Contents

Chapter 4

Quantum Mechanics in Three Dimensions

4.1 Separation of Variables

In three dimensions the Hamiltonian in the Schrödinger Equation is:

$$H = \frac{p^2}{2m} + V = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V(x, y, z) \tag{4.1}$$

where the momentum operators are:

$$p_x = \frac{\hbar}{i}\frac{\partial}{\partial x}, \qquad p_y = \frac{\hbar}{i}\frac{\partial}{\partial y}, \qquad p_z = \frac{\hbar}{i}\frac{\partial}{\partial z}, \tag{4.2}$$

In vector notation:

$$\mathbf{p} = \frac{\hbar}{i}\nabla \tag{4.3}$$

with:

$$p^2 = -\hbar^2\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] \equiv -\hbar^2\nabla^2 \tag{4.4}$$

The three-dimensional Schrödinger Equation is:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + V(x, y, z)\Psi = i\hbar\frac{\partial\Psi}{\partial t} \tag{4.5}$$

If V is independent of time, we can separate the space and time variables just as we did in one-dimension, writing:

$$\Psi(\mathbf{r}, t) = \psi_E(\mathbf{r})e^{-i\frac{E}{\hbar}t} \tag{4.6}$$

The possible values of E will depend on the potential. For bound states, the energies will be discrete. If we label them as E_n, a general solution will be a linear sum of eigenfunctions:

$$\Psi(\mathbf{r},t) = \sum_n c_n \psi_n(\mathbf{r}) e^{-i\frac{E_n}{\hbar}t} \tag{4.7}$$

If the potential allows unbound states, the allowed energies will be continuously distributed, and the sum over eigenstates becomes a three dimensional Fourier integral.

After separating out the time behavior, we are left with the time independent equation:

$$H\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{4.8}$$

or:

$$\nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\psi = 0 \tag{4.9}$$

The Laplacian operator, ∇^2, can be separated in many different coordinate systems. In particular it can be separated in rectangular, cylindrical, and spherical coordinates. The choice of coordinate system is generally based on the form of the potential and the nature of the boundary conditions that must be satisfied. For a central force, spherical coordinates are the natural choice.

4.2 Separation in Cartesian coordinates

4.2.1 Three dimensional infinite well

If the boundary conditions consist of specification of the wave function at the walls of a rectangular box, Cartesian coordinates are the natural choice. For the time-independent Schrödinger Equation to separate, the potential must have the separable form, $V(x,y,z) = V_x(x) + V_y(y) + V_z(z)$. The Schrödinger Equation is:

$$-\frac{\hbar^2}{2m}(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}) + (V_x(x) + V_y(y) + V_z(z)))\psi = E\psi \tag{4.10}$$

Separating the variables by writing $\psi(x,y,z) = X(x)Y(y)Z(z)$:

$$\frac{1}{X}\left(\frac{\partial^2 X}{\partial x^2} - \frac{2m}{\hbar^2}V_x(x)X\right) + \frac{1}{Y}\left(\frac{\partial^2 Y}{\partial y^2} - \frac{2m}{\hbar^2}V_y(y)Y\right)$$

$$+\frac{1}{Z}\left(\frac{\partial^2 Z}{\partial z^2}-\frac{2m}{\hbar^2}V_z(z)Z\right)+\frac{2m}{\hbar^2}E=0 \tag{4.11}$$

The separated one dimensional equations are:

$$\frac{1}{X}\left(\frac{\partial^2 X}{\partial x^2}-\frac{2m}{\hbar^2}V_x(x)X\right)=c_x \tag{4.12}$$

$$\frac{1}{Y}\left(\frac{\partial^2 Y}{\partial y^2}-\frac{2m}{\hbar^2}V_y(y)Y\right)=c_y \tag{4.13}$$

$$\frac{1}{Z}\left(\frac{\partial^2 Z}{\partial z^2}-\frac{2m}{\hbar^2}V_z(z)Z\right)=c_z \tag{4.14}$$

with:

$$c_x+c_y+c_z+\frac{2mE}{\hbar^2}=0 \tag{4.15}$$

Three dimensional infinite square well

The one dimensional infinite square well generalizes easily to three dimensions. Set $V=0$ inside a box with edges of length a, b, c and set $V=\infty$ outside the box. We choose the coordinate system with one vertex of the box at the origin, and with the inside of the box defined by:

$$0<x<a, \qquad 0<y<b, \qquad 0<z<c$$

The solutions are either Sines and Cosines if $c_q<0$ ($q=x$, y, or x) or exponential functions if $c_q>0$. The wave function must vanish outside the box, so that for continuity it must vanish at the edges of the box. To satisfy these boundary conditions, the possible solutions are restricted to negative values of c_i. The cosines are eliminated by the boundary condition at the origin, and we are left with:

$$X=\sqrt{\frac{2}{a}}\sin\left(\frac{l\pi x}{a}\right), \qquad Y=\sqrt{\frac{2}{b}}\sin\left(\frac{m\pi y}{b}\right), \qquad Z=\sqrt{\frac{2}{c}}\sin\left(\frac{n\pi z}{c}\right) \tag{4.16}$$

where l, m, and n are positive integers. With these restrictions, $c_x=-\frac{l^2\pi^2}{a^2}$, $c_y=-\frac{m^2\pi^2}{b^2}$, $c_z=-\frac{n^2\pi^2}{c^2}$. This leads to discrete values of the allowed energies:

$$E_{lmn}=\frac{\hbar^2\pi^2}{2m}\left(\frac{l^2}{a^2}+\frac{m^2}{b^2}+\frac{n^2}{c^2}\right) \tag{4.17}$$

If the box is a perfect cube, the eigenfunctions $\Psi_{lmn}(x,y,z,t)$ become highly degenerate:

$$E_{lmn} = \frac{\hbar^2\pi^2}{2ma^2}\left(l^2+m^2+n^2\right) \tag{4.18}$$

so that, for instance:

$$E_{211} = E_{121} = E_{112} \tag{4.19}$$

Clearly, the degeneracy is related to the cubic symmetry. If two sides are the same length, with the third different, the energy levels are still degenerate, but not to as high a degree. In general, degeneracy in the energy of quantum states is a consequence of a symmetry.

An arbitrary state in the box is represented by:

$$\Psi(x,y,z,t) = \sqrt{\frac{8}{abc}}\sum_{lmn} c_{lmn}\sin\left(\frac{l\pi x}{a}\right)\sin\left(\frac{m\pi y}{b}\right)\sin\left(\frac{n\pi z}{c}\right)e^{-iE_{lmn}t/\hbar} \tag{4.20}$$

The eigenstates are orthonormal, satisfying:

$$\int \psi_{lmn}(x,y,z)\ \psi_{l'm'n'}(x,y,z)\ dx\ dy\ dz = \delta_{ll'}\delta_{mm'}\delta_{nn'} \tag{4.21}$$

Using this condition, the coefficients c_{lmn} can be obtained by a straightforward generalization of the Fourier formula:

$$c_{lmn} = \sqrt{\frac{8}{abc}}$$

$$\int_0^a\int_0^b\int_0^c \Psi(x,y,z,t=0)\sin\left(\frac{l\pi x}{a}\right)\ \sin\left(\frac{m\pi y}{b}\right)\ \sin\left(\frac{n\pi z}{c}\right)\ dx\,dy\,dz \tag{4.22}$$

In terms of the notation of linear algebra, the eigenvectors are:

$$|lmn\rangle = \sqrt{\frac{8}{abc}}\sin\left(\frac{l\pi x}{a}\right)\sin\left(\frac{m\pi y}{a}\right)\sin\left(\frac{n\pi z}{a}\right)$$

These are orthonormal so that:

$$\langle l'm'n'|lmn\rangle = \delta_{ll'}\delta_{mm'}\delta_{nn'}$$

An arbitrary quantum state can be written as:

$$\Psi(x,t) = \sum_{lmn} c_{lmn}|lmn\rangle e^{-iE_{lmn}t/\hbar}$$

where:

$$c_{lmn} = \langle lmn|\psi\rangle$$

Thus:

$$|\Psi\rangle = \sum_{lmn} |lmn\rangle\langle lmn|\psi\rangle e^{-iE_{lmn}t/\hbar}$$

We will use the solution of the infinite square well in later examples. The finite square well does not generalize easily to three-dimensions in Cartesian coordinates.

4.3 Solution of the Schrödinger Equation Using Spherical Coordinates

If the potential function has spherical symmetry, such that $V(\mathbf{r}) = V(r)$, (a central force) it is natural to express the Schrödinger Equation in terms of spherical coordinates:

$$x = r\sin\theta\cos\phi, \qquad y = r\sin\theta\sin\phi, \qquad z = r\cos\theta \tag{4.23}$$

$$r \geq 0, \qquad 0 \leq \theta \leq \pi, \qquad 0 \leq \phi < 2\pi \tag{4.24}$$

with the inverse transformations:

$$r^2 = x^2 + y^2 + z^2, \qquad \cos\theta = \frac{z}{\sqrt{x^2+y^2+z^2}}, \qquad \tan(\phi) = \frac{y}{x} \tag{4.25}$$

A volume element in spherical coordinates is:

$$dV = d^3r = r^2\sin\theta\, dr\, d\theta\, d\phi \tag{4.26}$$

It is frequently convenient to make a change of variables, $\mu = \cos\theta$. Then $d\mu = -\sin\theta d\theta$. As θ varies from 0 to π, $\cos\theta$ varies from 1 to -1. In volume integrals:

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} f(r,\theta,\phi)\, r^2 \sin\theta\, dr\, d\theta\, d\phi$$
$$= -\int_0^\infty \int_1^{-1} \int_0^{2\pi} f(r,\mu,\phi) r^2 dr\, d\mu\, d\phi =$$
$$= \int_0^\infty \int_{-1}^{1} \int_0^{2\pi} f(r,\mu,\phi) r^2 dr\, d\mu\, d\phi$$

In spherical coordinates:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right) \tag{4.27}$$

Changing from θ to $\mu = \cos\theta$, so that:

$$\frac{\partial}{\partial\theta} = \frac{\partial}{\partial\mu}\frac{d\mu}{d\theta} = -\sin\theta\frac{\partial}{\partial\mu} \tag{4.28}$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\sin\theta\frac{\partial}{\partial\mu}\left(\sin^2\theta\frac{\partial}{\partial\mu}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right) \tag{4.29}$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\frac{\partial}{\partial \mu}\left((1-\mu^2)\frac{\partial}{\partial \mu}\right) + \frac{1}{r^2(1-\mu^2)}\left(\frac{\partial^2}{\partial \phi^2}\right) \tag{4.30}$$

We can now write the time-independent Schrödinger Equation as:

$$\begin{aligned}&\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi}{\partial r}\right) + \frac{1}{r^2}\frac{\partial}{\partial \mu}\left((1-\mu^2)\frac{\partial \psi}{\partial \mu}\right)\\ &+\frac{1}{r^2(1-\mu^2)}\left(\frac{\partial^2 \psi}{\partial \phi^2}\right) + \frac{2m}{\hbar^2}(E - V(r))\psi = 0\end{aligned} \tag{4.31}$$

Multiplying by r^2:

$$\begin{aligned}&\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi}{\partial r}\right) + \frac{2mr^2}{\hbar^2}(E - V(r))\psi\\ &+\frac{\partial}{\partial \mu}\left((1-\mu^2)\frac{\partial \psi}{\partial \mu}\right) + \frac{1}{(1-\mu^2)}\left(\frac{\partial^2 \psi}{\partial \phi^2}\right) = 0\end{aligned} \tag{4.32}$$

Using operator notation we can write this as:

$$\hat{D}(r)\psi + \hat{K}(\mu,\phi)\psi = 0 \tag{4.33}$$

$$\hat{D}(r) = \frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{2mr^2}{\hbar^2}(E - V(r))$$

$$\hat{K}(\mu,\phi) = +\frac{\partial}{\partial \mu}\left((1-\mu^2)\frac{\partial}{\partial \mu}\right) + \frac{1}{(1-\mu^2)}\left(\frac{\partial^2}{\partial \phi^2}\right)$$

The operator $\hat{D}$ depends only on r and the operator $\hat{K}$ depends only on the angle variables (μ and ϕ).

Clearly we can separate out the dependence on r by writing:

$$\psi = R(r)Y(\theta,\phi) = R(r)Y(\mu,\phi)$$

which by substitution into Eq. 4.33 yields:

$$\left(\hat{D}(r)R(r)\right)Y(\mu,\phi) + \left(\hat{K}(\mu,\phi)Y(\theta,\phi)\right)R(r) = 0$$

Dividing through by RY:

$$\frac{1}{R(r)}\hat{D}(r)R(r) + \frac{1}{Y(\mu,\phi)}\hat{K}(\mu.\phi)Y(\mu,\phi) = 0$$

This can be valid only if the two terms are equal and opposite constants. Denote the constant by C:

$$\hat{D}(r)R = CR, \qquad \hat{K}(\mu,\phi)Y = -CY$$

Looking ahead to the solution of the radial equation, we write the separation constant in the form, $C = l(l+1)$, where l at this point is just another constant. The explicit radial equation is:

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \left[\frac{2mr^2}{\hbar^2}(E - V(r)) - l(l+1)\right]R = 0 \tag{4.34}$$

4.3.1 The angular equation

The angular part of the equation is independent of the potential, provided of course that the potential is a central force potential depending only on r. Thus this part of the equation is the same for a large variety of problems, so we investigate its solution first. The angular equation is:

$$\frac{\partial}{\partial \mu}\left((1-\mu^2)\frac{\partial Y}{\partial \mu}\right) + \frac{1}{1-\mu^2}\left(\frac{\partial^2 Y}{\partial \phi^2}\right) = -l(l+1) \tag{4.35}$$

Multiplying by $1-\mu^2$:

$$(1-\mu^2)\frac{\partial}{\partial \mu}\left((1-\mu^2)\frac{\partial Y}{\partial \mu}\right) + l(l+1)(1-\mu^2)Y + \left(\frac{\partial^2 Y}{\partial \phi^2}\right) = 0 \tag{4.36}$$

which we can write in operator form as:

$$\hat{L}(\mu)Y + \hat{M}(\phi)Y = 0 \tag{4.37}$$

where:

$$\hat{L} \equiv (1-\mu^2)\frac{\partial}{\partial \mu}\left((1-\mu^2)\frac{\partial}{\partial \mu}\right) + l(l+1)(1-\mu^2)$$

and:

$$\hat{M} \equiv \frac{\partial^2 Y}{\partial \phi^2}$$

We can now write $Y = \Theta(\mu)\Phi(\phi)$ to obtain:

$$\frac{1}{\Theta}\hat{L}\Theta + \frac{1}{\Phi}\hat{M}\Phi = 0$$

Each term must separately be constant:

$$\frac{1}{\Phi}\hat{M}\Phi = C = -\frac{1}{\Theta}\hat{L}\Theta$$