MATHCHAPTER E

Spherical Coordinates

Although cartesian coordinates (x, y, and z) are suitable for many problems, there are many other problems for which they prove to be cumbersome. A particularly important type of such a problem occurs when the system being described has some sort of a natural center, as in the case of an atom, where the (heavy) nucleus serves as one. In describing atomic systems, as well as many other systems, it is most convenient to use spherical coordinates (Figure E.1).

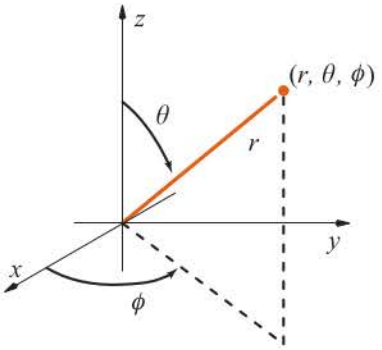


FIGURE E.1
A representation of a spherical coordinate system. A point is specified by the spherical coordinates r, θ, and ϕ.

Instead of locating a point in space by specifying the cartesian coordinates x, y, and z, we can equally well locate the same point by specifying the spherical coordinates r, θ, and ϕ. From Figure E.1, we can see that the relations between the two sets of coordinates are given by

$$
\begin{aligned}
x &= r \sin\theta \cos\phi \\
y &= r \sin\theta \sin\phi \qquad \text{(E.1)} \\
z &= r \cos\theta
\end{aligned}
$$

This coordinate system is called a *spherical coordinate system* because the graph of the equation $r = c =$ constant is a sphere of radius c centered at the origin.

Occasionally, we need to know r, θ, and ϕ in terms of x, y, and z. These relations are given by (Problem E–1)

$$\begin{aligned} r &= \left(x^2 + y^2 + z^2\right)^{1/2} \\ \cos\theta &= \frac{z}{(x^2 + y^2 + z^2)^{1/2}} \\ \tan\phi &= \frac{y}{x} \end{aligned} \tag{E.2}$$

Any point on the surface of a sphere of unit radius can be specified by the values of θ and ϕ. The angle θ represents the declination from the north pole, and hence $0 \le \theta \le \pi$. The angle ϕ represents the angle about the equator, and so $0 \le \phi \le 2\pi$. Although there is a natural zero value for θ (along the north pole), there is none for ϕ. Conventionally, the angle ϕ is measured from the x axis, as illustrated in Figure E.1. Note that r, being the distance from the origin, is intrinsically a positive quantity. In mathematical terms, $0 \le r < \infty$.

In Chapter 6, we will encounter integrals involving spherical coordinates. The differential volume element in cartesian coordinates is $dxdydz$, but it is not quite so simple in spherical coordinates. Figure E.2 shows a differential volume element in spherical coordinates, which can be seen to be

$$dV = (r \sin\theta d\phi)(r d\theta)dr = r^2 \sin\theta dr d\theta d\phi \tag{E.3}$$

Let's use Equation E.3 to evaluate the volume of a sphere of radius a. In this case, $0 \le r \le a$, $0 \le \theta \le \pi$, and $0 \le \phi \le 2\pi$. Therefore,

$$V = \int_0^a r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi = \left(\frac{a^3}{3}\right)(2)(2\pi) = \frac{4\pi a^3}{3}$$

Similarly, if we integrate only over θ and ϕ, then we obtain

$$dV = r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi = 4\pi r^2 dr \tag{E.4}$$

This quantity is the volume of a spherical shell of radius r and thickness dr (Figure E.3). The factor $4\pi r^2$ represents the surface area of the spherical shell and dr is its thickness.

The quantity

$$dA = r^2 \sin\theta d\theta d\phi \tag{E.5}$$

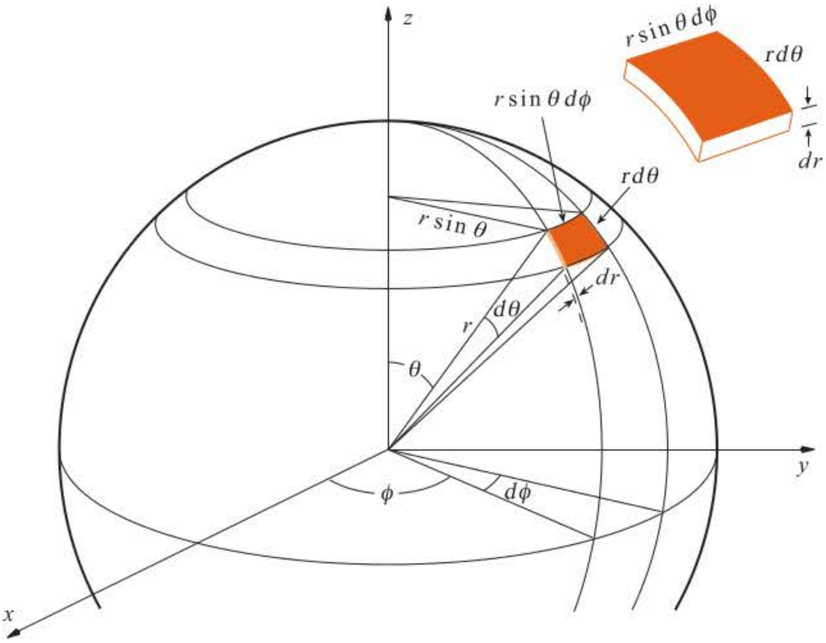


FIGURE E.2
A geometrical construction of the differential volume element in spherical coordinates.

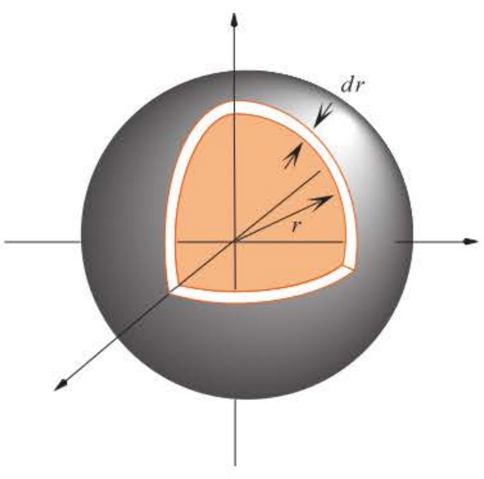


FIGURE E.3
A spherical shell of radius r and thickness dr. The volume of such a shell is $4\pi r^2 dr$, which is its area ($4\pi r^2$) times its thickness (dr).

is the differential area on the surface of a sphere of radius r. (See Figure E.2.) If we integrate Equation E.5 over all values of θ and ϕ, then we obtain $A = 4\pi r^2$, the area of the surface of a sphere of radius r.

Often, the integral we need to evaluate will be of the form

$$I = \int_0^\infty \int_0^\pi \int_0^{2\pi} F(r, \theta, \phi) r^2 \sin\theta dr d\theta d\phi \tag{E.6}$$

When writing multiple integrals, for convenience we use a notation that treats an integral like an operator. To this end, we write the triple integral in Equation E.6 in the form

$$I = \int_0^\infty dr r^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi F(r, \theta, \phi) \tag{E.7}$$

In Equation E.7, each integral "acts on" everything that lies to its right; in other words, we first integrate $F(r, \theta, \phi)$ over ϕ from 0 to 2π, then multiply the result by $\sin\theta$ and integrate over θ from 0 to π, and finally multiply that result by r^2 and integrate over r from 0 to ∞. The advantage of the notation in Equation E.7 is that the integration variable and its associated limits are always unambiguous. As an example of the application of this notation, let's evaluate Equation E.7 with

$$F(r, \theta, \phi) = \frac{1}{32\pi} r^2 e^{-r} \sin^2\theta \cos^2\phi$$

(We will learn in Chapter 7 that this function is the square of a $2p_x$ hydrogen atomic orbital.) If we substitute $F(r, \theta, \phi)$ into Equation E.7, we obtain

$$I = \frac{1}{32\pi} \int_0^\infty dr r^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi\, r^2 e^{-r} \sin^2\theta \cos^2\phi$$

The integral over ϕ gives

$$\int_0^{2\pi} d\phi \, \cos^2\phi = \pi$$

so that

$$I = \frac{1}{32} \int_0^\infty dr r^2 \int_0^\pi d\theta \, \sin\theta\, r^2 e^{-r} \sin^2\theta \tag{E.8}$$

The integral over θ, I_θ, is

$$I_\theta = \int_0^\pi d\theta \sin^3\theta$$

It is often convenient to perform a transformation of variables and let $x = \cos\theta$ in integrals involving θ. Then $\sin\theta d\theta$ becomes $-dx$ and the limits become $+1$ to -1, so in this case we have

$$I_\theta = \int_0^\pi d\theta \sin^3\theta = -\int_1^{-1} dx(1-x^2) = \int_{-1}^1 dx(1-x^2) = 2 - \frac{2}{3} = \frac{4}{3}$$

Using this result in Equation E.8 gives

$$I = \frac{1}{24}\int_0^\infty dr r^4 e^{-r} = \frac{1}{24}(4!) = 1$$

where we have used the general integral

$$\int_0^\infty x^n e^{-x} dx = n!$$

This final result for I simply shows that our above expression for a $2p_x$ hydrogen atomic orbital is normalized.

Frequently, the integrand in Equation E.7 will be a function only of r, in which case we say that the integrand is spherically symmetric. Let's look at Equation E.7 when $F(r, \theta, \phi) = f(r)$:

$$I = \int_0^\infty dr r^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi f(r) \tag{E.9}$$

Because $f(r)$ is independent of θ and ϕ, we can integrate over ϕ to get 2π and then integrate over θ to get 2:

$$\int_0^\pi \sin\theta d\theta = \int_{-1}^1 dx = 2$$

Therefore, Equation E.9 becomes

$$I = \int_0^\infty f(r) 4\pi r^2 dr \tag{E.10}$$

The point here is that if $F(r, \theta, \phi) = f(r)$, then Equation E.7 becomes effectively a one-dimensional integral with a factor of $4\pi r^2 dr$ multiplying the integrand. The quantity $4\pi r^2 dr$ is the volume of a spherical shell of radius r and thickness dr.

EXAMPLE E–1

We will learn in Chapter 7 that a 1s hydrogen atomic orbital is given by

$$f(r) = \frac{1}{(\pi a_0^3)^{1/2}} e^{-r/a_0}$$

Show that the square of this function is normalized.

SOLUTION: Realize that $f(r)$ is a spherically symmetric function of x, y, and z, where $r = (x^2 + y^2 + z^2)^{1/2}$. Therefore, we use Equation E.10 and write

$$I = \int_0^\infty f^2(r) 4\pi r^2 dr = \frac{4\pi}{\pi a_0^3} \int_0^\infty r^2 e^{-2r/a_0} dr$$

$$= \frac{4}{a_0^3} \cdot \frac{2}{(2/a_0)^3} = 1$$

If we restrict ourselves to the surface of a sphere of unit radius, then the angular part of Equation E.5 gives us the differential surface area

$$dA = \sin\theta d\theta d\phi \tag{E.11}$$

If we integrate over the entire spherical surface ($0 \le \theta \le \pi$, $0 \le \phi \le 2\pi$), then

$$A = \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi = 4\pi \tag{E.12}$$

which is the area of a sphere of unit radius.

We call the solid enclosed by the surface that connects the origin and the area dA a *solid angle*, as shown in Figure E.4. Because of Equation E.12, we say that a complete solid angle is 4π, just as we say that a complete angle of a circle is 2π. We often denote a solid angle by $d\Omega$, so that we sometimes write

$$d\Omega = \sin\theta d\theta d\phi \tag{E.13}$$

and Equation E.12 becomes

$$\int_{\text{sphere}} d\Omega = 4\pi \tag{E.14}$$

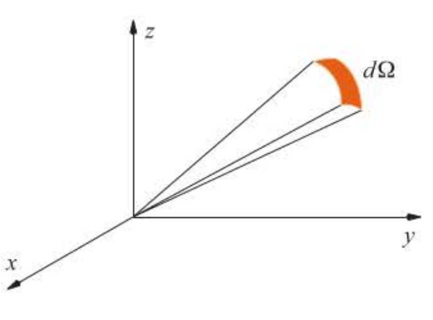


FIGURE E.4
The solid angle, $d\Omega$, subtended by the differential area element $dA = \sin\theta d\theta d\phi$.

In discussing the quantum theory of a hydrogen atom in Chapter 7, we will frequently encounter angular integrals of the form

$$I = \int_0^{\pi} d\theta \sin\theta \int_0^{2\pi} d\phi F(\theta, \phi) \tag{E.15}$$

Note that we are integrating $F(\theta, \phi)$ over the surface of a sphere. For example, we will encounter the integral

$$I = \frac{15}{8\pi} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta (\sin^2\theta \cos^2\theta) \sin\theta$$

The value of this integral is

$$\begin{aligned} I &= \left(\frac{15}{8\pi}\right) \int_0^{\pi} d\theta \sin^2\theta \cos^2\theta \sin\theta \int_0^{2\pi} d\phi \\ &= \frac{15}{4} \int_{-1}^{1} (1 - x^2)x^2 dx = \frac{15}{4}\left[\frac{2}{3} - \frac{2}{5}\right] = 1 \end{aligned}$$

EXAMPLE E–2

Show that

$$I = \int_0^{\pi} d\theta \sin\theta \int_0^{2\pi} d\phi \, Y_1^1(\theta, \phi)^* Y_1^{-1}(\theta, \phi) = 0$$

where

$$Y_1^1(\theta, \phi) = -\left(\frac{3}{8\pi}\right)^{1/2} e^{i\phi} \sin\theta$$

and

$$Y_1^{-1}(\theta, \phi) = \left(\frac{3}{8\pi}\right)^{1/2} e^{-i\phi} \sin\theta$$

SOLUTION:

$$I = -\frac{3}{8\pi} \int_0^{\pi} d\theta \, \sin^3\theta \int_0^{2\pi} d\phi \, e^{-2i\phi}$$

The integral over ϕ is an integral over a complete cycle of $\sin 2\phi$ and $\cos 2\phi$ and therefore $I = 0$. We say that $Y_1^1(\theta, \phi)$ and $Y_1^{-1}(\theta, \phi)$ are orthogonal over the surface of a unit sphere.

There is one final topic involving spherical coordinates that we should discuss here. The operator

$$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)f=\frac{\partial^2 f}{\partial x^2}+\frac{\partial^2 f}{\partial y^2}+\frac{\partial^2 f}{\partial z^2}$$

occurs frequently in physical problems. The operator

$$\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2} \tag{E.16}$$

is called the *Laplacian operator*. When dealing with problems involving a center of symmetry, so that we use spherical coordinates, we express ∇^2 in terms of spherical coordinates rather than cartesian coordinates. The conversion of ∇^2 from cartesian coordinates to spherical coordinates can be carried out starting with Equation E.1, but it is a long, tedious exercise involving partial derivatives that perhaps you should do once, but probably never again. The final result is (see Problems E–13 and E–14)

$$\nabla^2=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{E.17}$$

EXAMPLE E–3

Show that $u(r,\theta,\phi)=1/r$ is a solution to $\nabla^2 u=0$. (This equation is called *Laplace's equation*.)

SOLUTION: The fact that u depends only upon r means that $\nabla^2 u$ reduces to

$$\nabla^2 u=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial u}{\partial r}\right)$$

If we substitute $u=1/r$ into this expression, we find that $r^2\partial u/\partial r=-1$ and that $\nabla^2 u=0$.

EXAMPLE E–4

Show that $u(\theta,\phi)=Y_1^1(\theta,\phi)$ given in Example E–2 satisfies the equation $\nabla^2 u=\dfrac{c}{r^2}u$, where c is a constant. What is the value of c?

SOLUTION: Because $u(\theta,\phi)$ is independent of r, we start with

$$\nabla^2 u=\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial u}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2 u}{\partial\phi^2}$$

Substituting

$$u(\theta,\phi)=-\left(\frac{3}{8\pi}\right)^{1/2}e^{i\phi}\sin\theta$$

into $\nabla^2 u$ gives

$$\nabla^2 u = -\left(\frac{3}{8\pi}\right)^{1/2}\left[\frac{e^{i\phi}}{r^2\sin\theta}(\cos^2\theta - \sin^2\theta) - \frac{\sin\theta}{r^2\sin^2\theta}e^{i\phi}\right]$$

$$= -\left(\frac{3}{8\pi}\right)^{1/2}\frac{e^{i\phi}}{r^2}\left(\frac{1-2\sin^2\theta}{\sin\theta} - \frac{1}{\sin\theta}\right)$$

$$= 2\left(\frac{3}{8\pi}\right)^{1/2}\frac{e^{i\phi}\sin\theta}{r^2}$$

or $c = -2$.

Problems

E–1. Derive Equations E.2 from Equations E.1.

E–2. Express the following points given in cartesian coordinates in terms of spherical coordinates: (x, y, z): $(1, 0, 0)$; $(0, 1, 0)$; $(0, 0, 1)$; $(0, 0, -1)$.

E–3. Describe the graphs of the following equations:

(a) $r = 5$ (b) $\theta = \pi/4$ (c) $\phi = \pi/2$

E–4. Use Equation E.3 to determine the volume of a hemisphere of radius a.

E–5. Use Equation E.5 to determine the surface area of a hemisphere of radius a.

E–6. Evaluate the integral

$$I = \int_0^{\pi} \cos^2\theta \sin^3\theta d\theta$$

by letting $x = \cos\theta$.

E–7. We will learn in Chapter 7 that a $2p_y$ hydrogen atom orbital is given by

$$\psi_{2p_y} = \frac{1}{4\sqrt{2\pi}} re^{-r/2}\sin\theta\sin\phi$$

Show that ψ_{2p_y} is normalized. (Don't forget to square ψ_{2p_y} first.)

E–8. We will learn in Chapter 7 that a $2s$ hydrogen atomic orbital is given by

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}(2-r)e^{-r/2}$$

Show that ψ_{2s} is normalized.

E–9. Show that

$$Y_1^0(\theta, \phi) = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

$$Y_1^1(\theta, \phi) = -\left(\frac{3}{8\pi}\right)^{1/2} e^{i\phi} \sin\theta$$

and

$$Y_1^{-1}(\theta, \phi) = \left(\frac{3}{8\pi}\right)^{1/2} e^{-i\phi} \sin\theta$$

are orthonormal over the surface of a sphere.

E–10. Evaluate the average of $\cos\theta$ and $\cos^2\theta$ over the surface of a sphere.

E–11. We shall frequently use the notation $d\mathbf{r}$ to represent the volume element in spherical coordinates. Evaluate the integral

$$I = \int d\mathbf{r} e^{-r} \cos^2\theta$$

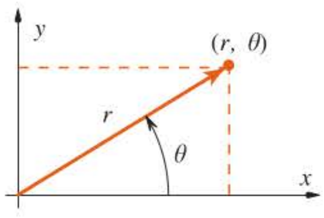
where the integral is over all space (in other words, over all possible values of r, θ, and ϕ).

E–12. Show that the two functions

$$f_1(r) = e^{-r} \cos\theta \quad \text{and} \quad f_2(r) = (2 - r)e^{-r/2} \cos\theta$$

are orthogonal over all space (in other words, over all possible values of r, θ, and ϕ).

E–13. Consider the transformation from cartesian coordinates to plane polar coordinates,



where

$$\begin{aligned} x &= r\cos\theta & r &= (x^2 + y^2)^{1/2} \\ y &= r\sin\theta & \theta &= \tan^{-1}\left(\frac{y}{x}\right) \end{aligned} \tag{1}$$

If a function $f(r, \theta)$ depends upon the polar coordinates r and θ, then the chain rule of partial differentiation says that

$$\left(\frac{\partial f}{\partial x}\right)_y = \left(\frac{\partial f}{\partial r}\right)_\theta \left(\frac{\partial r}{\partial x}\right)_y + \left(\frac{\partial f}{\partial \theta}\right)_r \left(\frac{\partial \theta}{\partial x}\right)_y \tag{2}$$

and that

$$\left(\frac{\partial f}{\partial y}\right)_x = \left(\frac{\partial f}{\partial r}\right)_\theta \left(\frac{\partial r}{\partial y}\right)_x + \left(\frac{\partial f}{\partial \theta}\right)_r \left(\frac{\partial \theta}{\partial y}\right)_x \tag{3}$$

For simplicity, we will assume that r is equal to a constant, l, so that we can ignore terms involving derivatives with respect to r. In other words, we will consider a particle that is constrained to move on the circumference of a circle. This system is sometimes called a *particle on a ring*. Using equations 1 and 2, show that

$$\left(\frac{\partial f}{\partial x}\right)_y = -\frac{\sin\theta}{l}\left(\frac{\partial f}{\partial \theta}\right)_r \qquad \text{and} \qquad \left(\frac{\partial f}{\partial y}\right)_x = \frac{\cos\theta}{l}\left(\frac{\partial f}{\partial \theta}\right)_r \tag{4}$$

Now apply equation 2 again to show that

$$\begin{aligned}\left(\frac{\partial^2 f}{\partial x^2}\right)_y &= \left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial x}\right)_y\right] = \left[\frac{\partial}{\partial \theta}\left(\frac{\partial f}{\partial x}\right)_y\right]_l \left(\frac{\partial \theta}{\partial x}\right)_y \\ &= \left\{\frac{\partial}{\partial \theta}\left[-\frac{\sin\theta}{l}\left(\frac{\partial f}{\partial \theta}\right)_r\right]\right\}_l \left(-\frac{\sin\theta}{l}\right) \\ &= \frac{\sin\theta\cos\theta}{l^2}\left(\frac{\partial f}{\partial \theta}\right) + \frac{\sin^2\theta}{l^2}\left(\frac{\partial^2 f}{\partial \theta^2}\right)\end{aligned}$$

Similarly, show that

$$\left(\frac{\partial^2 f}{\partial y^2}\right)_x = -\frac{\sin\theta\cos\theta}{l^2}\left(\frac{\partial f}{\partial \theta}\right) + \frac{\cos^2\theta}{l^2}\left(\frac{\partial^2 f}{\partial \theta^2}\right)$$

and that

$$\nabla^2 f = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} \longrightarrow \frac{1}{l^2}\left(\frac{\partial^2 f}{\partial \theta^2}\right)$$

E–14. Generalize Problem E–13 to the case of a particle moving in a plane under the influence of a central force; in other words, convert

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$$

to plane polar coordinates, this time without assuming that r is a constant. Use the method of separation of variables to separate the equation for this problem. Solve the angular equation.

E–15. Show that $u(r, \theta, \phi) = r \sin\theta \cos\phi$ satisfies Laplace's equation, $\nabla^2 u = 0$.

E–16. Show that $u(r, \theta, \phi) = r^2 \sin^2\theta \cos 2\phi$ satisfies Laplace's equation, $\nabla^2 u = 0$.