathbb{X} = \mathbb{B}$, where $\mathbb{B}$ is an $n\times 1$ column matrix, we saw that the (column) solution vector is equal to $\mathbb{X} = \mathbb{A}^{-1}\,\mathbb{B}$. Recalling our formal definition of the inverse matrix in terms of its adjoint, or in terms of its cofactors, we see that this is equivalent to writing

$$\mathbb{X} = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \\ \vdots \\ x_n \end{pmatrix} = \mathbb{A}^{-1}\,\mathbb{B} = \frac{1}{|\mathbb{A}|}\begin{pmatrix} \mathbf{C}(a_{11}) & \mathbf{C}(a_{21}) & \mathbf{C}(a_{31}) & \mathbf{C}(a_{41}) & \dots & \mathbf{C}(a_{n1}) \\ \mathbf{C}(a_{12}) & \mathbf{C}(a_{22}) & \mathbf{C}(a_{32}) & \mathbf{C}(a_{41}) & \dots & \mathbf{C}(a_{n1}) \\ \mathbf{C}(a_{13}) & \mathbf{C}(a_{23}) & \mathbf{C}(a_{33}) & \mathbf{C}(a_{41}) & \dots & \mathbf{C}(a_{n1}) \\ \mathbf{C}(a_{14}) & \mathbf{C}(a_{24}) & \mathbf{C}(a_{34}) & \mathbf{C}(a_{41}) & \dots & \mathbf{C}(a_{n1}) \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \end{pmatrix}\begin{pmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \\ \vdots \\ b_n \end{pmatrix}$$

From the definition of matrix multiplication with the j^{th} row of the adjoint matrix, we see that

$$x_j = \frac{1}{|\mathbb{A}|}\left[\, b_1\,\mathbf{C}(a_{1,j}) + b_2\,\mathbf{C}(a_{2,j}) + b_3\,\mathbf{C}(a_{3,j}) + b_4\,\mathbf{C}(a_{4,j}) + \cdots + b_n\,\mathbf{C}(a_{n,j})\,\right]$$

However, we can also see that the term in square brackets here is simply the definition of the determinant of the $n\times n$ matrix obtained on replacing the j^{th} columns of our origninal matrix $\mathbb{A}$ by the $n\times 1$ column matrix $\mathbb{B}$.

e.g.,

$$x_3 = \frac{1}{|\mathbb{A}|}\begin{vmatrix} a_{11} & a_{12} & b_1 & a_{14} & a_{15} & \dots\dots & a_{1n} \\ a_{21} & a_{22} & b_1 & a_{24} & a_{25} & \dots\dots & a_{2n} \\ a_{31} & a_{32} & b_1 & a_{34} & a_{35} & \dots\dots & a_{3n} \\ a_{41} & a_{42} & b_1 & a_{44} & a_{45} & \dots\dots & a_{4n} \\ \dots & \dots & \dots & \dots & \dots & \dots\dots & \dots \\ a_{n1} & a_{n2} & b_1 & a_{n4} & a_{n5} & \dots\dots & a_{nn} \end{vmatrix}$$

This result is called ***Cramer's Rule***.

Note, however, that a set of n non-homogeneous equations in n unknowns ***has no solution*** if the determinant of coefficients $|\mathbb{A}| = 0$

Returning to the example from p. 17:

$$\left.\begin{array}{rcl} x+2y+\ z &=& 1 \\ 2x+\ y+2z &=& 2 \\ 3x-y+\ z &=& -1 \end{array}\right\} \qquad \text{or} \qquad \begin{pmatrix} 1 & 2 & 1 \\ 2 & 1 & 2 \\ 3 & -1 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 1 \\ 2 \\ -1 \end{pmatrix}$$

B. For Homogeneous Linear Equations

This is the case

$$\begin{array}{rcl} a_{11}\,x_1 + a_{12}\,x_2 + a_{13}\,x_3 + \ldots + a_{1n}\,x_n &=& 0 \\ a_{21}\,x_1 + a_{22}\,x_2 + a_{23}\,x_3 + \ldots + a_{2n}\,x_n &=& 0 \\ a_{31}\,x_1 + a_{32}\,x_2 + a_{33}\,x_3 + \ldots + a_{3n}\,x_n &=& 0 \\ a_{41}\,x_1 + a_{42}\,x_2 + a_{43}\,x_3 + \ldots + a_{4n}\,x_n &=& 0 \\ \ldots\ldots & & \vdots \\ a_{n1}\,x_1 + a_{n2}\,x_2 + a_{n3}\,x_3 + \ldots + a_{nn}\,x_n &=& 0 \end{array} \qquad \text{or} \qquad \mathbb{A}\,\mathbb{X} = \mathbb{O}$$

As with homogeneous *differential* equations, one possible solution is always the "trivial" solution:

$$x_1 = 0 = x_2 = x_3 = \ldots = x_n = 0\ .$$

and if $|\mathbb{A}| \neq 0$, which means that $\mathbb{A}^{-1}$ exists, then the trivial solution is the *only possible* solution!

If $|\,\mathbb{A}\,| = 0$ then non-trivial solutions exist. Note, however, that if $\mathbb{X}$ is a solution, then so is $k\,\mathbb{X}$, for any scalar k .

Two possible methods of solving for such no-trivial solutions:

- solve by successive substitutions (can be *very* tedious!), or
- perform row reduction of the matrix of coefficients $\mathbb{A}$ to triangular form, and then solve by successive substitutions.

E.g., $\left.\begin{array}{rcl} x + 2y + z &=& 0 \\ 2x + y + 2z &=& 0 \\ x - y + z &=& 0 \end{array}\right\}$ is equivalent to $\begin{pmatrix} 1 & 2 & 1 \\ 2 & 1 & 2 \\ 1 & -1 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$

Since $|\,\mathbb{A}\,| =$

non-trivial solution(s) must exist!

***Summarizing*:**

5.6 Matrix Eigenvalue Problems

A matrix eigenvalue problem has the general form

$$\mathbb{A}\,\mathbb{X} = \begin{pmatrix} a_{11} & a_{12} & a_{13} & \dots & a_{1n} \\ a_{21} & a_{22} & a_{23} & \dots & a_{2n} \\ a_{31} & a_{32} & a_{33} & \dots & a_{3n} \\ a_{41} & a_{42} & a_{43} & \dots & a_{4n} \\ \dots & \dots & \dots & \dots & \dots \\ a_{n1} & a_{n2} & a_{n3} & \dots & a_{nn} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_2 \\ x_4 \\ \dots \\ x_n \end{pmatrix} = \lambda \begin{pmatrix} x_1 \\ x_2 \\ x_2 \\ x_4 \\ \dots \\ x_n \end{pmatrix} = \lambda\,\mathbb{X} \qquad \text{or} \qquad \mathbb{A}\,\mathbb{X} = \lambda\,\mathbb{X}$$

To solve it, for the given square matrix $\mathbb{A}$ of known (scalar) coefficients a_{ij}, we want to find the special column matrix $\mathbb{X}$ and scalar k such that the product $\mathbb{A}\,\mathbb{X}$ is a constant times the original column matrix $\mathbb{X}$.

Aside:

For *any* matrix $\mathbb{X}$, the definition of the unit matrix $\mathbb{I}$ means that $\mathbb{X} = \mathbb{X}\mathbb{I} = \mathbb{I}\,\mathbb{X}$. If we rearrange the compact version of the above matrix equation, and substitute this in for the last term, we obtain

$$\mathbb{A}\,\mathbb{X} - \lambda\,\mathbb{X} \;=\; \mathbb{A}\,\mathbb{X} - \lambda(\mathbb{I}\,\mathbb{X}) \;=\; \mathbb{A}\,\mathbb{X} - (\lambda\,\mathbb{I})\,\mathbb{X} \;=\; (\mathbb{A} - \lambda\,\mathbb{I})\,\mathbb{X} \;=\; 0$$

i.e.,
$$\left\{ \begin{pmatrix} a_{11} & a_{12} & a_{13} & \dots & a_{1n} \\ a_{21} & a_{22} & a_{23} & \dots & a_{2n} \\ a_{31} & a_{32} & a_{33} & \dots & a_{3n} \\ a_{41} & a_{42} & a_{43} & \dots & a_{4n} \\ \dots & \dots & \dots & \dots & \dots \\ a_{n1} & a_{n2} & a_{n3} & \dots & a_{nn} \end{pmatrix} - \lambda \begin{pmatrix} 1 & 0 & 0 & \dots & 0 \\ 0 & 1 & 0 & \dots & 0 \\ 0 & 0 & 1 & \dots & 0 \\ 0 & 0 & 0 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots & 1 \end{pmatrix} \right\} \begin{pmatrix} x_1 \\ x_2 \\ x_2 \\ x_4 \\ \dots \\ x_n \end{pmatrix} \;=\; 0$$

or
$$(\mathbb{A} - \lambda\,\mathbb{I})\,\mathbb{X} \;=\; \begin{pmatrix} (a_{11}-\lambda) & a_{12} & a_{13} & a_{14} & \dots & a_{1n} \\ a_{21} & (a_{22}-\lambda) & a_{23} & a_{24} & \dots & a_{2n} \\ a_{31} & a_{32} & (a_{33}-\lambda) & a_{34} & \dots & a_{3n} \\ a_{41} & a_{42} & a_{43} & (a_{4n}-\lambda) & \dots & a_{4n} \\ \dots & \dots & \dots & \dots & \dots & \dots \\ a_{n1} & a_{n2} & a_{n3} & a_{n4} & \dots & (a_{nn}-\lambda) \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_2 \\ x_4 \\ \dots \\ x_n \end{pmatrix} \;=\; 0$$

This is clearly just an example of a set of n linear *homogeneous* equations in n unknowns. As we saw previously, it can have non-trivial solutions if and only if the determinant of the matrix of coefficients *equals zero*. In the present case, that matrix of coefficients is $(\mathbb{A} - \lambda\,\mathbb{I})$. Hence, our set of linear equations $\mathbb{A}\,\mathbb{X} = \lambda\,\mathbb{X}$ only has non-trivial solution(s) if

$$\left|\, \mathbb{A} - \lambda\,\mathbb{I} \,\right| \;=\; 0$$

This is called the "***secular equation***" for the matrix $\mathbb{A}$.

- Since we know the two matrices $\mathbb{A}$ and $\mathbb{I}$, this equation serves to define the allowed values(s) of the "eigenvalue" λ.
- Because of the form of the determinant defining the secular equation,

$$\begin{vmatrix} (a_{11}-\lambda) & a_{12} & a_{13} & a_{14} & \dots & a_{1n} \\ a_{21} & (a_{22}-\lambda) & a_{23} & a_{24} & \dots & a_{2n} \\ a_{31} & a_{32} & (a_{33}-\lambda) & a_{34} & \dots & a_{3n} \\ a_{41} & a_{42} & a_{43} & (a_{4n}-\lambda) & \dots & a_{4n} \\ \dots & \dots & \dots & \dots & \dots & \dots \\ a_{n1} & a_{n2} & a_{n3} & a_{n4} & \dots & (a_{nn}-\lambda) \end{vmatrix} \;=\; 0 \;=\; \left\{ \, n^{th} \text{ order polynomial in } \lambda \right\}$$

  it is clear that for any given $n \times n$ matrix $\mathbb{A}$, there must exist exactly n individual possible eigenvalues: λ_1, λ_2, λ_3, λ_4, ... , λ_n.

Just as in our differential equation eigenvalue problems, each individual eigenvalue is associated with a unique different column (solution) vector, similarly, here we have:

i.e., $\lambda_j \leftrightarrow \mathbb{X}_j$, and each of these column vectors $\mathbb{X}_j$ must be solved for separately (see below).

Note that in some cases, two or more of the eigenvalues may be equal. When this occurs we refer to those eigenvalues as being "degenerate". However, if such a subset of 2 (or more generally, m) of the eigenvalues of a given matrix $\mathbb{A}$ are degenerate, we can determine m distinct orthogonal eigenvectors, all of which correspond to that common value of λ_j (see below).

- Once a particular value is known for $\lambda = \lambda_j$, we can substitute it in and solve the matrix equation

$$(\,\mathbb{A} - \lambda_j\,\mathbb{I}\,)\,\mathbb{X}_j \;=\; \mathbb{O}$$

to find the associated (column) solution matrix $\mathbb{X}_j$ (see example on p. 19).

- *Normalizing the Solutions.* If any given "eigenvector" $\mathbb{X}_j$ satisfies our eigenvalue equation

$$(\,\mathbb{A} - \lambda_j\,\mathbb{I}\,)\,\mathbb{X}_j \;=\; 0$$

it is clear that *any* scalar multiple of it $\mathbb{X}_j{}' = k\,\mathbb{X}_j$ must also satisfy that equation for the same eigenvalue λ_j ; aside from the scalar factor, these solution vectors will be identical. To remove ambiguity, it is convenient to require that each solution be normalized. To do this, we must determine the scalar k such that

$$\langle\,\mathbb{X}_j{}'\|\mathbb{X}_j{}'\,\rangle \;=\; \langle\,k\,\mathbb{X}_j\|k\,\mathbb{X}_j\,\rangle \;=\; k^*\,k\,\langle\,\mathbb{X}_j\|\mathbb{X}_j\,\rangle \;=\; |k|^2\,\langle\,\mathbb{X}_j\|\mathbb{X}_j\,\rangle \;=\; 1$$

Note that in matrix algebra, the inner product of two column matrices $\mathbb{B}$ and $\mathbb{C}$ is defined as $\langle\,\mathbb{B}\|\mathbb{C}\,\rangle \equiv \mathbb{B}^\dagger\,\mathbb{C}$, i.e., as the product of the Hermitian conjugate of the first (which makes in into a row vector) with the second.

This clearly shows that for any eigenvector $\mathbb{X}_j$, its normalized form is simply

---

E.g. (i) Find the eigenvalues and eigenvectors of the matrix $\mathbb{A} = \begin{pmatrix} 4 & 1 \\ 2 & 3 \end{pmatrix}$.

E.g. (ii) Find the eigenvalues and eigenvectors of the matrix $\mathbb{A} = \begin{pmatrix} 1 & -1 & -1 \\ 1 & -1 & 0 \\ 1 & 0 & -1 \end{pmatrix}$.

5.8 Some Properties of Matrix Eigenvalues

Recall that the secular equation for a given square matrix has the form

$$|\,\mathbb{A}-\lambda\,\mathbb{I}\,| \;=\; \begin{vmatrix} (a_{11}-\lambda) & a_{12} & a_{13} & a_{14} & \ldots & a_{1n} \\ a_{21} & (a_{22}-\lambda) & a_{23} & a_{24} & \ldots & a_{2n} \\ a_{31} & a_{32} & (a_{33}-\lambda) & a_{34} & \ldots & a_{3n} \\ a_{41} & a_{42} & a_{43} & (a_{4n}-\lambda) & \ldots & a_{4n} \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ a_{n1} & a_{n2} & a_{n3} & a_{n4} & \ldots & (a_{nn}-\lambda) \end{vmatrix} \;=\; 0$$

$$=\quad \left\{\; n^{th} \text{ order polynomial in } \lambda \;\right\}$$

$$=\quad f(\lambda) \;=\; (-1)^n \left\{\, \lambda^n - b_1\,\lambda^{n-1} + b_2\,\lambda^{n-2} - \ldots + (-1)^n\, b_n \,\right\} \;=\; 0$$

However, once we have solved and determined the n roots of the n^{th} order polynomial $f(\lambda)\,,\quad \lambda_1\,,\ \lambda_2\,,\ \lambda_3\,,\ \lambda_4\,,\ \ldots\,,\ \lambda_n\,,$ we can write

$$|\,\mathbb{A}-\lambda\,\mathbb{I}\,| \;=\; f(\lambda) \;=\; (\lambda_1-\lambda)(\lambda_2-\lambda)(\lambda_3-\lambda)(\lambda_4-\lambda)\;\ldots\;(\lambda_n-\lambda) \tag{19}$$

This means that the secular determinant $|\,\mathbb{A}-\lambda\,\mathbb{I}\,|$ may be treated as being a continuous function of the variable $\lambda\,$, which equals zero at the n special values $\lambda_1\,,\ \lambda_2\,,\ \lambda_3\,,\ \lambda_4\,,\ \ldots\ \lambda_n\,.$

Let us now consider some implications of this result.

1. Setting the variable λ in the above equation equal to zero shows than

   $$|\,\mathbb{A}\,| \;=\; \lambda_1\,\lambda_2\,\lambda_3\,\lambda_4\;\ldots\;\lambda_n$$

   i.e., for any square matrix, its determinant is equal to the product of its eigenvalues!

2. From the structure of the secular determinant, one can see that the coefficient of the terms in λ^n and λ^{n-1} can only arise from the product of the terms in its diagonal:

   $$(a_{11}-\lambda)(a_{22}-\lambda)(a_{33}-\lambda)(a_{44}-\lambda)\ldots(a_{nn}-\lambda) \tag{20}$$

   This is true because from the formal definition of a determinant given at the beginning of §5.3, we can see than any permutation of the column (or row) labels can only give terms involving powers of order $(n-2)$ or smaller. On applying the normal rules of algebra to the products in Eqs. (19) and (20) and requiring the coefficients of λ^{n-1} to be equal, we then obtain

   $$b_1 = (\,\lambda_1+\lambda_2+\lambda_3+\lambda_4+\;\ldots+\lambda_n) = (\,a_{11}+a_{22}+a_{33}+a_{44}+\;\ldots+a_{nn}) = \mathrm{Tr}(\,\mathbb{A}\,)$$

3. If $\mathbb{A}$ is an $n\times n$ matrix, then: $\quad |\,(\,\mathbb{A}-\lambda\,\mathbb{I}\,)\,| \;=\; \left|\widetilde{\mathbb{A}-\lambda\,\mathbb{I}}\right| \;=\; \left|\widetilde{\mathbb{A}}-\lambda\,\mathbb{I}\right|$

   which means that $\widetilde{\mathbb{A}}$ has the *same eigenvalues* as $\mathbb{A}\,.$ However, in general their eigenvectors will be different.

4. If $\mathbb{A}$ is a non-singular matrix (i.e., $\|\mathbb{A}\|$ is non-zero, so its inverse $\mathbb{A}^{-1}$ exists). then the eigenvalues of $\mathbb{A}^{-1}$ are the inverse of the eigenvalues of $\mathbb{A}$.

   Proof: If λ_j is an eigenvalue of $\mathbb{A}$, then

   $$0 \;=\; |\,\mathbb{A} - \lambda_j\,\mathbb{I}| =$$

Theorem 5.4 Eigenvalues corresponding to different eigenvalues are in general linearly independent.

Theorem 5.5 For a Hermitian matrix, all of its eigenvalues are purely real, and eigenvectors corresponding to different eigenvalues are *orthogonal*.

Theorem 5.6 If a given $n \times n$ square matrix $\mathbb{A}$ happens to have a number of its eigenvalues (say m) which are identical, there are m different orthogonal eigenvectors which correspond to that common m-fold degenerate eigenvalue. They generate a vector subspace of dimension m inside the full n-dimensional vector space generated by *all* of the eigenvectors of $\mathbb{A}$.

Find the eigenvalues and eigenvectors of the matrix $\begin{pmatrix} 2 & 0 & 1 \\ 0 & 3 & 0 \\ 1 & 0 & 2 \end{pmatrix}$.

First, solve the secular equation for this matrix:

$$\begin{vmatrix} 2-\lambda & 0 & 1 \\ 0 & 3-\lambda & 0 \\ 1 & 0 & 2-\lambda \end{vmatrix} \;=\; 0 \;=$$

[additional pages of work ...]

Application: Hückel Molecular Orbital Theory for the Propenyl Radical CH_2–CH–CH_2

Hückel molecular orbital theory is a model which provides a very good qualitative description of the relative energies and the nature of the associated molecular orbitals for the π-electron systems of simple conjugated hydrocarbons such as ethylene $CH_2 = CH_2$, cyclobutadiene C_4H_4, and benzene C_6H_6. We will introduce this theory and apply to to the case of the propenyl radical CH_2–CH–CH_2.

Recalling elementary molecular orbital theory, we can see that one very plausible structure would give each carbon atom three sp^2 orbitals to bond to its neighbours, plus one unpaired p orbital which is aligned perpendicular to the plane of its three bonds.

Let us label those (normalized) atomic p orbital wavefunctions $\phi_p(j)$ (or ϕ_j), where the index j identifies the atom that a particular p orbital is attached to. Treating them as basis functions, we can write the general expression for a molecular π orbital as

$$\psi_\pi \;=\; a_1\,\phi_p(1) + a_2\,\phi_p(2) + a_3\,\phi_p(3) \tag{21}$$

where a_1, a_2, a_3 are scalar constants. The desired eigenstates for the π electrons are solutions of the general Schrödinger equation

$$\hat{H}\;\psi_\pi \;=\; E\;\psi_\pi \tag{22}$$

in which $\hat{H}$ is the Hamiltonian operator and E is the energy of the π-electron system for our molecule. Substituting the wavefunction expansion of Eq. (21) into the Eq. (22) then yields

$$\hat{H}\,\{\,a_1\,\phi_p(1) + a_2\,\phi_p(2) + a_3\,\phi_p(3) + a_4\,\phi_p(4)\,\} \;=\; E\,\{\,a_1\,\phi_p(1) + a_2\,\phi_p(2) + a_3\,\phi_p(3) + a_4\,\phi_p(4)\,\} \tag{23}$$

In order to turn a differential equation-type problem into a matrix problem, we now multiply Eq. (23) from the left by the complex conjugate of one of the basis functions, $\phi_p(j)^*$, and integrate over all the coordinates of all three p electrons. However, we know that when an operator such as $\hat{H}$ is applied to a vector (or function), it changes it into another vector (or function): $\hat{H}\,\psi_\pi \rightarrow \psi'_\pi$. Thus, the operation described above effectively involves taking the inner product of this transformed vector (or function)

ψ'_π with one of the original basis function.

$$\begin{aligned}
\langle\, \phi_p(j) \| \hat{H} \| \psi_\pi \,\rangle \;&=\; \langle\, \phi_j \| \hat{H} \| \psi_\pi \,\rangle \;=\; E\, \langle\, \phi_j \| \psi_\pi \,\rangle \;=\; E\, \langle\, \phi_p(j) \| \psi_\pi \,\rangle \\
\Big\langle\, \phi_j | \hat{H} |\, \{a_1\, \phi_p(1) + a_2\, \phi_p(2) + a_3\, \phi_p(3)\} \,\Big\rangle \;&=\; E\, \langle\, \phi_j \| \{a_1\, \phi_p(1) + a_2\, \phi_p(2) + a_3\, \phi_p(3)\} \rangle \\
a_1\, \langle\, \phi_j \| \hat{H} \| \phi_1 \,\rangle + a_2\, \langle\, \phi_j \| \hat{H} \| \phi_2 \,\rangle + a_3\, \langle\, \phi_j \| \hat{H} \| \phi_3 \,\rangle \;&=\; E\, \{\, a_1\, \langle\, \phi_j \| \phi_1 \,\rangle + a_2\, \langle\, \phi_j \| \phi_2 \,\rangle + a_3\, \langle\, \phi_j \| \phi_3 \,\rangle \}
\end{aligned}$$

where the second and third versions of this equation have made use of the fact that the inner product of a sum is a sum of inner products, and that a constant factor (such as E) may be taken out on an inner product.

We now introduce the approximations which are the basis of Hückel theory.

(i) $\langle\, \phi_j \| \phi_k \,\rangle = \delta_{jk}$.

i.e., we assume that the p orbitals on different carbon atoms do not overlap at all ... that their orbital wavefunctions are unit normalized and mutually orthogonal.

(ii) $\langle\, \phi_j \| \hat{H} \| \phi_j \,\rangle = \alpha$ has the same value for all p orbitals j .

The quantity α represents the effective one-electron energy which one of these p electrons would have if no other p (or π) electrons were present

(iii) $\langle\, \phi_j \| \hat{H} \| \phi_k \,\rangle = -\beta$ has the same (non-zero) value for orbitals on *any* adjacent atoms j & k .

$\langle\, \phi_j \| \hat{H} \| \phi_k \,\rangle = 0$ for orbitals on any pair of *non*-adjacent atoms j and k .

Applying these three approximations to the above equation, for $i = 1,\ 2$ & 3, we obtain the set of linear equations:

$$\begin{aligned}
a_1\,\alpha \;-\; a_2\,\beta \;+\; a_3 \cdot 0 \;&=\; E\, a_1 \qquad \text{for} \qquad j = 1 \\
-a_1\,\beta \;+\; a_2\,\alpha \;-\; a_3\,\beta \;&=\; E\, a_2 \qquad \text{for} \qquad j = 1 \\
a_1 \cdot 0 \;-\; a_2\,\beta \;+\; a_3\,\alpha \;&=\; E\, a_2 \qquad \text{for} \qquad j = 1
\end{aligned}$$

or

$$\begin{pmatrix} \alpha & -\beta & 0 \\ -\beta & \alpha & -\beta \\ 0 & -\beta & \alpha \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} \;=\; E \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}$$

This is clearly a matrix eigenvalue problem for which the secular equation is

$$\begin{vmatrix} \alpha - E & -\beta & 0 \\ -\beta & \alpha - E & -\beta \\ 0 & -\beta & \alpha - E \end{vmatrix} \;=\; 0 \;=$$

Exercise 5.4 Evaluate the matrix product

$$\begin{pmatrix} 1 & -i & 1 & -i \end{pmatrix} \begin{pmatrix} 1 & -2 & 3 \\ 3 & 0 & 1 \\ 0 & 3 & -2 \\ -2 & 1 & 0 \end{pmatrix} \begin{pmatrix} i & 3 & 2i & 3 & i \\ 2 & i & 3 & 2i & 1 \\ 3i & 2 & i & 2 & 3i \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 1 \\ 0 \\ 1 \end{pmatrix}$$

Exercise 5.5 Evaluate the matrix product $\begin{pmatrix} 1 & 0 & 2 & 0 \\ 0 & 31 & 0 & 4 \\ 5i & 0 & 6 & 0 \\ 0 & 3i & 0 & 8 \end{pmatrix} \begin{pmatrix} 2 & 0 & 0 & 2 \\ 2 & 1 & 0 & 0 \\ 3 & 2 & 2 & 0 \\ 2 & 1 & 0 & -i \end{pmatrix}$

Exercise 5.6 Evaluate the determinants: (a) $\begin{vmatrix} 1 & -2-i & 1+i \\ -2+i & 1 & i \\ 1-i & -i & 1 \end{vmatrix}$ (b) $\begin{vmatrix} 1 & 0 & -1 & 1 \\ 0 & 2 & -2 & 2 \\ 3 & 6 & 0 & 4 \\ -4 & 2 & 5 & 3 \end{vmatrix}$

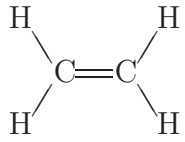
Exercise 5.7 Use matrix methods to find the solution (if one exists) of the set of equations

$$\begin{aligned} 4x - 3y + z &= 11 \\ 2x + y + 4z &= -1 \\ x + 2y - 2z &= 1 \end{aligned}$$

Exercise 5.8 Determine all of the eigenvalues and the associated normalized eigenvectors of the matrices:

(a) $\begin{pmatrix} 1 & 1+i \\ 1-i & 2 \end{pmatrix}$ (b) $\begin{pmatrix} 1 & 0 & 2i & 0 \\ 0 & 2 & 0 & -i \\ -2i & 0 & 1 & 0 \\ 0 & i & 0 & 2 \end{pmatrix}$ (c) $\begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \end{pmatrix}$

Exercise 5.9 Apply the Hückel molecular orbital method to the π electrons of ethylene and determine expressions for:



(i) the allowed orbital eigenvalues,

(ii) the associated eigenvectors, and

(iii) the overall π system ground-state energy, and

(iv) sketch the associated π orbital wavefunctions, clearly indicating the location(s) of any nodal surfaces.

Exercise 5.10 Repeat Q #5.9 for n-butadiene C_4H_6.

Exercise 5.11 Repeat Q #5.9 for cyclobutadiene C_4H_4.

Ans. eigencalues are $(\alpha - 2\beta)$, α, α, $(\alpha + 2\beta)$.

Exercise 5.12 Repeat Q #5.9 for benzene C_6H_6.

6. Symmetry and Group Theory

Group theory is a branch of mathematics which has a wide variety of forms and applications. In the brief introduction to it presented here, we focus on its application to the classification and description of molecular systems – either individual molecules, or extended solid crystalline lattices – according to their symmetry.

Our discussion of vector spaces began with a statement of a set of abstract conditions which determined whether a give set of objects constituted a "vector space". A somewhat similar set of rules defines whether or not a set of "objects" (e.g., numbers, square matrices, symmetry operations) forms a "group".

6.1 What is a "group"?

If a set of elements of some specified type form a ***group***, then there must exist some operation for "combining" any two elements of the set, and the following four rules must be satisfied.

(i) If any two elements of the set are "combined", the result is also one of the elements of the set.

(ii) The set must include an ***identity*** element, which is defined by the fact that when "combined" with any other element of the set, that other element is unchanged. This identity element is usually denoted by the symbol E or $\tilde{E}$ (or $\tilde{e}$, or $\mathbb{E}$ if it is a matrix).

(iii) The operation of "combining" pairs of elements of the set is *associative*; i.e., the result of the stepwise "combination" of element $\tilde{A}$ with the "combination" of $\tilde{B}$ with $\tilde{C}$, is identical to the net result of first "combining" $\tilde{A}$ with $\tilde{B}$ and then "combining" that result with $\tilde{C}$.

If the act of "combining" two elements is a type of multiplication, we can write this rule in the mathematical form

$$\tilde{A}(\tilde{B}\tilde{C}) = (\tilde{A}\tilde{B})\tilde{C}$$

(iv) Every element $\tilde{A}$ of the set has an "inverse" $\tilde{A}^{-1}$ which is also a member of that set. An "inverse" is defined by the property that when an element is "combined" with its "inverse", the result is the identity element $\tilde{E}$.

The *order* of a group is defined as the number of distinct elements comprising that group.

It is immediately clear that to define a particular *group*, it is necessary to specify both

- the type of element comprising the set, and
- the nature of the operation of "combining" two of those elements.

We will illustrate the nature of these definitions through some illustrative examples.

Examples of Groups

(1) Consider the set of all integers, with the "combination" law being ordinary operation of addition. Is it a group?

(2) Consider the set of all rational numbers with the "combining" law being the ordinary operation of scalar multiplication. Do they form a group?

(3) Consider the four elements $1,\ i,\ -1$ and $-i$ with the "combining" law being the ordinary operation of scalar multiplication. It is easy to show that this set comprises a *group*.

Moreover, we can see that it is a finite group of *order* 4.

This is an example of a ***cyclic group***, which is defined as any group whose elements may all be expressed as a power of a single element $\tilde{a}$, which is called the *generator* of that group.
[e.g., the pair of elements 1 and -1 under the operation of multiplication]

(4) Consider the set of four 2×2 matrices

$$\mathbb{E} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \qquad \mathbb{A} = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}, \qquad \mathbb{B} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}, \qquad \mathbb{C} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

For the "combining" operation of ordinary matrix multiplication, show that this set forms a *group* of order 4.

6.2 The 'Group Table' (or Group 'Multiplication' Table) for a Group

Although the we reserve the right to define the operation of "combining" two elements of a group in different ways, for the sake of convenience we will usually refer to it as being a type of 'multiplication', although it is often not the simple type of multiplication associated with taking products of scalar numbers.

For finite groups (groups with a finite number of distinct elements) it is usually very convenient to construct and understand the properties of their "multiplication table", a table which shows the result of combining any two elements in either order. Such tables are written as a matrix showing the result of "multiplying" the element at the beginning of each row (from the left) to the element at the head of each column. For Example (3) above, the multiplication table is (multiplication order – column element before row element):

	$\mathbb{E}=1$	i	-1	$-i$
1				
i				
-1				
$-i$				

The fact that the matrix of products is *symmetric* reflects the fact that for this *group* of scalars, the multiplication operation commutes. A group for which this is true is said to be "Abelian".

As a second example, construct the multiplication table for the four matrices from Example (4) from p. 2.

	$\mathbb{E}$	$\mathbb{A}$	$\mathbb{B}$	$\mathbb{C}$
$\mathbb{E}$				
$\mathbb{A}$				
$\mathbb{B}$				
$\mathbb{C}$				

This group of four matrices is clearly also Abelian.

As a third example, construct the multiplication table for the set of four 2×2 matrices:

$$\mathbb{E} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \qquad \mathbb{A} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}, \qquad \mathbb{B} = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}, \qquad \mathbb{C} = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$$

	$\mathbb{E}$	$\mathbb{A}$	$\mathbb{B}$	$\mathbb{C}$
$\mathbb{E}$				
$\mathbb{A}$				
$\mathbb{B}$				
$\mathbb{C}$				

Isomorphism

On comparing this multiplication table with that for the first example considered on the previous page, we see that they have *exactly the same structure*. In other words, there is a one-to-one correspondence between the elements of one group and those of the other, such that if $\mathbb{A}\,\mathbb{B} = \mathbb{C}$ for one, then $\mathbb{A}'\,\mathbb{B}' = \mathbb{C}'$ for the other. When this situation arises, those two groups are said to be ***isomorphic*** to one another.

A formal theorem of group theory shows that *all* groups of order four are *isomorphic* with one or the other of the two types of groups considered above.

Note (i): in all of the multiplication tables we have considered, each member of the group appears once in each row or column, but in a different position in each. This result is known as the ***rearrangement theorem***.

Note (ii): Not all groups are Abelian. For example, construct the multiplication table for the set of six matrices:

$$\mathbb{E} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \qquad \mathbb{A} = \begin{pmatrix} 0 & -1 \\ 1 & -1 \end{pmatrix}, \qquad \mathbb{B} = \begin{pmatrix} -1 & 1 \\ -1 & 0 \end{pmatrix},$$

$$\mathbb{C} = \begin{pmatrix} 1 & -1 \\ 0 & -1 \end{pmatrix}, \qquad \mathbb{D} = \begin{pmatrix} -1 & 0 \\ -1 & 1 \end{pmatrix}, \qquad \mathbb{F} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

	$\mathbb{E}$	$\mathbb{A}$	$\mathbb{B}$	$\mathbb{C}$	$\mathbb{D}$	$\mathbb{F}$
$\mathbb{E}$						
$\mathbb{A}$						
$\mathbb{B}$						
$\mathbb{C}$						
$\mathbb{D}$						
$\mathbb{F}$						

Overview

The truly central characterizing property of any group is the structure of its multiplication table. Many superficially different sets of objects can be shown to be 'isomorphic groups', since they have the same multiplication table.

Groups of Order 2. All possible groups of order 2 are cyclic groups. For example:

- the pair of numbers 0 and $+1$ under the operation of addition modulo 2.
- the pair of numbers 1 and -1 under the operation of multiplication.
- the pair of 3×3 matrices $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ and $\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$
- the pair of functions $\tilde{f}_1(x) = x$ and $\tilde{f}_2(x)$ for which the law of combination is to substitute one function into the other. e.g., $\tilde{f}_2\,\tilde{f}_2 = \dfrac{1}{1/x}$.

All of these groups have a generator $\tilde{a}$, and the multiplication table:

	$\tilde{e}$	$\tilde{a}$
$\tilde{e}$	$\tilde{e}^2 = \tilde{e}$	$\tilde{e}\,\tilde{a} = \tilde{a}$
$\tilde{a}$	$\tilde{a}\,\tilde{e} = \tilde{a}$	$\tilde{a}^2 = \tilde{e}$

Groups of Order 3. All possible groups of order 3 are cyclic groups with the multiplication table:

	$\tilde{e}$	$\tilde{a}$	$\tilde{a}^2$
$\tilde{e}$	$\tilde{e}$	$\tilde{a}$	$\tilde{a}^2$
$\tilde{a}$	$\tilde{a}$	$\tilde{a}^2$	$\tilde{e}$
$\tilde{a}^2$	$\tilde{a}^2$	$\tilde{e}$	$\tilde{a}$

e.g.,
- the group of complex numbers with generator $\tilde{a} = -\frac{1}{2} + i\,\frac{\sqrt{3}}{2}$ with the combination operation being multiplication.
- the numbers 0, 1 and 2 under the operation of addition modulo 3 .

Groups of Order 4. Two types of multiplication tables are possible for groups of order 4.

- Cyclic groups with the multiplication table $\Longrightarrow$

	$\tilde{e}$	$\tilde{a}$	$\tilde{a}^2$	$\tilde{a}^3$
$\tilde{e}$	$\tilde{e}$	$\tilde{a}$	$\tilde{a}^2$	$\tilde{a}^3$
$\tilde{a}$	$\tilde{a}$	$\tilde{a}^2$	$\tilde{a}^3$	$\tilde{e}$
$\tilde{a}^2$	$\tilde{a}^2$	$\tilde{a}^3$	$\tilde{e}$	$\tilde{a}$
$\tilde{a}^3$	$\tilde{a}^3$	$\tilde{e}$	$\tilde{a}$	$\tilde{a}^2$

  e.g., (i) First example on p. 3: the numbers 1, i, -1 and $-i$ under multiplication.
  (ii) The example at the top of p. 4.
  [What is the 'generator' for each of these cases?]

- The 'V group' or 'Four Group' consisting of four distinct elements $\tilde{e}$, $\tilde{a}$, $\tilde{b}$ and $\tilde{c}$, with the multiplication table seen on the bottom of p. 3.

Cyclic Groups of any order n are formed by generators with the form $e^{2\pi\, i/n}$ under the combination operation of multiplication.

Exercise 6.1 Consider the set of the six functions

$$f_1(x) = x\ , \quad f_2(x) = 1 - x\ , \quad f_3(x) = \frac{x-1}{x}\ , \quad f_4(x) = \frac{1}{x}\ , \quad f_5(x) = \frac{1}{1-x}\ , \quad f_6(x) = \frac{x}{x-1}$$

(a) For a 'law of combination' which consists of substituting one function into another [i.e., the "product" $f_i(x)\, f_j(x)$ is $f_i\,(x = f_j(x))$] show that this set of functions is a *group*.

(b) Construct the multiplication table for this group.

(c) If this an Abelian group? [justify your answer!]

(d) What is the identity element of this group?

(e) What is the inverse of element $f_3(x)$?

Exercise 6.2 Consider the set of operations consisting of the identity operator and rotation by π about each of three mutually perpendicular intersecting axes.

(a) Show what this is a *group* of order 4.

(b) What is the multiplication table for this group?

(c) Is this a cyclic group?

(d) Is this an Abelian group?

(e) Is this group isomorphic with the group of elements $\{1, -1, i, -i\}$ for which the combination operation is simple multiplication?

6.3 Groups of Symmetry Operators

Up to this point we have considered groups consisting of sets of conventional mathematical objects – numbers or matrices – with a combination law which is the conventional definition of multiplication for such objects. We now extend the discussion to include more abstract objects – *symmetry operators* – for which there is no simple general numerical coordinate representation. Operators of this type are not identified by their form or structure, as is the case for differential operators, which transform one function into another, or for square matrix operators, which convert one column vector into another. Rather, they are identified as a "set of instructions" which change the object or system on which they act.

In the preliminary discussion herein, we will consider the special case of ***point symmetry operators***, a class of symmetry operators which can be defined in terms of how they act on *points* in 3-dimensional space. Operators of this type do not move a point if it is located at the origin of the coordinate system. In applications to the description of molecules, we usually place that coordinate origin at the centre of mass, or centre of symmetry of the system. However, this is not necessary for the definition of those operators.

$\hat{E}$ is the identity operator; it leaves the system unchanged.

$\hat{C}_n^k$ is the operation of performing a clockwise rotation through an angle $2\pi/n$, k times, about an axis identified as a C_n axis. This type of rotation is sometimes called a "proper" rotation. For a given value of n there are $n-1$ operators of this type: $\hat{C}_n^1(=\hat{C}_n)$, $\hat{C}_n^2$, $\hat{C}_n^3$ $\ldots$, $\hat{C}_n^{n-1}$.

$\hat{\sigma}$ is the operation of performing a reflection in some specified plane. Since more than one reflection operation is often possible, these operators often have subscripts to distinguish the plane of reflection from another; e.g., $\hat{\sigma}_v$ or $\hat{\sigma}_h$.

$\hat{S}_n$ is the "improper" rotation operator which consists of clockwise rotation rotation by an angle $2\pi/n$ about an axis identified as a C_n axis, followed by reflection in a plane perpendicular to that axis. It is clear that $\hat{S}_n^k = (\sigma_h \hat{C}_n)^k = \hat{C}_n^k (\sigma_h)^k$, where the subscript h (for horizontal) defined the plane of reflection as being perpendicular to the axis of rotation. Thus, for even values of k, $\hat{S}_n^k = \hat{C}_n^k$.

$\hat{i}$ is the inversion operator, which causes all coordinates of the system to be inverted through the centre of symmetry of the system. One can readily see that $\hat{i} = \hat{S}_2^1 = \hat{\sigma}_h \hat{C}_2^1$.

These symmetry operations are defined by their effect on the coordinates of a point in space. Thus, for the case of axis of rotation along the z spatial axis, we can write:

$$\hat{C}_4 \{x_1, y_1, z_1\} = \qquad \hat{C}_4^2 \{x_1, y_1, z_1\} =$$

$$\hat{C}_4^3 \{x_1, y_1, z_1\} = \qquad \hat{C}_4^4 \{x_1, y_1, z_1\} =$$

$$\hat{\sigma}_h \{x_1, y_1, z_1\} = \qquad (\hat{\sigma}_h)^2 \{x_1, y_1, z_1\} =$$

$$\hat{S}_4 \{x_1, y_1, z_1\} = \qquad \hat{S}_4^2 \{x_1, y_1, z_1\} =$$

$$\hat{i} \{x_1, y_1, z_1\} = \qquad \hat{i}^2 \{x_1, y_1, z_1\} =$$

If a symmetry operator is applied to a system, it acts on all of the coordinates of all of the particles comprising the system.

If, after applying a symmetry operation to a given system or object, all of the particles of each type are in the same overall configuration as before, except for the exchange of identical particles, we say that *that symmetry operator "belongs"* to that system or object.

Every rigid object or system has a set of symmetry operators that *belong* to it. For a completely unsymmetric object, that set will consist of only the identity operator $\hat{E}$, but a symmetric object possesses at least one or more additional symmetry operators. The symmetry properties of any rigid object or system of particles can be specified by listing all of the symmetry operators that *belong* to it. It can be shown that such a set of symmetry operators form a *group*.

Exercise 6.3 What is the set of symmetry operators which *belong* to: (a) the water molecule; (b) the ammonia molecule.

Exercise 6.4 What is the multiplication table for the symmetry operations which *belong* to (a) the water molecule, and (b) the ammonia molecule.