5 Ordinary Differential Equations

Differential equations are usually classified as "ordinary" or "partial". In the former case only one independent variable is involved and its differential is exact. Thus there is a relation between the dependent variable, say $y(x)$, its various derivatives, as well as functions of the independent variable x. Partial differential equations contain several independent variables, and hence partial derivatives.

The order of an ordinary differential equation is the order of its highest derivative. Thus, an ordinary differential equation of order n is an equation of the form

$$F(x, y, y', \dots, y^{(n)}) = 0. \tag{1}$$

If the dependent variable $y(x)$ and all of its derivatives occur in the first degree and do not appear as products, the equation is said to be linear. In effect, the solution of a differential equation of order n necessitates n integrations, each of which involves an arbitrary constant. However, in some cases one or more of these constants may be assigned specific values. The results, which are also solutions of the differential equation, are referred to as particular solutions. The general solution, however, includes all of the n constants of integration, whose evaluation requires additional information associated with the application.

5.1 FIRST-ORDER DIFFERENTIAL EQUATIONS

A first-order differential equation can always be solved, although its solution is not necessarily easy to obtain. If the variables are separable, the equation can be reduced to the form

$$f(x)\mathrm{d}x = g(y)\mathrm{d}y, \tag{2}$$

and the integration can usually be carried out by one of the methods illustrated in Section 3.3.

Furthermore, as shown in Section 3.5, a differential equation such as

$$N(x,y)\mathrm{d}x + M(x,y)\mathrm{d}y = 0 \tag{3}$$

can be integrated directly if the left-hand side is an exact differential. Although most differential equations of this type are not exact, in principle they can be made so by the introduction of a suitable integrating factor. If the equation is linear, which is often the case, it can be written as

$$\frac{dy}{dx} + yp(x) = q(x). \tag{4}$$

Now, if a function $\mu(x)$ is chosen so that

$$p(x) = \frac{\mu'(x)}{\mu(x)} = \frac{d}{dx} ln\ \mu(x), \tag{5}$$

this function is

$$\mu(x) = e^{\int p(x)dx}, \tag{6}$$

and Eq. (4) becomes

$$\frac{dy}{dx} + y\frac{\mu'(x)}{\mu(x)} = q(x). \tag{7}$$

If both sides are multiplied by $\mu(x)$, Eq. (7) can be written as

$$\mu(x)y' + y\mu'(x) = \frac{d}{dx}[\mu(x)y] = \mu(x)q(x). \tag{8}$$

Thus,

$$\mu(x)y = \int \mu(x)q(x)dx + C, \tag{9}$$

and the function $\mu(x) = e^{\int p(x)dx}$ is the desired integrating factor.

As an example, consider the differential equation

$$\frac{dy}{dx} - yx = x. \tag{10}$$

By comparison with Eq. (4), $p = -x$, $q = x$ and the integrating factor is the Gaussian function $\mu = e^{-\frac{1}{2}x^2}$. With the introduction of this factor in Eq. (10),

$$e^{-\frac{1}{2}x^2}\frac{dy}{dx} - xe^{-\frac{1}{2}x^2}y = xe^{-\frac{1}{2}x^2} \tag{11}$$

and

$$\frac{d}{dx}(e^{-\frac{1}{2}x^2}y) = xe^{-\frac{1}{2}x^2}. \tag{12}$$

The solution to Eq. (10) is then obtained from

$$e^{-\frac{1}{2}x^2}y = \int xe^{-\frac{1}{2}x^2}\mathrm{d}x = -e^{-\frac{1}{2}x^2} + C, \tag{13}$$

or, simply,

$$y = Ce^{\frac{1}{2}x^2} - 1, \tag{14}$$

as can be easily verified by substitution.

5.2 SECOND-ORDER DIFFERENTIAL EQUATIONS

Many second-order differential equations arise in physical problems. Fortunately, most of them can be cast into a relatively simple form, namely,

$$P(x)\frac{\mathrm{d}^2y}{\mathrm{d}x^2} + Q(x)\frac{\mathrm{d}y}{\mathrm{d}x} + R(x)y = 0, \tag{15}$$

where $P(x)$, $Q(x)$ and $R(x)$ are polynomials. As the right-hand side of Eq. (15) is equal to zero in this case, the equation is said to be homogeneous and the method of series solution can be applied. This method is illustrated as follows.

5.2.1 Series solution

The dependent variable $y(x)$ is written in a power series, *viz.*

$$y(x) = a_0 + a_1x + a_2x^2 + \cdots = \sum_n a_nx^n. \tag{16}$$

Successive differentiation yields

$$\frac{\mathrm{d}y}{\mathrm{d}x} = a_1 + 2a_2x + 3a_3x^2 + \cdots = \sum_n na_nx^{n-1} \tag{17}$$

and

$$\frac{\mathrm{d}^2y}{\mathrm{d}x^2} = 2a_2 + 6a_3x + 12a_4x^2 \cdots = \sum_n n(n-1)a_nx^{n-2}. \tag{18}$$

The polynomial coefficients are of the form

$$P(x) = p_0 + p_1x + p_2x^2 \cdots , \tag{19}$$

$$Q(x) = q_0 + q_1x + q_2x^2 \cdots \tag{20}$$

and

$$R(x) = r_0 + r_1 x + r_2 x^2 \cdots. \tag{21}$$

The result of the substitution of Eqs. (16) to (21) into the differential equation [Eq. (15)] can be collected in powers of x. The constants, that is, the coefficients of x^0, lead to the relation

$$2a_2 p_0 + a_1 q_0 + a_0 r_0 = 0. \tag{22}$$

Thus,

$$a_2 = -\frac{a_1 q_0 + a_0 r_0}{2p_0}, \tag{23}$$

a function of the two coefficients a_0 and a_1. Equating the coefficients of x will yield an expression for a_3, namely

$$a_3 = \frac{1}{6p_0}\left\{\left[\frac{r_0(p_1+q_0)}{p_0} - r_1\right]a_0 + \left[\frac{q_0(p_1+q_0)}{p_0} - (q_1+r_0)\right]a_1\right\}, \tag{24}$$

where the expression for a_2 given by Eq. (23) has been employed. In principle, this procedure can be continued to obtain successive coefficients a_n as functions of only a_0 and a_1, two constants of integration.

An over-simplified example of this method is provided by the differential equation

$$\frac{d^2y}{dx^2} - y = 0. \tag{25}$$

Here, by comparison with Eq. (15) $P(x) = 1$, $Q(x) = 0$ and $R(x) = -1$; thus, all three coefficients in Eq. (15) are independent of x. The dependent variable $y(x)$ and its derivatives are developed as above [Eqs. (16) and (18)]. Substitution into Eq. (25) yields the relations $a_2 = a_0/2, a_3 = a_1/6$, *etc.*, which can be generalized in the form of a recursion formula for the coefficients,

$$a_{n+2} = \frac{a_n}{(n+1)(n+2)}. \tag{26}$$

A particular solution to Eq. (25) can be obtained by posing $a_0 = a_1 = 1$; then,

$$y_1 = 1 + x + \tfrac{1}{2}x^2 + \tfrac{1}{6}x^3 + \cdots = e^x, \tag{27}$$

where the identification of the series as the exponential has been made [see Eq. (1-10)]. It is easily verified by substitution that the exponential is a solution. However, it is also easy to show that the function $y_2 = e^{-x}$ is another solution to Eq. (25). As the ratio of these two solutions, $y_1/y_2 = e^{2x} \neq 0$, they are independent particular solutions. The general solution can then be written as

$$y = Ay_1 + By_2 = Ae^x + Be^{-x}, \tag{28}$$

where the constants of integration, A and B, are to be determined by the appropriate boundary conditions. From the definitions of the hyperbolic functions *sinh* x and *cosh* x [Eqs. (1-44) and (1-45)], it should be evident that the solution given by Eq. (28) can also be expressed in terms of these functions (see problem 3).

If in Eq. (15), $R = +1$, Eq. (25) becomes

$$\frac{d^2y}{dx^2} + y = 0, \tag{29}$$

and the particular solutions in this case are of the form $e^{\pm ix}$, as can be verified by substitution. It should be noted that the particular solutions are in this case periodic. The general solution

$$y(x) = Ae^{ix} + Be^{-ix} \tag{30}$$

can be expressed in terms of the functions *sin* x and *cos* x by application of Euler's relation [Eq. (1-32)]. Here again, the constants of integration are determined by the boundary conditions imposed on the general solution.

5.2.2. The classical harmonic oscillator

The example presented above will now be developed, as it is a problem which arises frequently in many applications. The vibrations of mechanical systems and oscillations in electrical circuits are illustrated by the following simple examples. The analogous subject of molecular vibrations is treated with the use of matrix algebra in Chapter 9.

Consider a physical pendulum, as represented in Fig. 1. A mass m is attached by a spring to a rigid support. The spring is characterized by a force

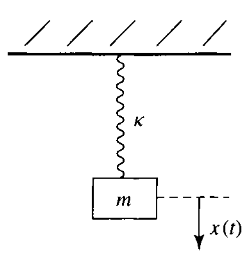


Fig. 1 Simple mechanical oscillator.

constant κ such that the force acting on the mass is described by Hooke's law,*

$$f = -\kappa x, \tag{31}$$

where $x(t)$ is the displacement of the mass from its equilibrium position and f is the force opposing this displacement (see Fig. 1).† Assuming that the force of gravity is independent of the small displacement $x(t)$, Newton's second law can be written in the form

$$f = m\ddot{x} = -\kappa x. \tag{32}$$

The equation of motion is then

$$\ddot{x} + \frac{\kappa}{m}x = 0. \tag{33}$$

In Eqs. (32) and (33) Newton's notation has been employed; the dot above a symbol indicates that its time derivative has been taken. Thus, $\mathrm{d}^2x/\mathrm{d}t^2 \equiv \ddot{x}$ is the second derivative of x with respect to time.

Aside from a constant and some changes in notation, Eq. (33) is of the same form as Eq. (29). Thus, particular solutions would be expected such as $e^{\pm i\omega_0 t}$, where $\omega_0 = 2\pi\nu^0$ is a constant and ν^0 is the natural frequency of oscillation. Substitution of this expression into Eq. (33) leads to the identification $\omega_0^2 = \kappa/m$. The general solution of Eq. (33) is then of the form

$$x(t) = Ae^{i\omega_0 t} + Be^{-i\omega_0 t}, \tag{34}$$

where A and B are two constants of integration. An alternative form of Eq. (34) is obtained from Euler's relation (Section 1.6), namely,

$$x = (A + B)\,cos\,\omega_0 t + i(A - B)\,sin\,\omega_0 t = C\,cos\,\omega_0 t + D\,sin\,\omega_0 t \tag{35}$$

and the constants C and D can also serve as the two integration constants.

Returning to the problem illustrated in Fig. 1, the question is: How is the pendulum put into motion at an initial time t_0?

(i) If at $t = t_0$ the mass is displaced by a distance x_0, and it is not given an initial velocity ($\dot{x}_0 = 0$), $C = x_0$ and $D = 0$. The solution is then given by

$$x = x_0\,cos\,\omega_0 t. \tag{36}$$

*Robert Hooke, English astronomer and mathematician (1635–1703).

†As shown in Section 5.14, in a conservative system the force can be represented by a potential function. The force is then given by $f = -\mathrm{d}V(x)/\mathrm{d}x$, where $V(x) = \frac{1}{2}\kappa x^2$ for this one-dimensional harmonic oscillator.

(ii) If at $t = t_0$ the mass is not displaced, but an initial velocity $\dot{x}_0 = v_0$ is imparted to it, as the derivative of Eq. (35) is

$$\dot{x} = -C\omega_0 \sin \omega_0 t + D\omega_0 \cos \omega_0 t, \tag{37}$$

$v_0 = D\omega_0$ and

$$x = \frac{v_0}{\omega_0} \sin \omega_0 t. \tag{38}$$

An alternative form of Eq. (35) can be obtained by substituting $C = \rho \cos \alpha$ and $D = \rho \sin \alpha$. Then,

$$x = \rho(\cos \alpha \cos \omega_0 t + \sin \alpha \sin \omega_0 t) = \rho \cos(\omega_0 t - \alpha). \tag{39}$$

The two constants of integration are now ρ and α, which are the amplitude and the phase angle, respectively. The initial conditions can be imposed as before.

5.2.3 The damped oscillator

Now suppose that the harmonic oscillator represented in Fig. 1 is immersed in a viscous medium. Equation (32) will then be modified to include a damping force which is usually assumed to be proportional to the velocity, $-h\dot{x}$. Thus, the equation of motion becomes

$$\ddot{x} + \frac{h}{m}\dot{x} + \frac{\kappa}{m}x = 0, \tag{40}$$

where the constant h depends on the viscosity of the medium.

The solution to Eq. (40) can be obtained with the substitution $x(t) = z(t)e^{\lambda t}$. The result is

$$e^{\lambda t}\left[\ddot{z} + \left(2\lambda + \frac{h}{m}\right)\dot{z} + \left(\lambda^2 + \frac{h\lambda}{m} + \frac{\kappa}{m}\right)z\right] = 0. \tag{41}$$

As the factor $e^{\lambda t} \neq 0$, the expression in brackets in Eq. (41) must be equal to zero. Furthermore, the parameter λ can be chosen so that the coefficient of $\dot{z}$ vanishes. Thus, $\lambda = -h/2m$ and Eq. (40) reduces to

$$\ddot{z} + \left(\frac{\kappa}{m} - \frac{h^2}{4m^2}\right)z = 0. \tag{42}$$

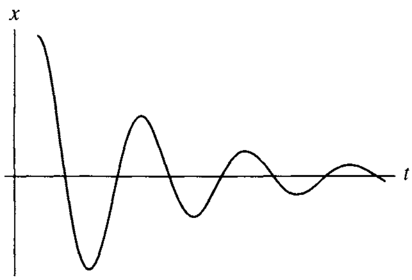


Fig. 2 Exponentially damped oscillation.

Here, two distinct situations arise depending on the relative magnitudes of the two terms in parentheses. If $\kappa/m > h^2/4m^2$, Eq. (42) is of the same form as Eq. (29), whose solutions can be written as $C\,cos\,\omega_1 t + D\,sin\,\omega_1 t$, with $\omega_1^2 = \kappa/m - h^2/4m^2$. Note that the presence of the damping term h/m modifies the natural (angular) frequency of the system. Then,

$$x = e^{-(h/2m)t}(C\,cos\,\omega_1 t + D\,sin\,\omega_1 t). \tag{43}$$

The two constants of integration, C and D, are determined as before by the initial conditions. This solution is oscillatory, although the amplitude of the oscillations decreases exponentially in time, as shown in Fig. 2.

On the other hand if $\kappa/m < h^2/4m^2$, the equation for $z(t)$ is of the form of Eq. (25) and the solutions are in terms of exponential functions of real arguments or hyperbolic functions. In this case $x(t)$ is not oscillatory and will simply decrease exponentially with time.

A third, very specific case occurs when $\kappa/m = h^2/4m^2$. The system is then said to be critically damped.

The mechanical problem treated above has its electrical analogy in the circuit shown in Fig. 3. It is composed of three elements, an inductance L, a capacitance C and a resistance R. If there are no other elements in the closed

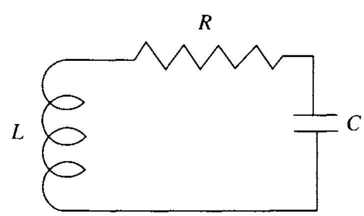


Fig. 3 Damped electrical oscillator.

circuit, according to Kirchhoff's second law,* the sum of the voltage drops across each of these three elements is equal to zero. The differential equation is then

$$L\frac{d\iota}{dt} + R\iota + \frac{q}{C} = 0, \tag{44}$$

where ι is the current and q is the charge on the capacitance. As the current is given by $\iota = dq/dt$, Eq. (44) becomes

$$\frac{d^2q}{dt^2} + \frac{R}{L}\frac{dq}{dt} + \frac{1}{LC}q = 0, \tag{45}$$

which is of the same form as Eq. (40). Clearly, the resistance is responsible for the damping, while L and $1/C$ are analogous to the mass and force constant, respectively, which characterize the mechanical problem. This example will be treated in Chapter 11 with the use of the Laplace transform.

5.3 THE DIFFERENTIAL OPERATOR

The problems presented above can be solved with the use of an alternative method which employs operators of the type $\hat{\mathcal{D}} \equiv d/dx$. While the notion of operators will be developed in more detail in Chapter 7, it is sufficient here to point out that $\hat{\mathcal{D}}$ may be considered to be an abbreviation. This method can be applied in the case where $P(x)$, $Q(x)$ and $R(x)$ in Eq. (15) are constants, as in the examples considered above.

5.3.1 Harmonic oscillator

With the use of the differential operator the equation of motion for the harmonic oscillator [Eq. (29)], can be expressed as

$$(\hat{\mathcal{D}}^2 + 1)y = 0, \tag{46}$$

where the symbol $\hat{\mathcal{D}}^2$ is understood to mean two successive applications of the derivative. Formally, Eq. (46) can be factored, *viz.*

$$(\hat{\mathcal{D}} - r_1)(\hat{\mathcal{D}} - r_2)y = 0, \tag{47}$$

*Gustav Robert Kirchhoff, German physicist (1824–1887).

where r_1 and r_2 are the roots. Clearly, if y satisfies the equation

$$(\hat{\mathcal{D}} - r_1)y = 0, \tag{48}$$

its solution, $y = c_1 e^{r_1 x}$ is a particular solution of Eq. (46). An analogous argument for the second factor in Eq. (47) will lead to a second, independent particular solution of Eq. (46). The general solution is then of the form

$$y = c_1 e^{r_1 x} + c_2 e^{r_2 x}, \tag{49}$$

where both r_1 and r_2 are imaginary. With the changes in notation indicated above, this result is equivalent to Eq. (34) for the classical harmonic oscillator. This method can be easily extended to the example of the damped oscillator (see problem 7).

5.3.2 Inhomogeneous equations

If the right-hand side of Eq. (15) is not equal to zero, solutions are more difficult to obtain. Consider a second-order equation of the form

$$y'' + a_1 y' + a_2 y = f(x). \tag{50}$$

In terms of the differential operator it becomes

$$(\hat{\mathcal{D}}^2 + a_1 \hat{\mathcal{D}} + a_2)y = f(x), \tag{51}$$

or

$$(\hat{\mathcal{D}} - r_1)(\hat{\mathcal{D}} - r_2)y = f(x), \tag{52}$$

where r_1 and r_2 are the roots of the left-hand side of Eq. (51). It is convenient to make the substitution $u = (\hat{\mathcal{D}} - r_2)y$, which results in $(\hat{\mathcal{D}} - r_1)u = f(x)$, a linear first-order differential equation. It can be solved by application of the method outlined in Section 3.5. The integrating factor is then $exp(-\int r_1 \mathrm{d}x)$ and

$$u = e^{r_1 x} \int f(x) e^{-r_1 x} \mathrm{d}x + c_1 e^{r_1 x}. \tag{53}$$

The definition of u above, then leads to the relation

$$(\hat{\mathcal{D}} - r_2)y = e^{r_1 x}[g(x) + c_1], \tag{54}$$

where $g(x) = \int f(x) e^{-r_1 x} \mathrm{d}x$. Equation (54) can now be solved by the same procedure with the identification of $exp(-\int r_2 \mathrm{d}x)$ as the integrating factor. The result is

$$y = e^{r_2 x} \int g(x) e^{-(r_2 - r_1)x} \mathrm{d}x + \frac{c_1}{r_1 - r_2} e^{r_1 x} + c_2 e^{r_2 x}. \tag{55}$$

The coefficient in the second term on the right-hand side of Eq. (55) is a constant, so the sum of the second and third terms corresponds to the general solution of the homogeneous equation [Eq. (30)]. The first term is a particular integral which results from the nonzero term on the right-hand side of Eq. (50), *i.e.* the inhomogenuity. With the application of integration by parts, it can be written in the form

$$I = \frac{1}{r_1 - r_2}\left[e^{r_1 x}\int f(x)e^{-r_1 x}\mathrm{d}x - e^{r_2 x}\int f(x)e^{-r_2 x}\mathrm{d}x\right] \tag{56}$$

(see problem 8).

The reader is warned that the use of differential operators may lead to difficulties in certain cases. Specifically, if the coefficients appearing in Eq. (15) are functions of x, the method fails. Furthermore, it must be modified if two (or more) roots are equal.

5.3.3 Forced vibrations

An important example in mechanical and electrical systems is that of forced oscillations of a vibrational system. If an external force $f(t)$ is imposed on the mechanical oscillator considered above, Eq. (40) becomes

$$\ddot{x} + \frac{h}{m}\dot{x} + \frac{\kappa}{m}x = \frac{1}{m}f(t). \tag{57}$$

In practice, the right-hand side of Eq. (57) is often periodic in time, *e.g.* $f(t)/m = F_0 \sin \omega t$. The frequency ν of the applied force is equal to $\omega/2\pi$. Then, from Eq. (40) the inhomogeneous equation of interest is

$$\ddot{x} + \frac{h}{m}\dot{x} + \frac{\kappa}{m}x = F_0 \sin \omega t. \tag{58}$$

The general solution for the homogeneous part is given by Eq. (43) for the oscillatory (underdamped) case. The particular integral given by Eq. (56) can be developed as

$$I = \frac{1}{\left(\frac{\kappa}{m} - \omega^2\right)^2 + \frac{\omega^2 h^2}{m^2}}\left[\left(\frac{\kappa}{m} - \omega^2\right)\sin \omega t - \frac{h\omega}{m}\cos \omega t\right]. \tag{59}$$

The factor before the square brackets is of course the amplitude of the oscillation. It reaches a maximum value when the square of the angular frequency of the forcing function is given by

$$\omega^2 = \frac{\kappa}{m} - \frac{h^2}{2m^2}. \tag{60}$$

It should be noted that in the case of a damped oscillator, the condition given by Eq. (60) yields a resonant frequency that does not correspond to its natural frequency, as

$$\omega_1^2 = \omega_0^2 - \frac{h^2}{4m^2}. \tag{61}$$

The expression given by Eq. (59) is of particular importance in both mechanical and electrical systems. In the absence of damping, the amplitude of the forced oscillations approaches infinity at resonance. This result has been the origin of a number of well-known disasters, for example the collapse of the Tacoma Narrows bridge in the state of Washington in 1940. The turbulence created by strong winds in the narrow gorge produced periodic oscillations of the bridge which were, unfortunately, in resonance with the structure. A more classic example is that of the walls of Jericho that "came tumbling down", so it seems, because of resonance with the sound of the trumpets.

In electrical circuits the above analysis can be applied by adding an alternating voltage of angular frequency ω in series with the circuit shown in Fig. 3. However, the results in this case are normally less dramatic. In fact the condition of resonance, at which

$$\omega^2 = \frac{1}{LC} - \frac{R^2}{2L^2} \tag{62}$$

allows the resonant circuit of a radio receiver, for example, to be adjusted to correspond to the frequency of the detected signal. Usually, it is the capacitance, C, that is varied to achieve this condition.

5.4 APPLICATIONS IN QUANTUM MECHANICS

Most students are introduced to quantum mechanics with the study of the famous problem of the particle in a box. While this problem is introduced primarily for pedagogical reasons, it has nevertheless some important applications. In particular, it is the basis for the derivation of the translational partition function for a gas (Section 10.8.1) and is employed as a model for certain problems in solid-state physics.

5.4.1 The particle in a box

Consider a particle of mass m which is constrained to remain inside a one-dimensional "box" of width ℓ. The potential function which represents this system corresponds to

$$V(x) = \begin{cases} 0, & 0 < x < \ell \\ \infty, & x = 0, \ell \end{cases}. \tag{63}$$

In other words, there is no force acting on the particle except at the "walls" of the box. Schrödinger's second equation* for this problem (see Chapter 7) is then of the form

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = \varepsilon\psi, \tag{64}$$

where, $\hbar \equiv h/2\pi$, h is Planck's constant† and ε is the energy of the single-particle system. The symbol ψ is by tradition used to represent the wavefunction, which describes the stationary (time-independent) states of the system.

In the interior of the box the particle is free; thus, $V(x) = 0$ and Eq. (64) becomes

$$\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0, \tag{65}$$

where $\alpha^2 = 2m\varepsilon/\hbar^2$. Equation (65) is clearly of the same form (aside from notation) as Eq. (33). One form of its general solution is then

$$\psi(x) = \mathcal{A}\, sin(\alpha x + \eta), \tag{66}$$

by analogy with Eq. (39). The constant α can now be identified as $2\pi/\lambda$, where λ is the wavelength of a wave in the space of x. It is known in wave mechanics as the deBroglie‡ descriptive wave, with a wavelength given by

$$\lambda = \frac{2\pi}{\alpha} = \frac{\hbar}{\sqrt{2m\varepsilon}} = \frac{\hbar}{mv}. \tag{67}$$

In Eq. (67) the classical energy of a free particle, $\varepsilon = \frac{1}{2}mv^2$, has been substituted, with v its velocity and mv its momentum. Equation (67) is of course the well-known relation of deBroglie.

The solution of this problem, as given by Eq. (66), must now be analyzed with consideration of the boundary conditions at $x = 0$ and $x = \ell$. At these two points the potential function, $V(x)$, becomes infinite. Therefore, for the product $V(x)\ \psi(x)$ in Eq. (64) to remain finite at these two points, the wavefunction $\psi(x)$ must vanish. Clearly, if η, which is one of the arbitrary constants of integration, is chosen equal to zero in Eq. (66), the wavefunction will vanish at $x = 0$. However, at $x = \ell$ the situation is somewhat more complicated. A little reflection will show that if the argument of the sine

*Erwin Schrödinger, Austrian physicist (1887–1961).

†Max Planck, German physicist (1858–1947).

‡Louis deBroglie, French physicist (1892–1987).

function is equated to $n\pi x/\ell$, the wavefunction will vanish at $x = \ell$ for all values of the integer n. The acceptable solutions to this problem are then of the form

$$\psi_n(x) = \mathcal{A} \sin \frac{n\pi x}{\ell}, \tag{68}$$

with $n = 1, 2, 3, \ldots$. The second constant of integration is the amplitude, $\mathcal{A}$, which is usually determined by normalizing $\psi(x)$.* Thus, the amplitude in Eq. (68) is determined by the condition that

$$\int_0^\ell |\psi_n(x)|^2 \mathrm{d}x = \mathcal{A}^2 \int_0^\ell \sin^2\left(\frac{n\pi x}{\ell}\right) \mathrm{d}x = 1, \tag{69}$$

which yields $\mathcal{A} = \sqrt{2/\ell}$. The integral in Eq. (69) can be easily evaluated with the substitution $\sin^2 y = \frac{1}{2}(1 - \cos 2y)$. The wavefunctions for the first few values of n are represented in Fig. 4a.

With $\eta = 0$, the comparison of Eqs. (66) and (68) shows that $\alpha = n\pi/\ell$, and from Eq. (67) the energy is given by $\varepsilon = h^2n^2/8m\ell^2$, with $n = 1, 2, 3, \ldots$. Thus, the energy of the system is quantized due to the required boundary conditions on the solutions.

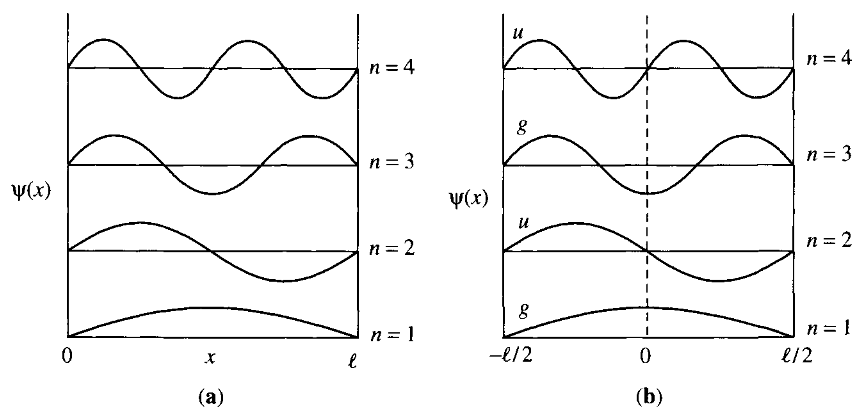


Fig. 4 Wavefunctions for the particle in a box: (**a**) without symmetry considerations; (**b**) the symmetric box.

*The normalization condition allows the quantity $\psi_v^*(\xi)\psi_v(\xi)\mathrm{d}\xi$ to be interpreted as the probability of finding the particle in the region of space $\mathrm{d}\xi$ (see Section 6.6.2).

5.4.2 Symmetric box

In the above treatment of the problem of the particle in a box, no consideration was given to its natural symmetry. As the potential function is symmetric with respect to the center of the box, it is intuitively obvious that this position should be chosen as the origin of the abscissa. In Fig. 4b, $x = 0$ at the center of the box and the walls are symmetrically placed at $x = \pm\ell/2$. Clearly, the analysis must in this case lead to the same result as above, because the particle does not "know" what coordinate system has been chosen! It is sufficient to replace x by $x + \ell/2$ in the solution given by Eq. (68). This operation is a simple translation of the abscissa, as explained in Section 1.2. The result is shown in Fig. 4b, where the wave function is now given by

$$\psi_n(x) = \mathcal{A}\,sin\left(\frac{n\pi x}{\ell} + \frac{n\pi}{2}\right). \tag{70}$$

It is easily verified that Eq. (70) satisfies the boundary conditions at the walls.

Although the net results obtained above for the particle in a box are physically the same, the mathematical consequences are quite different. From Fig. 4b it can be seen that the wavefunction is either even or odd, depending on the parity of n. Specifically, $\psi_n(x) = \pm\psi_n(-x)$, where the plus sign is appropriate when n is odd and the minus sign when n is even. As Eq. (70) contains the sine of the sum of two terms, it can be rewritten in the form

$$\psi_n(x) = \mathcal{A}\left(sin\,\frac{n\pi x}{\ell}\,cos\,\frac{n\pi}{2} + cos\,\frac{n\pi x}{\ell}\,sin\,\frac{n\pi}{2}\right); \tag{71}$$

then,

$$\psi_n^{(g)}(x) = \pm\mathcal{A}\,cos\,\frac{n\pi x}{\ell} \qquad \text{if } n \text{ is odd} \tag{72}$$

and

$$\psi_n^{(u)}(x) = \pm\mathcal{A}\,sin\,\frac{n\pi x}{\ell} \qquad \text{if } n \text{ is even.} \tag{73}$$

In spectroscopic applications the letters g and u (German: *Gerade, Ungerade*) are used to specify the symmetry of the functions under the inversion operation, $x \to -x$. Note that the normalization constant is given by $\mathcal{A} = \sqrt{2/\ell}$, as before.

The symmetry properties of the wavefunctions, as given by Eqs. (72) and (73) are extremely useful in the evaluation of certain integrals arising in quantum mechanics. First of all, it is evident that

$$\int_{-\ell/2}^{+\ell/2} \psi_n^{(g)}(x)\psi_n^{(u)},\,dx = 0 \tag{74}$$

for all values of n and n'. Other integrals of the type

$$\int_{-\ell/2}^{+\ell/2} \psi_n(x) f(x) \psi_{n'}(x) \mathrm{d}x \tag{75}$$

depend on the overall symmetry of the triple product in the integrand of Eq. (75). If the integrand is of symmetry "u", the integral is equal to zero. Clearly, the relations $g \times g = g, u \times u = g$ and $g \times u = u$ are applicable. These principles, which are the bases for the determination of spectroscopic selection rules, are developed in Sections 8.10 and 12.3.

5.4.3 Rectangular barrier: The tunnel effect

A relatively simple problem which has a direct application in the theory of chemical reaction rates is that of the rectangular barrier. A particle of mass m and energy $\varepsilon < V'$ approaches the barrier of height V' from the left (Fig. 5). Before the encounter with the barrier the amplitude of the deBroglie wave is equal to A, and after reflection by the barrier it is B. The wavefunction in region ①, where $x < 0$, is then $\psi_{①} = Ae^{i\alpha x} + Be^{-i\alpha x}$. The solution is periodic in this region, as $V = 0$ and $\alpha^2 = 2m\varepsilon/\hbar^2 > 0$. In region ②, with $\varepsilon < V'$, the solution is exponential, *viz.* $\psi_{②} = Ce^{\beta x} + De^{-\beta x}$, where $\beta^2 = 2m(V' - \varepsilon)/\hbar^2 > 0$. To the right of the barrier the solution is once again periodic, because $V = 0$, and the wavefunction is of the form $\psi_{③} = Fe^{i\alpha x}$, if it is assumed that the particle is not reflected at $x = \infty$.

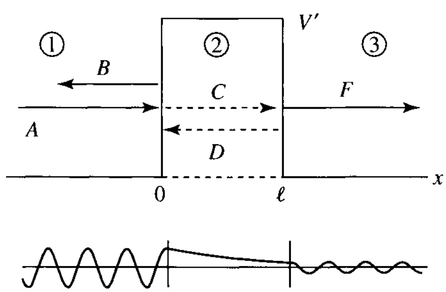


Fig. 5 Particle with a rectangular barrier.

At each boundary, $x = 0$ and $x = \ell$, both the function and its derivative must be continuous. These conditions impose the following relations:

$$\psi_{①}(0) = \psi_{②}(0), \left[\frac{d\psi_{①}}{dx}\right]_{x=0} = \left[\frac{d\psi_{②}}{dx}\right]_{x=0} \tag{76}$$

and

$$\psi_{②}(\ell) = \psi_{③}(\ell), \left[\frac{d\psi_{②}}{dx}\right]_{x=\ell} = \left[\frac{d\psi_{③}}{dx}\right]_{x=\ell}. \tag{77}$$

The application of Eqs. (76) and (77) to the solutions indicated above results in a system of four simultaneous equations:

(i) At $x = 0$,

$$\begin{aligned} A + B &= C + D \\ i\alpha A - i\alpha B &= \beta C - \beta D, \end{aligned} \tag{78}$$

and

(ii) At $x = \ell$,

$$\begin{aligned} Ce^{\beta\ell} + De^{-\beta\ell} &= Fe^{\beta\ell} \\ \beta Ce^{\beta\ell} - \beta De^{-\beta\ell} &= \alpha Fe^{\beta\ell}. \end{aligned} \tag{79}$$

As these functions cannot be normalized, it is sufficient here to pose $|A|^2 = 1$ and calculate the relative probability densities in each succeeding step. Then, $R = |B|^2$ represents the reflection coefficient and $T = |F|^2$ the transmission coefficient. Assuming that the particle cannot remain trapped within the barrier, the relation

$$|B|^2 + |F|^2 = 1 \tag{80}$$

represents the conservation of probability density in the system [see Eq. (69)].

After a bit of algebra it is found that the transmission coefficient is given by

$$T = \frac{1}{cosh^2\beta\ell + \frac{1}{4}\left(\frac{\alpha}{\beta} - \frac{\beta}{\alpha}\right)^2 sinh^2\beta\ell}. \tag{81}$$

Equation (81) can be verified by calculation of $R = |B|^2$ from the simultaneous equations for the coefficients and substitution in Eq. (80). The result represented by Eq. (81) shows that the transmission coefficient decreases as the height V' or the thickness ℓ of the barrier increases.

The possibility that a particle with energy less than the barrier height can penetrate is a quantum-mechanical phenomenon known as the tunnel effect. A number of examples are known in physics and chemistry. The problem illustrated here with a rectangular barrier was used by Eyring* to estimate the rates of chemical reactions. It forms the basis of what is known as the absolute reaction-rate theory. Another, more recent example is the inversion of the ammonia molecule, which was exploited in the ammonia maser – the forerunner of the laser (see Section 9.4.1).

5.4.4 The harmonic oscillator in quantum mechanics

One of the most important second-order, homogeneous differential equations is that of Hermite.† It arises in the quantum mechanical treatment of the harmonic oscillator. Schrödinger's equation for the harmonic oscillator leads to the differential equation

$$\frac{d^2\psi}{d\xi^2} + (\sigma - \xi^2)\psi = 0, \tag{82}$$

where $\psi(\xi)$ is the wavefunction and σ is a constant. As a first step in the solution of this problem, it is useful to look for what is called the asymptotic solution, that is, the solution to Eq. (82) in the limit as $\xi^2 \to \infty$. Since in this case $\sigma \ll \xi^2$, Eq. (82) reduces to

$$\frac{d^2\psi}{d\xi^2} - \xi^2\psi = 0, \tag{83}$$

with approximate solutions of the form $\psi(\xi) \approx Ce^{\pm\frac{1}{2}\xi^2}$. This function can be tested by consideration of its second derivative

$$\frac{d^2\psi}{d\xi^2} = Ce^{\pm\frac{1}{2}\xi^2}(\xi^2 \pm 1) \approx C\xi^2 e^{\pm\frac{1}{2}\xi^2}. \tag{84}$$

This asymptotic solution suggests that the substitution $\psi(\xi) = \mathcal{H}_v(\xi)e^{\pm\frac{1}{2}\xi^2}$ in Eq. (82) should be tried. If the resulting differential equation for $\mathcal{H}(\xi)$ can be solved, the expression for $\psi(\xi)$ might be valid for all values of the independent variable ξ.

*Henry Eyring, American physical chemist (1901–1981).

†Charles Hermite, French mathematician (1822–1901).

The substitution proposed above leads to the well-known equation of Hermite,

$$\frac{d^2\mathcal{H}}{d\xi^2} - 2\xi\frac{d\mathcal{H}}{d\xi} + (\sigma - 1)\mathcal{H} = 0. \tag{85}$$

This equation can be solved by the method described in Section 5.2.1. The dependent variable is developed in a power series,

$$\mathcal{H}(\xi) = \sum_n a_n \xi^n, \tag{86}$$

by analogy with Eq. (16). Its first and second derivatives are found by term-by-term differentiation [see Eqs. (17) and (18)]. The substitution of these results in Eq. (85) leads directly to the expression

$$\sum_n n(n-1)a_n\xi^{n-2} - 2\sum_n na_n\xi^n + (\sigma - 1)\sum_n a_n\xi^n = 0. \tag{87}$$

It must be emphasized that the indices n appearing in each summation in Eq. (87) are independent. Thus, to collect the coefficients of, say, ξ^n, the index in the first term can be advanced, independently of the indices in the second and third terms. If in the first term n is replaced by $n + 2$, it becomes $\sum_n (n+1)(n+2)a_{n+2}\xi^n$. Then, Eq. (87) can be written as a function of a single index, namely,

$$\sum_n \left[(n+1)(n+2)a_{n+2} - 2na_n + (\sigma - 1)a_n\right]\xi^n = 0. \tag{88}$$

Clearly, for this sum to vanish for all values of ξ, the coefficient in brackets must vanish for all values of n. Thus,

$$(n+1)(n+2)a_{n+2} - 2na_n + (\sigma - 1)a_n = 0 \tag{89}$$

and

$$a_{n+2} = \frac{2n - \sigma + 1}{(n+1)(n+2)}a_n. \tag{90}$$

This result is the recursion formula which allows the coefficient a_{n+2} to be calculated from the coefficient a_n. Starting with either a_0 or a_1 an infinite series can be constructed which is even or odd, respectively. These two coefficients are of course the two arbitrary constants in the general solution of a second-order differential equation. If one of them, say, a_0 is set equal to zero, the remaining series will contain the constant a_1 and be composed only of odd powers of ξ. On the other hand, if $a_1 = 0$, the even series will result. It can be shown, however, that neither of these infinite series can be accepted as solutions to the harmonic oscillator problem in quantum mechanics, as they are not convergent for large values of ξ.

The problem of convergence of the infinite series developed above can be circumvented by stopping the chosen series after a given finite number of terms. To break off the series at the term where $n = v$, it is sufficient to replace n by v in Eq. (90) and pose $2v - \sigma + 1 = 0$. The coefficient a_{v+2} then vanishes, yielding a polynomial of degree v. These functions are known as the Hermite polynomials. The factor $e^{\pm\frac{1}{2}\xi^2}$ introduced above will assure the required convergence if the negative sign is chosen in the exponent. The solution to Eq. (82) is then of the form $\psi(\xi) = \mathcal{H}_v(\xi)e^{-\frac{1}{2}\xi^2}$, where $\mathcal{H}_v(\xi)$ is the Hermite polynomial of degree v.

In the quantum mechanical application, the constant σ, is proportional to ε, the energy of the oscillator; namely,

$$\sigma = \frac{2\varepsilon}{h\nu^0}, \tag{91}$$

where h is Planck's constant and ν^0 is the frequency of the classical oscillator (see Section 5.2.2). The condition applied above, *viz.* $2v - \sigma + 1 = 0$ then leads to the well-known result

$$\varepsilon = h\nu^0 \left(v + \tfrac{1}{2}\right), \tag{92}$$

where $v = 0, 1, 2, \ldots$, identified here as the degree of the Hermite polynomial. It is known to spectroscopists as the vibrational quantum number. It should be emphasized that this quantization of the energy is not determined by the differential equation in question, but by the condition imposed to assure the acceptability of its solution.

5.5 SPECIAL FUNCTIONS

The Hermite polynomials introduced above represent an example of special functions which arise as solutions to various second-order differential equations. After a summary of some of the properties of these polynomials, a brief description of a few others will be presented. The choice is based on their importance in certain problems in physics and chemistry.

5.5.1 Hermite polynomials

While the Hermite polynomials can be developed with the use of the recursion formula [Eq. (90)], it is more convenient to employ one of their fundamental definitions, *e.g.*

$$\mathcal{H}_v(\xi) \equiv (-1)^v e^{\xi^2} \frac{\mathrm{d}^v e^{-\xi^2}}{\mathrm{d}\xi^v}. \tag{93}$$

An alternative definition involves the use of a generating function. This method is especially convenient for the evaluation of certain integrals of the Hermite polynomials and can be applied to other polynomials as well. For the Hermite polynomials the generating function can be written as

$$S(\xi, s) \equiv e^{\xi^2-(s-\xi)^2} \equiv \sum_{v=0}^{\infty} \frac{\mathcal{H}_v(\xi)}{v!} s^v. \tag{94}$$

The variable s is a dummy variable in the sense that it does not enter the final result. Thus, if the exponential function in Eq. (94) is expanded in a power series in s, the coefficients of successive powers of s are just the Hermite polynomials $\mathcal{H}_v(\xi)$ divided by $v!$. It is not too difficult to show that Eqs. (93) and (94) are equivalent definitions of the Hermite polynomials.

Certain relations between the Hermite polynomials and their derivatives can be obtained from Eq. (94). First, the partial derivative of Eq. (94) with respect to s is

$$\frac{\partial S}{\partial s} = -2(s-\xi)S = \sum_{v=1}^{\infty} \frac{\mathcal{H}_v(\xi)}{v!} v s^{v-1} \tag{95}$$

and

$$-2(s-\xi)\sum_{v=0}^{\infty} \frac{\mathcal{H}_v(\xi)}{v!} s^v = \sum_{v=1}^{\infty} \frac{\mathcal{H}_v(\xi)}{(v-1)!} s^{v-1}. \tag{96}$$

By collecting the coefficients of a given power of s,

$$\sum_{\nu=0}^{\infty} \left[\frac{\mathcal{H}_{v+1}(\xi)}{v!} + \frac{2\mathcal{H}_{v-1}(\xi)}{(v-1)!} - \frac{2\xi\mathcal{H}_v(\xi)}{v!} \right] s^v = 0 \tag{97}$$

As this relation is correct for all values of s, the coefficients in brackets must vanish. The result yields the important recursion formula for the Hermite polynomials,

$$\mathcal{H}_{v+1}(\xi) - 2\xi\mathcal{H}_v(\xi) + 2v\mathcal{H}_{v-1}(\xi) = 0, \quad v = 1, 2, 3, \ldots \tag{98}$$

which is usually written in the form

$$\xi\mathcal{H}_v(\xi) = \tfrac{1}{2}\mathcal{H}_{v+1}(\xi) + v\mathcal{H}_{v-1}(\xi). \tag{99}$$

This relation can also be derived from the definition given by Eq. (93), which represents the series

$$\mathcal{H}_v(\xi) = (2\xi)^v - \frac{v(v-1)}{1!}(2\xi)^{v-2} + \frac{v(v-1)(v-2)(v-3)}{2!}(2\xi)^{v-4} - \cdots. \tag{100}$$

It breaks off at $(2\xi)^0$ or $(2\xi)^1$, depending on the parity of v. Differentiation of Eq. (100) leads to the expressions

$$\frac{d\mathcal{H}_v(\xi)}{d\xi} = 2v\mathcal{H}_{v-1}(\xi) \tag{101}$$

and

$$\frac{d^2\mathcal{H}_v(\xi)}{d\xi^2} = 2v\frac{d\mathcal{H}_{v-1}(\xi)}{d\xi} = 4v(v-1)\mathcal{H}_{v-2}(\xi). \tag{102}$$

Clearly, expressions for higher derivatives can be derived by the same method. Substitution of Eqs. (101) and (102) into Hermite's equation [Eq. (85)], with $\sigma - 1$ replaced by $2v$, leads to Eq. (99) (see problems 15 and 16).

In quantum mechanics it is customary to multiply the wavefunctions introduced in Eq. (82) by a normalizing factor, $\mathcal{N}_v$. Then,

$$\psi_v(\xi) = \mathcal{N}_v e^{-\frac{1}{2}\xi^2}\mathcal{H}_v(\xi) \tag{103}$$

and these functions form an orthonormal set for all values of ξ such that

$$\int_{-\infty}^{\infty} \psi_{v'}^*(\xi)\psi_v(\xi)d\xi = \delta_{v',v} = \begin{cases} 1 & \text{if} \quad v' = v \\ 0 & \text{if} \quad v' \neq v \end{cases}, \tag{104}$$

where the symbol $\delta_{v',v}$ is known as the delta of Kronecker. If the $v' \neq v$, the integral in Eq. (104) is equal to zero and the functions are orthogonal. On the other hand, if $v' = v$, it is equal to one and the functions are normal – hence the term "orthonormal". This geometrical interpretation is derived from vector analysis (see Section 4.3).

Now take $v' < v$ and consider the integral

$$I = \int_{-\infty}^{\infty} \mathcal{H}_{v'}(\xi)\mathcal{H}_v(\xi)e^{-\xi^2}d\xi = (-1)^v \int_{-\infty}^{\infty} \mathcal{H}_{v'}(\xi)\frac{d^v(e^{-\xi^2})}{d\xi^v}d\xi. \tag{105}$$

Integration by parts (see Section 3.3.2) yields

$$I = (-1)^v \left[\mathcal{H}_{v'}(\xi)\frac{d^{v-1}(e^{-\xi^2})}{d\xi^{v-1}}\right]_{-\infty}^{\infty} - (-1)^v \int_{-\infty}^{\infty} \frac{d\mathcal{H}_{v'}(\xi)}{d\xi}\frac{d^{v-1}(e^{-\xi^2})}{d\xi^{v-1}}d\xi. \tag{106}$$

The first term on the right-hand side of Eq. (106) vanishes, as the Gaussian function and its derivatives are equal to zero at $\xi = \pm\infty$. From Eq. (101) $\mathrm{d}\mathcal{H}_{v'}(\xi)/\mathrm{d}\xi = 2v'\mathcal{H}_{v'-1}(\xi)$ and Eq. (106) becomes

$$I = 2v'(-1)^{v+1}\int_{-\infty}^{\infty}\mathcal{H}_{v'-1}(\xi)\frac{\mathrm{d}^{v-1}(e^{-\xi^2})}{\mathrm{d}\xi^{v-1}}\mathrm{d}\xi. \tag{107}$$

If this process is continued, the result is

$$I = 2^{v'}(-1)^{v+v'}v'!\int_{-\infty}^{\infty}\mathcal{H}_0(\xi)\frac{\mathrm{d}^{v-v'}(e^{-\xi^2})}{\mathrm{d}\xi^{v-v'}}\mathrm{d}\xi, \tag{108}$$

$$= 2^{v'}(-1)^{v+v'}v'!\left[\frac{\mathrm{d}^{v-v'-1}(e^{-\xi^2})}{\mathrm{d}\xi^{v-v'-1}}\right]_{-\infty}^{\infty} = 0. \tag{109}$$

If $v = v'$, Eq. (105) becomes

$$\int_{-\infty}^{\infty}[\mathcal{H}_v(\xi)]^2 e^{-\xi^2}\mathrm{d}\xi = 2^v(-1)^{2v}v!\int_{-\infty}^{\infty}e^{-\xi^2}\mathrm{d}\xi = 2^v v!\sqrt{\pi} \tag{110}$$

and Eq. (104) is verified if the normalizing factor is taken to be

$$\mathcal{N}_v = \frac{1}{\sqrt{2^v v!\sqrt{\pi}}}. \tag{111}$$

Some of the Hermite polynomials and the corresponding harmonic-oscillator wave functions are presented in Table 1. The importance of the parity of these functions under the inversion operation, $\xi \to -\xi$ cannot be overemphasized.

5.5.2 Associated Legendre* polynomials

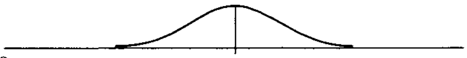
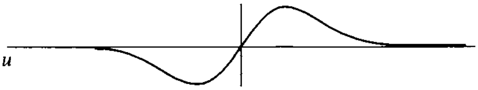
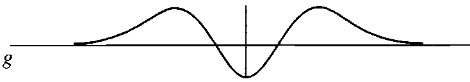
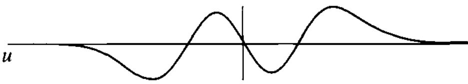
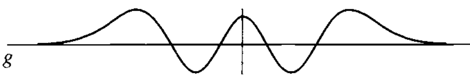
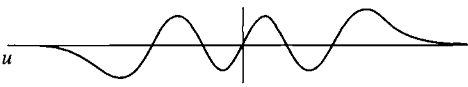
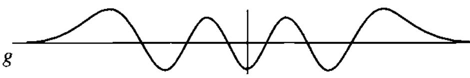
As shown in Chapter 6, these functions arise in all central-force problems, that is, systems composed of two interacting spherical objects in free space. The fundamental differential equation involved is

$$(1 - z^2)\frac{\mathrm{d}^2P(z)}{\mathrm{d}z^2} - 2z\frac{\mathrm{d}P(z)}{\mathrm{d}z} + \left(\beta - \frac{m^2}{1 - z^2}\right)P(z) = 0, \tag{112}$$

where β is a constant and $m = 0, \pm1, \pm2, \ldots$ (see Section 6.4.2). If m is equal to zero, this equation can be solved by the development of $P(z)$ in

*Adrien-Marie Le Gendre, French mathematician (1752–1833).

Table 1 The Hermite polynomials and the harmonic-oscillator wavefunctions.

$\mathcal{H}_v(\xi)$	Symmetry	$\psi_v = \mathcal{N}_v e^{-\frac{1}{2}\xi^2}\mathcal{H}_v(\xi)$
$\mathcal{H}_0(\xi) = 1$	g	 ξ
$\mathcal{H}_1(\xi) = 2\xi$	u	 ξ
$\mathcal{H}_2(\xi) = 4\xi^2 - 2$	g	 ξ
$\mathcal{H}_3(\xi) = 8\xi^3 - 12\xi$	u	 ξ
$\mathcal{H}_4(\xi) = 16\xi^4 - 48\xi^2 + 12$	g	 ξ
$\mathcal{H}_5(\xi) = 32\xi^5 - 160\xi^3 + 120\xi$	u	 ξ
$\mathcal{H}_6(\xi) = 64\xi^6 - 480\xi^4 + 720\xi^2$	g	 ξ

a power series, as before. However, if $m \neq 0$, the problem becomes more difficult due to the presence of the term with $(1 - z^2)$ in the denominator. At the points where $z = \pm 1$ this term becomes infinite. At these points, which are called singular points, the method of integration in series usually breaks down. However, if these points correspond to nonessential singularities (or regular points), it is often possible to avoid this problem with the use of appropriate substitutions. Here, with

$$P(z) = (1 - z^2)^s G(z) \tag{113}$$

the so-called index $s \geq 0$ is determined by inserting Eq. (113) in Eq. (112). The resulting terms in $(1 - z^2)^{s-1} = (1 - z^2)^s/1 - z^2$ are

$$\frac{4z^2 s(s-1) + 4z^2 s - m^2}{1 - z^2} = \frac{4z^2 s^2 - m^2}{1 - z^2} = -m^2. \tag{114}$$

With a little reflection it can be seen that the second equality results if s is chosen so that $4s^2 = m^2$ or $s = \pm m/2$. Thus the troublesome factor $(1 - z^2)^{-1}$

has been eliminated. Furthermore, the condition that $s \geq 0$ then imposes the result $s = |m|/2$ and Eq. (113) becomes

$$P(z) = (1 - z^2)^{|m|/2} G(z). \tag{115}$$

The differential equation for $G(z)$ is

$$(1 - z^2)\frac{d^2G(z)}{dz^2} - 2z(1 + |m|)\frac{dG(z)}{dz} + [\beta - |m|(|m| + 1)]G(z) = 0, \tag{116}$$

which can be solved directly by the series method.

The substitution $G(z) = \sum_n b_n z^n$ results in the relation

$$\sum_n n(n-1)b_n z^{n-2} - \sum_n n(n-1)b_n z^n - 2\sum_n (1 + |m|)nb_n z^n$$
$$+ \sum_n [\beta - |m|(|m| + 1)]b_n z^n = 0. \tag{117}$$

Here again the indices n are independent in each summation, so that n can be replaced by $n + 2$ in the first term. Then, by posing the coefficient of z^n equal to zero, the recursion formula becomes

$$b_{n+2} = \frac{(n + |m|)(n + |m| + 1) - \beta}{(n + 1)(n + 2)} b_n. \tag{118}$$

Once again there is a problem of convergence, this time at the points $z = \pm 1$. It is therefore necessary to break off the series at the term $n = n'$, where

$$\beta = (n' + |m|)(n' + |m| + 1) = \ell(\ell + 1). \tag{119}$$

The new integer $\ell = n' + |m| = |m|, |m| + 1, |m| + 2, \ldots$ is therefore related to m by the condition $|m| \leq \ell$ or

$$m = 0, \pm 1, \pm 2, \ldots \pm \ell. \tag{120}$$

It will be identified in Chapter 6 as the azimuthal quantum number, which is characteristic of the two-body problem.

The associated Legendre polynomials can be defined by the generating function

$$T_{|m|}(z, t) \equiv \frac{(2|m|)!(1 - z^2)^{|m|/2} t^{|m|}}{2^{|m|}(|m|)!(1 - 2zt + t^2)^{|m| + \frac{1}{2}}} \equiv \sum_{\ell = |m|}^{\infty} P_\ell^{|m|}(z) t^\ell. \tag{121}$$

It is analogous to the generating function for the Hermite polynomials [Eq. (94)], although somewhat more complicated. It can be used to obtain the useful recursion relations

$$zP_\ell^{|m|}(z) = \frac{(\ell + |m|)}{(2\ell + 1)} P_{\ell-1}^{|m|}(z) + \frac{(\ell - |m| + 1)}{(2\ell + 1)} P_{\ell+1}^{|m|}(z), \quad (122)$$

$$(1 - z^2)^{\frac{1}{2}} P_\ell^{|m|-1}(z) = \frac{1}{(2\ell + 1)} P_{\ell+1}^{|m|}(z) - \frac{1}{(2\ell + 1)} P_{\ell-1}^{|m|}(z) \quad (123)$$

and

$$(1 - z^2)^{\frac{1}{2}} P_\ell^{|m|+1}(z) = \frac{(\ell + |m|)(\ell + |m| + 1)}{(2\ell + 1)} P_{\ell-1}^{|m|}(z) - \frac{(\ell - |m|)(\ell - |m| + 1)}{(2\ell + 1)} P_{\ell+1}^{|m|}(z) \quad (124)$$

(see problem 20).

An alternative definition, but equally useful, of the associated Legendre polynomials is of the form

$$P_\ell^m(z) = \frac{(1 - z^2)^{m/2}}{2^n \ell!} \frac{\mathrm{d}^{\ell+m}}{\mathrm{d}z^{\ell+m}} (z^2 - 1)^\ell. \quad (125)$$

It is analogous to the definition of the Hermite polynomials, as given by Eq. (93).

When the associated Legendre polynomials are normalized they are written in the form

$$\Theta_{\ell,m}(\theta) = \sqrt{\frac{(2\ell + 1)}{2} \frac{(\ell - |m|)!}{(\ell + |m|)!}} P_\ell^{|m|}(\cos\theta), \quad (126)$$

where the independent variable z has been replaced by $\cos\theta$ and the normalizing constant has been evaluated by much the same procedure as that employed for the Hermite polynomials. The functions $\Theta_{\ell,m}(\theta)$ form an orthonormal set in the sense that

$$\int_0^\pi \Theta_{\ell',m}(\theta)\Theta_{\ell,m}(\theta) \sin\theta \, \mathrm{d}\theta = \delta_{\ell',\ell}. \quad (127)$$

The explicit form of the normalized associated Legendre polynomials is given by

$$\Theta_{\ell,m}(\theta) = \frac{(-1)^\ell}{2^\ell \ell!} \sqrt{\frac{2\ell + 1}{2} \frac{(\ell - |m|)!}{(\ell + |m|)!}} \sin^{|m|}\theta \frac{\mathrm{d}^{\ell+|m|}(\sin^{2\ell}\theta)}{(\mathrm{d}\cos\theta)^{\ell+|m|}}. \quad (128)$$

They often appear as products of the function $1/\sqrt{2\pi}e^{im\varphi}$. The angles θ and φ are just the two angles defined in spherical coordinates, as shown in Fig. 6-5. The function *sin* θ appearing in the integral arises from the appropriate volume element. The functions

$$Y_\ell^m(\theta, \varphi) = \Theta_{\ell,m}(\theta)\frac{1}{\sqrt{2\pi}}e^{im\varphi} \tag{129}$$

are known as spherical harmonics (see Appendix III).

5.5.3 The associated Laguerre polynomials*

Consider the differential equation

$$\frac{\mathrm{d}^2R(\rho)}{\mathrm{d}\rho^2} + \frac{2}{\rho}\frac{\mathrm{d}R(\rho)}{\mathrm{d}\rho} + \left[\frac{\gamma}{\rho} - \frac{\ell(\ell+1)}{\rho^2} - \frac{1}{4}\right]R(\rho) = 0, \tag{130}$$

where γ is a constant and $\ell = 0, 1, 2 \ldots$. As in the problem of the harmonic oscillator (Section 4.4.4), it is of interest to discuss first the asymptotic solution as $\rho \to \infty$. In this limit the terms in $1/\rho$ approach zero and Eq. (130) becomes

$$\frac{\mathrm{d}^2R(\rho)}{\mathrm{d}\rho^2} - \frac{1}{4}R(\rho) = 0. \tag{131}$$

Particular solutions to Eq. (131) are $R(\rho) = e^{\pm\rho/2}$, where only the negative exponent yields an acceptable function at infinity. This result suggests the substitution $R(\rho) = e^{-\rho/2}S(\rho)$, which results in the differential equation

$$\frac{\mathrm{d}^2S(\rho)}{\mathrm{d}\rho^2} + \left(\frac{2}{\rho} - 1\right)\frac{\mathrm{d}S(\rho)}{\mathrm{d}\rho} + \left[\frac{\gamma-1}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right]S(\rho) = 0. \tag{132}$$

This equation cannot be solved by expansion in series, as the coefficients of $S(\rho)$ and its first derivative result in a singularity at $\rho = 0$. Because this point is regular, the substitution $S(\rho) = \rho^s\mathcal{L}(\rho)$ is suggested. If the coefficient of ρ^{s-2} is set equal to zero, the resulting indicial equation is

$$2s + s(s-1) - \ell(\ell+1) = 0. \tag{133}$$

Its solutions are

$$s = \ell, -\ell - 1. \tag{134}$$

The second solution in Eq. (134) is not compatible with the condition $s \geq 0$. Therefore, the substitution $S(\rho) = \rho^\ell\mathcal{L}(\rho)$ is introduced into Eq. (130), leading

*Edmond Laguerre, French mathematician (1834–1886).

to the differential equation

$$\rho\frac{d^2\mathcal{L}(\rho)}{d\rho^2} + [2(\ell+1) - \rho]\frac{d\mathcal{L}(\rho)}{d\rho} + (\gamma - \ell - 1)\mathcal{L}(\rho) = 0. \tag{135}$$

This equation is of the form of Eq. (15) and hence can be solved by the power-series expansion $\mathcal{L}(\rho) = \sum_k a_k\rho^k$. The resulting recursion formula is

$$a_{k+1} = \frac{k+\ell+1-\gamma}{k(k+1)+2(\ell+1)(k+1)}a_k. \tag{136}$$

Unlike the previous two examples, this is a one-term recursion formula. Hence, the series that is constructed from the value of a_0 is a particular solution of Eq. (135). Once again, however, because of the problem of convergence, the series must be terminated after a finite number of terms. The condition for it to break off after the term in $\rho^{k'}$ is given by

$$k' + \ell + 1 - \gamma = 0. \tag{137}$$

As the integers k' and ℓ both begin at zero, $\gamma = 1, 2, 3\ldots$ can of course be identified as the principal quantum number n for the hydrogen atom (see Section 6.6.1). Thus, the quantization of the energy is due to the termination of the series, a condition imposed to obtain an acceptable solution. The associated Laguerre polynomials provide quantitative descriptions of the radial part of the wave functions for the hydrogen atom, as described in Appendix IV.

5.5.4 The gamma function

The gamma function is a generalization of the factorial introduced in Section 1.4. There, the notation $n! = 1\cdot 2\cdot 3\cdot 4\cdot\ldots n$ was employed, with n a positive integer (or zero). The gamma function in this case is chosen so that $\Gamma(n) = (n-1)!$. However, a general definition due to Euler states that

$$\Gamma(z) = \lim_{n\to\infty}\frac{1\cdot 2\cdot 3\cdots(n-1)}{z(z+1)\cdots(z+n-1)}n^z. \tag{138}$$

Several properties of the gamma function follow from this definition, *e.g.*

$$\Gamma(z+1) = z\Gamma(z), \tag{139}$$

$$\Gamma(1) = \lim_{n\to\infty}\frac{n!}{n!} = 1 \tag{140}$$

and, if n is a positive integer,

$$\Gamma(n) = (n-1)! \tag{141}$$

as stated above. It is also apparent that from the definition given by Eq. (138) that $\Gamma(z)$ becomes infinite at $z = 0, -1, -2, \ldots$, but is continuous (analytic) everywhere else.

An alternative expression for the gamma function is

$$\Gamma(z) = \int_0^\infty e^{-t} t^{z-1} \mathrm{d}t, \tag{142}$$

which is valid when the real part of z is positive. The evaluation of some of the gamma functions give $\Gamma(0) = \infty$, $\Gamma(1) = 1$, $\Gamma(2) = 1$, $\Gamma(3) = 2!$, $\Gamma(4) = 3!$, *etc.*. Furthermore, if $\Gamma(z)$ is known for $0 < z < 1$, $\Gamma(z)$ can be calculated for all real, positive values of z with the use of Eq. (139). Finally, for half-integer values of the argument, starting with $z = \frac{1}{2}$, Eq. (142) becomes

$$\Gamma(\tfrac{1}{2}) = \int_0^\infty e^{-t} t^{-1/2} \mathrm{d}t = 2\int_0^\infty e^{-x^2} \mathrm{d}x = \sqrt{\pi} \tag{143}$$

and similarly, $\Gamma(\frac{3}{2}) = \frac{1}{2}\sqrt{\pi}$, $\Gamma(\frac{5}{2}) = \frac{3}{4}\sqrt{\pi}$, $\Gamma(\frac{7}{2}) = \frac{15}{8}\sqrt{\pi}$, *etc.*

5.5.5 Bessel functions*

Bessel's equation can be written in the form

$$x^2 y'' + xy' + (x^2 - k^2)y = 0, \tag{144}$$

where k is a constant. The substitution $y(x) = x^\ell$ leads to the indicial equation $\ell^2 = k^2$. The roots are then $\pm k$. A particular solution is of the form

$$y = J_k(x) = \sum_{\lambda=0}^{\infty} \frac{(-1)^\lambda}{\Gamma(\lambda+1)\Gamma(\lambda+k+1)} \left(\frac{x}{2}\right)^{k+2\lambda}, \tag{145}$$

where $J_k(x)$ is the Bessel function of order k. It can be shown that if the difference between the values of the two roots $\pm k$ obtained above is not an integer, the general solution is given by

$$y(x) = AJ_k(x) + BJ_{-k}(x). \tag{146}$$

Even in the case where $k = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \cdots$ a general solution of the type given in Eq. (146) can be found. In fact, this case is of particular importance in many physical problems, as these Bessel functions are closely related to the ordinary trigonometric functions.

*Friedrich Wilhelm Bessel, German astronomer (1784–1846).

To illustrate this relationship, substitute $y = ux^{-\frac{1}{2}}$ in Eq. (144). The result is another form of Bessel's equation, namely,

$$u'' + \left(1 - \frac{4p^2 - 1}{4x^2}\right) u = 0. \tag{147}$$

In the special case in which $p = \pm\frac{1}{2}$ Eq. (147) reduces to

$$\frac{d^2u}{dx^2} + u = 0, \tag{148}$$

whose solution is sinusoidal [see Eq. (30)]. More generally, if p is finite, Eq. (147) becomes Eq. (148) in the limit as $x \to \infty$. Specifically, the Bessel functions of half-integer order are then given by

$$\lim_{x\to\infty} J_{n+\frac{1}{2}}(x) = \sqrt{\frac{2}{\pi x}}\, sin(x - \tfrac{1}{2}n\pi), \tag{149}$$

where n is an integer. The corresponding functions of negative order are often referred to as Neumann functions.* Certain linear combinations of the Bessel and Neumann functions are known as Hankel functions.† The reader is referred to advanced texts for the various recurrence relations among these functions, as well as their integral representations.

5.5.6 Mathieu functions‡

These functions arise in a certain number of problems in electromagnetic theory and acoustics – in particular, those involving the vibrations of elliptical drum heads and the waves on approximately elliptical lakes. For the physical chemist, their interest is primarily in the treatment of the problem of internal rotation in a molecule. For example, the methyl group, CH_3, can assume three equivalent minimal positions around the single bond with which it is attached to the rest of a molecule (see Section 9.4.2). In general, if α represents the angle of internal rotation, the potential function for the rotation of a given functional group can be written in a first approximation in the form

$$V(\alpha) = \frac{V_N}{2}(1 - cos\, N\alpha). \tag{150}$$

*Johann (John) von Neumann, American mathematician (1903–1957).

†Hermann Hankel, German mathematician (1839–1873).

‡Emile Léonard Mathieu, French mathematician (1835–1890).

Here N represents the order of the rotation axis, *i.e.* $N = 3$ for the hindered rotation of a methyl group about its C_3 symmetry axis (see Chapter 9).

The Schrödinger equation for the hindered rotator can be written in the form

$$\frac{\hbar^2}{2I}\frac{d^2\psi(\alpha)}{d\alpha^2} + \left[\varepsilon - \frac{V_N}{2}(1 - \cos N\alpha)\right]\psi(\alpha) = 0, \tag{151}$$

where I is the moment of inertia of the rotator* and ε is the energy. Comparison of Eq. (151) with the general form of Mathieu's equation,

$$\frac{d^2y}{dx^2} + (a - 16b\cos 2x)y = 0, \tag{152}$$

yields the relations: $y = \psi(\alpha), x = N\alpha/2$,

$$a = \frac{8I(\varepsilon - \frac{1}{2}V_N)}{\hbar^2N^2} \text{ and } b = -\frac{IV_N}{4\hbar^2N^2}.$$

Although Eq. (152) can in principle be solved by the development of $y(x)$ in a power series, the periodicity of the argument of cosine, namely, $2x = N\alpha$ complicates the problem. The most important application of Mathieu's equation to internal rotation in molecules is in the analysis of the microwave spectra of gases and vapors. The needed solutions to equations such as Eq. (152) are usually obtained numerically.

5.5.7 The hypergeometric functions

A differential equation due to Gauss is of the form

$$x(x-1)\frac{d^2y}{dx^2} + [(1 + \alpha + \beta)x - \gamma]\frac{dy}{dx} + \alpha\beta y = 0, \tag{153}$$

where α, β and γ are constants. Substitution of a power series, $y = \sum_{n=0}^{\infty} a_n x^n$ leads to the one-term recursion formula

$$a_{n+1} = \frac{(\alpha + n)(\beta + n)}{(n + \gamma)(n + 1)}a_n. \tag{154}$$

The resulting series is a particular solution to Eq. (153) known as the hypergeometric series. It converges for $|x| < 1$. It is usually denoted as $F(\alpha,\beta;\gamma,x)$.

*Strictly speaking, I is the reduced moment of inertia for the relative rotational motion of the system. For the case of a relatively light rotor such as CH_3 it is the moment of inertia of the hindered rotor that appears in Eq. (143).

Although the hypergeometric functions are useful in spectroscopy, as they describe the rotation of a symmetric top molecule (Section 9.2.4), their importance is primarily due to their generality. If, for example, $\alpha = 1$ and $\beta = \gamma$, Eq. (154) becomes $a_{n+1} = a_n$ for all values of n. The result is the ordinary geometric series

$$y = 1 + x + x^2 + x^3 \dots . \tag{155}$$

If the substitution $x = \frac{1}{2}(1 - z)$ is made in Eq. (153), the result is the differential equation of Legendre, with $\alpha = \ell + 1$, $\beta = -1$ and $\gamma = 1$ [see Eq. (112) with $m = 0$].

The Chebyshev polynomials,* which occur in quantum chemistry and in certain numerical applications, can be obtained from the hypergeometric functions by placing $\alpha = -\beta$, an integer, and $\gamma = \frac{1}{2}$. Finally, the hypergeometric functions reduce to the Jacobi polynomials† of degree n if $n = -\alpha$ is a positive integer.

PROBLEMS

1. Verify that $y = Ce^{\frac{1}{2}x^2} - 1$ is a solution to Eq. (10).

2. Derive Eq. (24).

3. Express Eq. (28) in terms of hyperbolic functions.
Ans. $y = (A + B)\cosh x + (A - B)\sinh x$

4. Verify that Eq. (30) is one form of the general solution to Eq. (29).

5. Verify Eqs. (35) and (39).

6. Show that the two particular solutions proposed for Eq. (46) are independent.

7. Solve Eq. (45) with the use of the operator $\hat{\mathcal{D}} = \mathrm{d}/\mathrm{d}t$ and find the condition for critical damping.
Ans. $R = 2\sqrt{L/C}$

8. Verify Eqs. (55) and (56).

9. Derive Eq. (59), verify Eq. (60) and show that Eq. (61) expresses the resonance condition.

10. With the use of Eqs. (66) and (68) show that the energy of the particle in the box is given by $\varepsilon = hn^2/8m\ell^2$, with $n = 1, 2, 3, \dots$.

*Pafnuty Lvovich Chebyshev (or Tschebyscheff), Russian mathematician (1821–1894).

†Carl Jacobi, German mathematician (1804–1851).

11. Apply Eq. (75) to evaluate $\int_{-\ell/2}^{+\ell/2} \psi_1(x)x\psi_2(x)\mathrm{d}x$ and $\int_{-\ell/2}^{+\ell/2} \psi_1(x)x^2\psi_2(x)\mathrm{d}x$.
Ans. $16\ell/9\pi^2, 0$

12. Derive Eq. (81).

13. Show that $\xi^2 e^{-\frac{1}{2}\xi^2}$ is an asymptotic solution to Eq. (83) that leads to Hermite's equation.

14. Derive the recursion relation for the Hermite polynomials [Eq. (90)].

15. Derive Eqs. (97) and (99).

16. Develop Eqs. (101) and (102) and show that their substitution in Eq. (85) yields Eq. (99).

17. With the use of Eq. (111) prove Eq. (104).

18. Substitute Eq. (113) in Eq. (112) and derive Eq. (114).

19. Derive the recursion relation given by Eq. (118).

20. With the use of Eq. (121) derive Eqs. (122) to (124).

21. Develop the indicial equation for the associated Laguerre polynomials [Eq. (133)].

22. Derive the recursion relation [Eq. (136)] for the associated Laguerre polynomials.

23. Verify the relations between Eqs. (151) and (152).

24. Substitute $y = u\sqrt{x}$ in Eq. (144) to obtain Eq. (147).