The Chemistry Maths Book

Erich Steiner

University of Exeter

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Solutions

Section 14.2

1. Show that the function $f(x,t) = a\sin(bx)\cos(vbt)$ **(i)** satisfies the 1-dimensional wave equation (14.1), **(ii)** has the form $f(x,t) = F(x+vt) + G(x-vt)$.

(i) We have $\quad f(x,t) = a\sin(bx)\cos(vbt)$

Then
$$\frac{\partial f}{\partial x} = ba\cos(bx)\cos(vbt), \quad \frac{\partial^2 f}{\partial x^2} = -b^2 a\sin(bx)\cos(vbt) = -b^2 f$$
$$\frac{\partial f}{\partial t} = vba\sin(bx)\sin(vbt), \quad \frac{\partial^2 f}{\partial t^2} = -v^2 b^2 a\sin(bx)\sin(vbt) = -v^2 b^2 f$$

Therefore
$$\frac{\partial^2 f}{\partial x^2} = -\frac{1}{v^2}\frac{\partial^2 f}{\partial t^2}$$

(ii) We have
$$\sin A\cos B = \frac{1}{2}\Big[\sin(A+B) + \sin(A-B)\Big]$$

Therefore
$$f(x,t) = a\sin(bx)\cos(vbt) = \frac{a}{2}\Big[\sin(bx+vbt) + \sin(bx-vbt)\Big]$$

2. The diffusion equation $\dfrac{\partial f}{\partial t} = D\dfrac{\partial^2 f}{\partial x^2}$ provides a model of, for example, the transfer of heat from a hot region of a system to a cold region by conduction when $f(x,t)$ is a temperature field, or the transfer of matter from a region of high concentration to one of low concentration when f is the concentration. Find the functions $V(x)$ for which $f(x,t) = V(x)e^{ct}$ is a solution of the equation.

We have
$$f(x,t) = V(x)e^{ct}, \quad \frac{\partial f}{\partial t} = cV(x)e^{ct}, \quad \frac{\partial^2 f}{\partial x^2} = \frac{d^2V}{dx^2}e^{ct}$$

Then
$$\frac{\partial f}{\partial t} = D\frac{\partial^2 f}{\partial x^2} \;\to\; cV(x)e^{ct} = D\frac{d^2V}{dx^2}e^{ct}$$
$$\to\; \frac{d^2V}{dx^2} = \frac{c}{D}V$$

The type solution depends on the value of c/D:

(a) $c/D = 0 \qquad \dfrac{d^2V}{dx^2} = 0 \;\to\; V = a + bx$

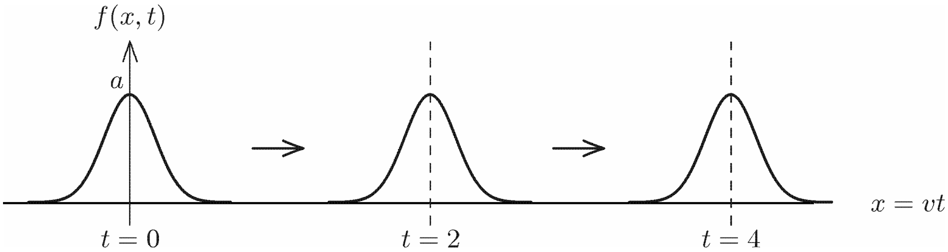
(b) $c/D = \lambda^2 > 0 \qquad c/D = \lambda > 0 \;\to\; V = ae^{\lambda x} + be^{-\lambda x}$

(c) $c/D = \lambda^2 > 0 \qquad V = a\cos\lambda x + b\sin\lambda x$

3. **(i)** It is shown in Example 14.2 that the function $f(x,t) = a\exp[-b(x-vt)^2]$ is a solution of the wave equation (14.1). Sketch graphs of $f(x,t)$ as a function of *x* at times $t=0$, $t=2/v$, $t=4/v$ (use, for example, $a=b=1$) to demonstrate that the function represents a wave travelling to the right (in the positive *x*–direction) at constant speed v.
(ii) Verify that $g(x,t) = a\exp[-b(x+vt)^2]$ is also a solution of the wave equation, and hence that every superposition $F(x,t) = f(x,t)+g(x,t)$ is a solution. **(iii)** Sketch appropriate graphs of $f(x,t)+g(x,t)$ to demonstrate how this function develops in time.

(i) The function $f(x,t) = a\exp[-b(x-vt)^2]$ represents a Gaussian wave whose centre lies at $x = vt$. The centre moves to the right (the positive *x*-direction) with constant speed $dx/dt = v$. Figure 1 shows the wave at times $t=0$, $t=2/v$, $t=4/v$.

Figure 1



(ii) Function $g(x,t)$ is obtained from $f(x,t)$ by replacement if v by $-v$, and has the same second derivative with respect to time *t*, proportional to v^2, as in Example 14.2. Thus

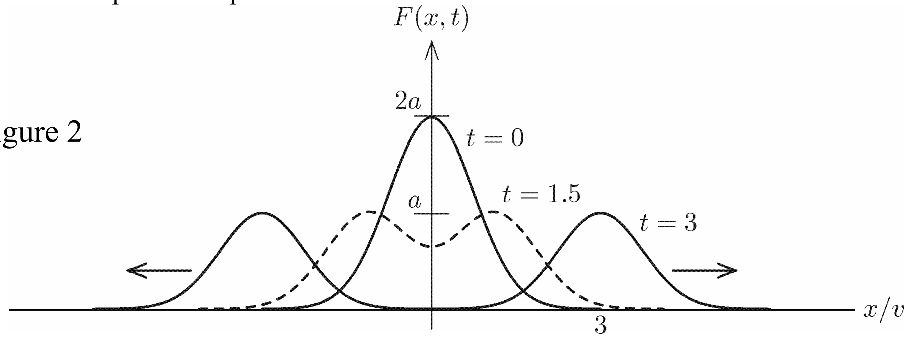
$$\frac{\partial^2 g}{\partial x^2} = \frac{1}{(-v)^2}\frac{\partial^2 g}{\partial t^2} = \frac{1}{v^2}\frac{\partial^2 g}{\partial t^2}$$

Then
$$\frac{\partial^2 F}{\partial x^2} = \frac{\partial^2}{\partial x^2}(af+bg) = a\frac{\partial^2 f}{\partial x^2} + b\frac{\partial^2 g}{\partial x^2} = \frac{a}{v^2}\frac{\partial^2 f}{\partial t^2} + \frac{b}{v^2}\frac{\partial^2 g}{\partial t^2}$$

$$= \frac{1}{v^2}\frac{\partial^2}{\partial t^2}(af+bg) = \frac{1}{v^2}\frac{\partial^2 F}{\partial t^2}$$

(iii) In Figure 2, the component *f* of $F = f+g$ moves to the right with constant speed v, the component *g* to the left with the same speed; that is, the components separate as *t* increases. The amplitude of the total wave at $t=0$ is twice that of the components, but decrease with *t* to that of the separate components.

Figure 2



Section 14.3

Find solutions of the following equations by the method of separation of variables:

4. $2\dfrac{\partial f}{\partial x}+\dfrac{\partial f}{\partial t}=0$

Let $f(x,t)=F(x)\times G(t)$

Then $\dfrac{\partial f}{\partial x}=\dfrac{dF(x)}{dx}\times G(t),\quad \dfrac{\partial f}{\partial t}=F(x)\times\dfrac{dG(t)}{dt}$

and $2\dfrac{\partial f}{\partial x}+\dfrac{\partial f}{\partial t}=0 \;\to\; 2\dfrac{dF(x)}{dx}G(t)+F(x)\dfrac{dG(t)}{dt}=0$

Division throughout by $f=F(x)\times G(y)$ gives

$$\left[\frac{2}{F(x)}\frac{dF(x)}{dx}\right]+\left[\frac{1}{G(t)}\frac{dG(t)}{dt}\right]=0$$

The two sets of terms in square brackets must be separately constant if *x* and *t* are independent variables. Therefore, if the first set of terms equals the constant *C* then the second set is equal to $-C$ (for the total to be zero). The resulting ordinary first-order equation in variable *x* is

$$\left[\frac{2}{F(x)}\frac{dF(x)}{dx}\right]=C \;\to\; \frac{dF(x)}{dx}=\frac{C}{2}F(x)$$

with general solution $F(x)=ae^{Cx/2}$. The corresponding equation in variable *t* is

$$\left[\frac{1}{G(t)}\frac{dG(t)}{dt}\right]=-C \;\to\; \frac{dG(t)}{dt}=-CG(t)$$

with general solution $G(t)=be^{-Ct}$. A complete solution is therefore

$$\begin{aligned} f(x,t)&=F(x)\times G(t)\\ &=ae^{Cx/2}\times be^{-Ct}=abe^{C(x/2-t)}\\ &=Ae^{B(x-2t)}\end{aligned}$$

where *A* and *B* are arbitrary constants.

5. $y\dfrac{\partial f}{\partial x} - x\dfrac{\partial f}{\partial y} = 0$

Let $\quad f(x, y) = F(x)\times G(y) \;\to\; \dfrac{\partial f}{\partial x} = \dfrac{dF}{dx}\times G, \;\; \dfrac{\partial f}{\partial y} = F\times\dfrac{dG}{dy}$

Then $\quad y\dfrac{\partial f}{\partial x} - x\dfrac{\partial f}{\partial t} = 0 \;\to\; y\dfrac{dF}{dx}G - xF\dfrac{dG}{dy} = 0$

$$\to \left[\frac{1}{xF}\frac{dF}{dx}\right] - \left[\frac{1}{yG}\frac{dG}{dy}\right] = 0$$

Putting each set of terms equal to constant C, we have (see Section 11.3)

$$\frac{dF}{dx} = CxF \;\to\; \int\frac{dF}{F} = C\int x\,dx \;\to\; \ln F = C\frac{x^2}{2} + c$$

$$\to\; F = ae^{Cx^2/2}$$

Similarly, $\quad \dfrac{dg}{dy} = CyG \;\to\; G = be^{Cy^2/2}$

Therefore $\quad f(x, y) = abe^{C(x^2+y^2)/2} = Ae^{B(x^2+y^2)}$

6. $\dfrac{\partial^2 f}{\partial x^2} + \dfrac{\partial^2 f}{\partial y^2} = 0$

Let $\quad f(x, y) = F(x)\times G(y) \;\to\; \dfrac{\partial^2 f}{\partial x^2} = \dfrac{d^2F}{dx^2}\times G, \;\; \dfrac{\partial^2 f}{\partial y^2} = F\times\dfrac{d^2G}{dy^2}$

Then $\quad \dfrac{\partial^2 f}{\partial x^2} + \dfrac{\partial^2 f}{\partial y^2} = 0 \;\to\; \dfrac{d^2F}{dx^2}\times G + F\times\dfrac{d^2G}{dy^2} = 0 \;\to\; \left[\dfrac{1}{F}\dfrac{d^2F}{dx^2}\right] + \left[\dfrac{1}{G}\dfrac{d^2G}{dy^2}\right] = 0$

and $\quad \dfrac{d^2F}{dx^2} = CF, \qquad \dfrac{d^2G}{dy^2} = -CG$

As in Exercise 2, there are three possible types of solutions:

(a) $C = 0$: $\quad \begin{cases} F(x) = a + bx \\ G(y) = c + dy \end{cases} \;\to\; f(x, y) = (a + bx)(c + dy)$

(b) $C = \lambda^2 > 0$: $\quad \begin{cases} F(x) = ae^{\lambda x} + be^{-\lambda x} \\ G(y) = c\cos\lambda y + d\sin\lambda y \end{cases} \;\to\; f(x, y) = (ae^{\lambda x} + be^{-\lambda x})(c\cos\lambda y + d\sin\lambda y)$

(c) $C = \lambda^2 < 0$: $\quad \begin{cases} F(x) = a\cos\lambda x + b\sin\lambda x \\ G(y) = ce^{\lambda y} + de^{-\lambda y} \end{cases} \;\to\; f(x, y) = (a\cos\lambda x + b\sin\lambda x)(ce^{\lambda y} + de^{-\lambda y})$

7. $\dfrac{\partial^2 f}{\partial x \partial y} + f = 0$

We have $f(x, y) = F(x) \times G(y) \;\; \rightarrow \;\; \dfrac{\partial^2 f}{\partial x \partial y} = \dfrac{dF}{dx} \times \dfrac{dG}{dy}$

Then $\dfrac{\partial^2 f}{\partial x \partial y} + f = \dfrac{dF}{dx} \times \dfrac{dG}{dy} + FG = 0$ when $\left[\dfrac{1}{F}\dfrac{dF}{dx}\right]\left[\dfrac{1}{G}\dfrac{dG}{dy}\right] + 1 = 0$

and $\dfrac{dF}{dx} = CF \;\; \rightarrow \;\; F = ae^{Cx}, \qquad \dfrac{dG}{dy} = -\dfrac{1}{C}G \;\; \rightarrow \;\; G = be^{-y/C}$

Therefore $f(x, y) = Ae^{(Cx - y/C)}$

Section 14.4

8. Show that the wave functions (14.23) satisfy the orthonormality conditions

$$\int_0^b \int_0^a \psi_{p,q}(x, y)\psi_{r,s}(x, y)\, dx dy = \begin{cases} 1 & \text{if } p = r \text{ and } q = s \\ 0 & \text{otherwise} \end{cases}$$

We have $\psi_{p,q} = \sqrt{\dfrac{2}{a}} \sin\left(\dfrac{p\pi x}{a}\right) \times \sqrt{\dfrac{2}{b}} \sin\left(\dfrac{q\pi y}{b}\right), \quad \psi_{r,s} = \sqrt{\dfrac{2}{a}} \sin\left(\dfrac{r\pi x}{a}\right) \times \sqrt{\dfrac{2}{b}} \sin\left(\dfrac{s\pi y}{b}\right)$

Then
$$\begin{aligned} I &= \int_0^b \int_0^a \psi_{p,q}(x, y)\psi_{r,s}(x, y)\, dx dy \\ &= \frac{2}{a}\int_0^a \sin\left(\frac{p\pi x}{a}\right)\sin\left(\frac{r\pi x}{a}\right) dx \times \frac{2}{b}\int_0^b \sin\left(\frac{q\pi y}{b}\right)\sin\left(\frac{s\pi y}{b}\right) dy = I_{p,r} \times I_{q,s} \end{aligned}$$

Remember $\sin Ax \sin Bx = \dfrac{1}{2}\Big[\cos(A - B)x - \cos(A + B)\Big]x$

Then, if $A = p\pi/a$, $B = r\pi/a$, where p and r are integers,

$$I_{p,r} = \frac{2}{a}\int_0^a \sin\left(\frac{p\pi x}{a}\right)\sin\left(\frac{r\pi x}{a}\right) dx = \begin{cases} \left[\dfrac{\sin(p-q)\pi}{(p-q)\pi} - \dfrac{\sin(p+q)\pi}{(p+q)\pi}\right] = 0 & \text{if } p \neq r \\ \dfrac{2}{a}\displaystyle\int_0^a \sin^2\left(\frac{p\pi x}{a}\right) dx = \left[1 - \frac{\sin 2p\pi}{2p\pi}\right] = 1 & \text{if } p = r \end{cases}$$

and similarly for $I_{q,s}$.

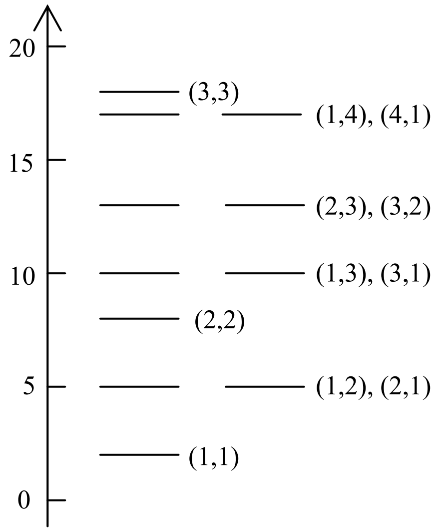
9. **(i)** Find the energies (in units of $h^2/8ma^2$) of the lowest 11 states of the particle in a square box of side a, and sketch an appropriate energy-level diagram. **(ii)** The six diagrams in Figure 14.2 are maps of the signs and nodes of the wave functions (14.27) for the lowest six states, using the real forms of the angular functions. Sketch the corresponding diagrams for the next five lowest states.

(i) By equation (14.26),

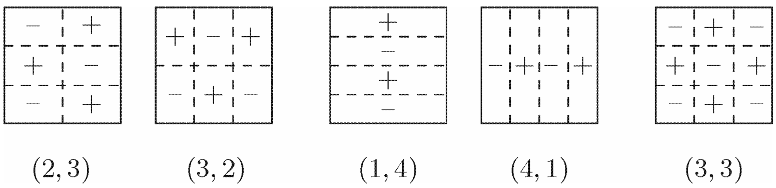
$$E_{p,q} = \frac{h^2}{8ma^2}(p^2 + q^2),$$

and the energies of the lowest 11 states are given by the corresponding lowest values of $p^2 + q^2$:

p	q	$p^2 + q^2$
1	1	2
1	2	5
2	1	5
2	2	8
1	3	10
3	1	10
2	3	13
3	2	13
1	4	17
4	1	17
3	3	18



(ii) Figure 3



10. (i) Solve the Schrödinger equation for the particle in a three-dimensional rectangular box with potential energy function

$$V(x,\, y,\, z) = \begin{cases} 0 & \text{for} \quad 0 < x < a, \quad 0 < y < b, \quad 0 < z < c \\ \infty & \text{elsewhere} \end{cases}$$

(ii) What are the possible degeneracies of the eigenvalues for a cubic box?

The Schrödinger equation for a particle of mass *m* moving in three 3dimensions is

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z) + V(x,y,z)\psi(x,y,z) = E\psi(x,y,z)$$

where ∇^2 is the 3-dimensional Laplacian operator. For the particle within the box, we have the boundary value problem

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) = E\psi$$

with boundary conditions

$$\psi(0,y,z) = \psi(a,y,z) = 0 \qquad (\psi = 0 \text{ when } x = 0 \text{ and } x = a)$$

$$\psi(x,0,z) = \psi(x,b,z) = 0 \qquad (\psi = 0 \text{ when } y = 0 \text{ and } y = b)$$

$$\psi(x,y,0) = \psi(x,y,c) = 0 \qquad (\psi = 0 \text{ when } z = 0 \text{ and } z = c)$$

As for the 2-dimensional rectangular box, but with 3 components for motion along the *x*, *y*, and *z* directions,

let $\quad \psi(x,y,z) = X(x)\times Y(y)\times Z(z)$

then $\quad \psi_{p,q,r}(x,y,z) = \sqrt{\frac{2}{a}}\sin\left(\frac{p\pi x}{a}\right)\times\sqrt{\frac{2}{b}}\sin\left(\frac{q\pi y}{b}\right)\times\sqrt{\frac{2}{c}}\sin\left(\frac{r\pi z}{c}\right),$

$$E_{p,q,r} = \frac{h^2}{8m}\left(\frac{p^2}{a^2} + \frac{q^2}{b^2} + \frac{r^2}{c^2}\right)$$

(ii) For a cubic box,

$$E_{p,q,r} = \frac{h^2}{8ma^2}(p^2 + q^2 + r^2), \qquad p,\, q,\, r = 1,\, 2,\, 3,\, 4,\, \ldots$$

with degeneracies: 1 if p, q and r are all equal (e.g. $E_{2,2,2}$)

3 if two only equal (e.g. $E_{1,1,2}$, $E_{1,2,1}$, $E_{2,1,1}$)

6 if all are different (e.g. $E_{1,2,3}$, $E_{1,3,2}$, $E_{2,3,1}$, $E_{2,1,3}$, $E_{3,1,2}$, $E_{3,2,1}$)

Section 14.5

11. Some zeros of the Bessel functions $J_n(x)$ are:

$J_0(x) = 0$ for $x = 2.4048, 5.5201, 8.6537$
$J_1(x) = 0$ $x = 3.8317, 7.0156, 10.1736$
$J_2(x) = 0$ $x = 5.1356, 8.4172$
$J_3(x) = 0$ $x = 6.3802, 9.7610$
$J_4(x) = 0$ $x = 7.5883$

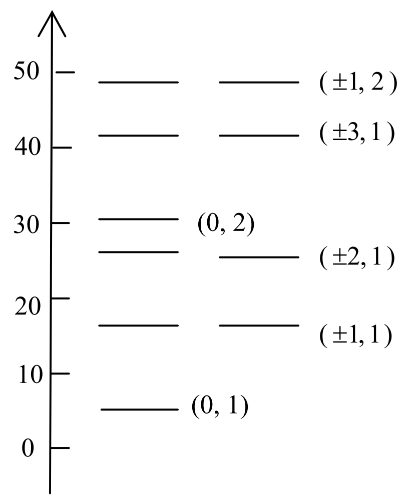
(i) Find the energies (in units of $\hbar^2/2ma^2$) of the lowest 10 states of the particle in a circular box of radius a, and sketch an appropriate energy-level diagram. **(ii)** The six diagrams in Figure 14.3 are maps of the signs and nodes of the wave functions (14.47) for the lowest six states, using the real forms of the angular functions. Sketch the corresponding diagrams for the next four states.

(i) By equation (14.46),

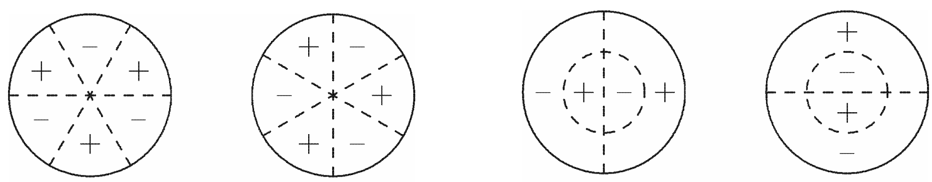
$$E_{n,k} = \alpha_{n,k}^2 \frac{\hbar^2}{2m} = x_{n,k}^2 \frac{\hbar^2}{2ma^2}, \qquad n = 0, \pm 1, \pm 2, \ldots, \quad k = 1, 2, 3, \ldots$$

The energies of the lowest 10 states are given by the corresponding lowest values of $x_{n,k}^2$:

n	k	$x_{n,k}^2$
0	1	5.783
±1	1	14.682
±2	1	26.374
0	2	30.472
±3	1	40.707
±1	2	49.219



(ii) Figure 4



$n = \pm 3,\ k = 1$ $n = \pm 1,\ k = 2$

Section 14.6

12. **(i)** Make use of Tables 14.1 and 14.2 to write down the total wave function $\psi_{1,0,0}$ for the hydrogen-like atom. **(ii)** Substitute this wave function into the Schrödinger equation (14.52), and confirm that it is a solution of the equation with E given by (14.82).

(i) We have $n = 1, l = 0,\ m = 0,\ \rho = 2Zr$

Then $$\psi_{1,0,0}(r,\theta,\phi) = R_{1,0}(r)\times Y_{0,0}(\theta,\phi) = 2Z^{3/2}\,e^{-Zr}\times\left(\frac{1}{4\pi}\right)^{1/2}$$

$$= \left(\frac{Z^3}{\pi}\right)^{1/2} e^{-Zr}$$

(ii) The Schrödinger equation, equation (14.52), is

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2Z}{r}\psi + 2E\psi = 0$$

The wave function depends only on the radial variable r. Therefore $\dfrac{\partial\psi}{\partial\theta} = \dfrac{\partial\psi}{\partial\phi} = 0$, and

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) + \left(\frac{2Z}{r} + 2E\right)\psi = 0$$

which is the radial equation (4.55) with $l = 0$. We have

$$\frac{d\psi}{dr} = -Z\psi,\quad \frac{d^2\psi}{dr^2} = Z^2\psi$$

Therefore $$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) + \left(\frac{2Z}{r} + 2E\right)\psi = \frac{d^2\psi}{dr^2} + \frac{2}{r}\frac{d\psi}{dr} + \left(\frac{2Z}{r} + 2E\right)\psi$$

$$= Z^2\psi - \frac{2Z}{r}\psi + \frac{2Z}{r}\psi + 2E\psi$$

$$= 0 \text{ when } E = -\frac{Z^2}{2}$$

and this is $E_n = -\dfrac{Z^2}{2n^2}$ for $n = 1$.

13. Repeat Exercise 12 for the wave function $\psi_{2,1,0}$.

(i) We have $n=2, l=1, m=0, \rho = Zr$

Then $$\psi_{2,1,0}(r,\theta,\phi) = R_{2,1}(r)\times Y_{1,0}(\theta,\phi) = \frac{1}{2\sqrt{6}} Z^{5/2} r\, e^{-Zr/2} \times \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

$$= \left(\frac{Z^5}{32\pi}\right)^{1/2} r\, e^{-Zr/2} \cos\theta$$

(ii) The Schrödinger equation, equation (14.52), is

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2Z}{r}\psi + 2E\psi = 0$$

We have, for the unnormalized wave function, $\psi = re^{-Zr/2}\cos\theta$,

$$\psi = re^{-Zr/2}\cos\theta \;\to\; \frac{\partial\psi}{\partial r} = \left[e^{-Zr/2} - \frac{Z}{2}re^{-Zr/2}\right]\cos\theta = \left[\frac{1}{r} - \frac{Z}{2}\right]\psi$$

$$\frac{\partial^2\psi}{\partial r^2} = \left[-\frac{1}{r^2}\right]\psi + \left[\frac{1}{r} - \frac{Z}{2}\right]^2\psi = \left[\frac{Z^2}{4} - \frac{Z}{r}\right]\psi$$

$$\frac{\partial\psi}{\partial\theta} = -re^{-Zr/2}\sin\theta = -\tan\theta\,\psi$$

$$\frac{\partial^2\psi}{\partial\theta^2} = -\psi$$

$$\frac{\partial\psi}{\partial\phi} = \frac{\partial^2\psi}{\partial\phi^2} = 0$$

Therefore $$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) = \left[\frac{Z^2}{4} - \frac{2Z}{r} + \frac{2}{r^2}\right]\psi$$

$$\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) = \frac{1}{r^2}\frac{\partial^2\psi}{\partial\theta^2} + \frac{1}{r^2\tan\theta}\frac{\partial\psi}{\partial\theta} = -\frac{2}{r^2}\psi$$

and $$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2Z}{r}\psi + 2E\psi$$

$$= \left[\frac{Z^2}{4} + 2E\right]\psi = 0 \text{ when } E = -\frac{Z^2}{8}$$

and this is $E_n = -\dfrac{Z^2}{2n^2}$ for $n = 2$.

14. Show that the radial functions $R_{1,0}$ and $R_{2,0}$ in Table 14.2 satisfy the orthogonality condition (14.81).

We have $R_{1,0}(r) = 2Z^{3/2}\, e^{-Zr}$

$$R_{2,0}(r) = \frac{1}{2\sqrt{2}}\, Z^{3/2}(2 - Zr)\, e^{-Zr/2}$$

Then, ignoring the normalization constants, and making use of the standard integral

$$\int_0^\infty r^n e^{-ar}\, dr = \frac{n!}{a^{n+1}}$$

we have $$I = \int_0^\infty R_{1,0}(r) R_{2,0}(r) r^2\, dr = \int_0^\infty (2r^2 - Zr^3)\, e^{-3Zr/2}\, dr$$

$$= \left[2\frac{2!}{(3Z/2)^3} - Z\frac{3!}{(3Z/2)^4}\right] = \frac{1}{(3Z/2)^4}\left[4\times\frac{3Z}{2} - 6Z\right]$$

$$= 0$$

15. The Schrödinger equation for the particle in a spherical box of radius a is

$$-\left(\hbar^2/2m\right)\nabla^2\psi + V\psi = E\psi \ ,$$

with potential energy function

$$V(x, y, z) = 0 \ \text{ for } \ r = \sqrt{x^2+y^2+z^2} < a \ \text{ and } \infty \text{ elsewhere.}$$

(i) Show that the equation is separable in spherical polar coordinates, with the same angular wave functions, the spherical harmonics (14.68), as for the hydrogen atom. **(ii)** Show that the radial equation reduces to the Bessel equation (13.60) for spherical Bessel functions $j_l(x)$ where, as in Section 14.5 for the particle in a circular box, $x = \sqrt{2mE/\hbar^2}\, r$. **(iii)** Use the boundary condition to find an expression for the quantized energy in terms of the zeros of the Bessel functions. **(iv)** Find the wave function and energy of the ground state.

Put $\qquad \psi(r,\theta,\phi) = R(r)\times Y(\theta,\phi)$

Then as in Section 14.6 for the hydrogen-like atom, but with $V = -Ze^2/4\pi\varepsilon_0 r$ replaced by $V = 0$ inside the box, the Schrödinger equation separates into a radial equation,

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left(-\frac{l(l+1)}{r^2} + \frac{2mE}{\hbar^2}\right)R = 0 \qquad \text{(equation 1)}$$

and an angular equation

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} + l(l+1)Y = 0 \qquad \text{(equation 2)}$$

(i) Equation 2 for $Y(\theta,\phi)$ is the same as equation (14.56) so that the angular functions are the spherical harmonics $Y_{l,m}(\theta,\phi)$.

(ii) Equation 1 is

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \left(\alpha^2 - \frac{l(l+1)}{r^2}\right)R = 0$$

where $\alpha^2 = 2mE/\hbar^2$. Let $x = \alpha r$. Then $\dfrac{dR}{dr} = \alpha\dfrac{dR}{dx}$ and $\dfrac{d^2R}{dr^2} = \alpha^2\dfrac{d^2R}{dx^2}$. Equation 1 can then be written as

$$\alpha^2\left[\frac{d^2R}{dx^2} + \frac{2}{x}\frac{dR}{dx} + \left(1 - \frac{l(l+1)}{x^2}\right)R\right] = 0$$

or $\qquad x^2R'' + 2xR' + \left[x^2 - l(l+1)\right]R = 0$

This is the Bessel equation (13.60) for the Bessel functions of half-integral order $j_l(x)$ and $\eta_l(x)$, of which only the spherical Bessel functions $j_l(x)$ are finite for all $x \ge 0$. The radial wave functions for the particle in a spherical box are therefore

$$R_l(r) = j_l(\alpha r), \quad l = 0, 1, 2, \ldots$$

(iii) As for the particle in a circular box, Section 14.5, the wave function is subject to the boundary condition $R_l(r) = 0$ when $r = a$. Therefore

$$R_l(a) = j_l(\alpha a) = 0$$

so that the possible values of αa are the zeros of the Bessel function. If the zeros are labelled $x_{1,l}, x_{2,l}, x_{3,l}, \ldots$, the allowed values of $\alpha = \sqrt{2mE/\hbar^2}$ are

$$\alpha_{n,l} = x_{n,l}/a, \quad n = 1, 2, 3, \ldots$$

The energy is therefore quantized, with values

$$E_{n,l} = \alpha_{n,l}^2 \frac{\hbar^2}{2m} = x_{n,l}^2 \frac{\hbar^2}{2ma^2}, \qquad n = 1, 2, 3, \ \ldots, \ l = 0, 1, 2, \ \ldots$$

and the corresponding wave functions are

$$\psi_{n,l,m}(r, \theta) = R_{n,l}(r) Y_{l,m}(\theta, \phi)$$

where $\qquad R_{n,l}(r) = A\, j_l(x_{n,l} r/a) \qquad$ (A is a normalization constant)

(iv) For the ground state, $Y_{0,0} = 1/\sqrt{4\pi}$. From equations (13.55) and (13.59), $j_0(x) = \dfrac{\sin x}{x}$.

Therefore $\qquad R_{1,0}(r) = A\, j_0(x_{1,0} r/a) = A \dfrac{\sin(x_{1,0} r/a)}{(x_{1,0} r/a)}$

The first zero of $j_0(x) = \dfrac{\sin x}{x}$ is $x_{1,0} = \pi$, when $\sin x_{1,0} = \sin \pi = 0$. Then

$$R_{1,0}(r) = A \frac{\sin(\pi r/a)}{(\pi r/a)}$$

and the total ground-state wave function is

$$\psi_{1,0,0}(r, \theta) = R_{1,0}(r) Y_{0,0}(\theta, \phi) = A' \frac{\sin(\pi r/a)}{r}$$

(normalization of the wave function gives $A' = 1/\sqrt{2\pi a}$). The corresponding energy of the ground state is

$$E_{1,0} = \frac{\pi^2 \hbar^2}{2ma^2} = \frac{h^2}{8ma^2}$$

Section 14.7

16. Find the solution of the wave equation for the vibrating string that satisfies the initial conditions $y(x,0) = 3\sin \pi x/l$ and $(\partial y/\partial t)_{t=0} = 0$.

By equation (14.103), the general solution of the vibrating string discussed in Section 14.7 is

$$y(x,t) = \sum_{n=1}^{\infty} \sin \frac{n\pi x}{l}\Big[A_n \cos \omega_n t + B_n \sin \omega_n t\Big]$$

where $\omega_n = n\pi v/l$.

(a) For initial condition $y(x,0) = 3\sin \pi x/l$:

$$y(x,0) = \sum_{n=1}^{\infty} \sin \frac{n\pi x}{l}\Big[A_n \cos 0 + B_n \sin 0\Big]$$

$$= \sum_{n=1}^{\infty} A_n \sin \frac{n\pi x}{l}$$

$$= 3\sin \frac{\pi x}{l} \quad \text{when } A_1 = 3 \text{ and } A_n = 0 \text{ for } n > 1$$

Therefore $$y(x,t) = 3\sin \frac{\pi x}{l} \cos \omega_1 t + \sum_{n=1}^{\infty} B_n \sin \frac{n\pi x}{l} \sin \omega_n t \qquad \text{(equation 1)}$$

(b) For initial condition $(\partial y/\partial t)_{t=0} = 0$:

From Equation 1, we have

$$\frac{\partial y}{\partial t} = -3\omega_1 \sin \frac{\pi x}{l} \sin \omega_1 t + \sum_{n=1}^{\infty} B_n \omega_n \sin \frac{n\pi x}{l} \cos \omega_n t$$

Therefore $$\left(\frac{\partial y}{\partial t}\right)_{t=0} = -3\omega_1 \sin \frac{\pi x}{l} \sin 0 + \sum_{n=1}^{\infty} B_n \omega_n \sin \frac{n\pi x}{l} \cos 0$$

$$= \sum_{n=1}^{\infty} B_n \omega_n \sin \frac{n\pi x}{l}$$

$$= 0 \text{ when } B_n = 0 \text{ for all } n$$

Therefore $$y(x,t) = 3\sin \frac{\pi x}{l} \cos \omega_1 t = 3\sin \frac{\pi x}{l} \cos \frac{\pi v t}{l}$$

and this is the fundamental mode of vibration with amplitude 3.

17. A homogeneous thin bar of length *l* and constant cross-section is perfectly insulated along its length with the ends kept at constant temperature $T = 0$ (on some temperature scale). The temperature profile of the bar is a function $T(x,t)$ of position *x* ($0 \le x \le l$) and of time *t*, and satisfies the heat-conduction (diffusion) equation $\dfrac{\partial T}{\partial t} = D\dfrac{\partial^2 T}{\partial x^2}$ where *D* is the thermal diffusivity of the material. The boundary conditions are $T(0,t) = T(l,t) = 0$. Find the solution of the equation for initial temperature profile $T(x,0) = 3\sin \pi x/l$.

We consider the solution in 4 steps.

(1) Separation of variables:

Put $T(x,t) = F(x)\times G(t)$, substitute in the diffusion equation, divide by $T = F\times G$. Then

$$\frac{1}{F}\frac{d^2F}{dx^2} = \frac{1}{DG}\frac{dG}{dt} = C \quad \rightarrow \quad \frac{d^2F}{dx^2} = CF, \quad \frac{dG}{dt} = CDG$$

(2) Solution of the equation in *x*:

The boundary conditions $T(0,t) = T(l,t) = 0$ mean, for *x*, that $F(0) = F(l) = 0$. These are the boundary conditions for the particle in a box discussed in Section 12.6, and of the vibrating string in Section 12.7. The allowed values of the separation constant are therefore $C_n = -n^2\pi^2/l^2$ and particular solutions are

$$F_n(x) = \sin\frac{n\pi x}{l}$$

(3) Solution of the equation in *t* for each value of *n*:

$$\frac{dG}{dt} = -\frac{n^2\pi^2 D}{l^2}G \quad \rightarrow \quad G_n(t) = e^{-n^2\pi^2 Dt/l^2}$$

(4) Application of the initial condition.

The particular solution for each *n* is $T_n(x,t) = F_n(x)G_n(t)$ and the general solution is

$$T(x,t) = \sum_{n=1}^{\infty} A_n F_n(x)G_n(t) = \sum_{n=1}^{\infty} A_n \sin\frac{n\pi x}{l} e^{-n^2\pi^2 Dt/l^2}$$

Now $$T(x,0) = \sum_{n=1}^{\infty} A_n \sin\frac{n\pi x}{l}$$

$$= 3\sin\frac{\pi x}{l} \quad \text{when } A_1 = 3 \text{ and } A_n = 0 \text{ for } n > 1$$

The solution that satisfies both boundary and initial conditions is therefore

$$T(x,t) = 3\sin\frac{n\pi x}{l} e^{-\pi^2 Dt/l^2}$$

Heat leaks out of the ends of the rod, and T decreases exponentially at each point.

18. **(i)** Find the general solution of the Laplace equation $\dfrac{\partial^2 u}{\partial x^2}+\dfrac{\partial^2 u}{\partial y^2}=0$ in the rectangle

$$0\le x\le a,\ 0\le y\le b$$

subject to the boundary conditions

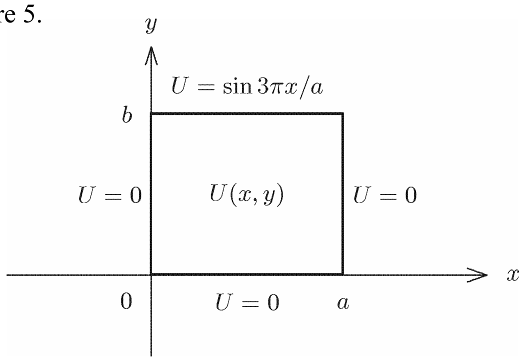
$$u(0,y)=0,\quad u(a,y)=0$$

$$u(x,0)=0,\quad u(x,b)=f(x)$$

where $f(x)$ is an arbitrary function of x. **(ii)** Find the particular solution for $f(x)=\sin\dfrac{3\pi x}{a}$.

The boundary conditions are shown in Figure 5.

Figure 5



(i) We consider the solution in 4 steps.

(1) Separation of variables:

Put $u(x,y)=F(x)\times G(y)$. Then

$$\frac{\partial^2 u}{\partial x^2}+\frac{\partial^2 u}{\partial y^2}=0 \quad\to\quad \frac{d^2F}{dx^2}=CF,\quad \frac{d^2G}{dy^2}=-CG$$

(2) Solution of the equation in x:

The boundary conditions $u(0,y)=u(a,y)=0$ mean, for x, that $F(0)=F(a)=0$. Then, as in Exercise 17, the allowed values of the separation constant are therefore $C_n=-n^2\pi^2/a^2$ and particular solutions are

$$F_n(x)=\sin\frac{n\pi x}{a}$$

(3) Solution of the equation in y for each value of n:

$$\frac{d^2G}{dy^2}=\frac{n^2\pi^2}{a^2}G \quad\to\quad G_n(y)=A_n e^{n\pi y/a}+B_n e^{-n\pi y/a}$$

The boundary condition $u(x,0)=0$ means, for y, that

$$G_n(0)=A_n+B_n=0 \quad\to\quad B_n=-A_n$$

Therefore $\quad G_n(y)=A_n\left(e^{n\pi y/a}-e^{-n\pi y/a}\right)$

$$=2A_n\sinh\frac{n\pi y}{a}$$

(4) The particular solution for each n is $u_n(x, y) = F_n(x)G_n(y)$ and a general solution that satisfies the same boundary conditions is

$$u(x, y) = \sum_{n=1}^{\infty} A_n \sin\frac{n\pi x}{a} \sinh\frac{n\pi y}{a}$$

The coefficients A_n are determined by the boundary condition $u(x, b) = f(x)$.

(ii) If $f(x) = \sin\frac{3\pi x}{a}$ then

$$u(x, b) = \sum_{n=1}^{\infty} A_n \sin\frac{n\pi x}{a} \sinh\frac{n\pi b}{a}$$

$$= \sin\frac{3\pi x}{a} \quad \text{if } A_3 \sinh\frac{3\pi b}{a} = 1 \text{ and } A_n = 0 \text{ for } n \neq 3$$

Therefore $$u(x, y) = \sin\frac{3\pi x}{a} \times \frac{\sinh\left(\frac{3\pi y}{a}\right)}{\sinh\left(\frac{3\pi b}{a}\right)}$$