

4 The Schrödinger wave equation

We have noted in previous lectures that all particles, both light and matter, can be described as a localised wave packet.

- De Broglie suggested a relationship between the effective wavelength of the wave function associated with a given matter or light particle its the momentum. This relationship was subsequently confirmed experimentally for electrons.
- Consideration of the two slit experiment has provided an understanding of what we can and cannot achieve with the wave function representing the particle: The wave function Ψ is not observable. According to the statistical interpretation of Born, the quantity $\Psi^*\Psi = |\Psi|^2$ is observable and represents the probability density of locating the particle in a given elemental volume.

To understand the wave function further, we require a **wave equation** from which we can study the evolution of wave functions as a function of position and time, in general within a **potential field** (e.g. the potential fields associated with the Coulomb or strong nuclear force).

As we shall see, manipulation of the wave equation will permit us to calculate “most probable” values of a particle’s position, momentum, energy, etc. These quantities form the study of **mechanics** within classical physics. Our quantum theory has now become **quantum mechanics** – the description of mechanical physics on the quantum scale. The particular sub-branch of quantum mechanics accessible via wave theory is sometimes referred to as wave mechanics.

The **time-dependent Schrödinger wave equation** is the quantum wave equation

$$i\hbar \frac{\partial \Psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + V(x, t) \Psi(x, t), \quad (1)$$

where $i = \sqrt{-1}$, m is the mass of the particle, $\hbar = h/2\pi$, $\Psi(x, t)$ is the wave function representing the particle and $V(x, t)$ is a potential energy function. It is straight forward to extend the Schrödinger equation to three spatial dimensions

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) + V \Psi. \quad (2)$$

The Schrödinger equation is postulated – it is not derived – yet the predictions based upon it are verified via experiment. It provides a correct description of physical observables. The same could be said for Newton’s equation

$$F = m \frac{d^2 x}{dt^2}. \quad (3)$$

This is another example of an equation that is postulated – not derived – yet provides a correct description of physical observables. However, Newton’s equation is valid at macroscopic scales, whereas the Schrödinger is valid at microscopic, or quantum scales.

Note that the Schrödinger equation as presented here is **non-relativistic**. A relativistic form of the Schrödinger equation exists but is not considered in this course.

4.1 Investigating the Schrödinger equation

The Schrödinger is nominally similar to the classical wave equation

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 \Psi}{\partial t^2}, \quad (4)$$

with the exception that the Schrödinger equation contains only a 1st order time derivative. This is the first clue that wave solutions to the Schrödinger equation will not be identical to solutions of the classical wave equation.

T–Rex Example 6.1: Is the Schrödinger equation linear?

If the Schrödinger equation is linear, then, if Ψ_1 and Ψ_2 represent valid solutions, there must exist a valid solution of the form

$$\Psi(x, t) = a \Psi_1(x, t) + b \Psi_2(x, t), \quad (5)$$

where a and b are (real or complex) constants. The derivatives of Ψ may be written as

$$\begin{aligned} \frac{\partial \Psi}{\partial t} &= a \frac{\partial \Psi_1}{\partial t} + b \frac{\partial \Psi_2}{\partial t} \\ \frac{\partial \Psi}{\partial x} &= a \frac{\partial \Psi_1}{\partial x} + b \frac{\partial \Psi_2}{\partial x} \\ \frac{\partial^2 \Psi}{\partial x^2} &= a \frac{\partial^2 \Psi_1}{\partial x^2} + b \frac{\partial^2 \Psi_2}{\partial x^2}. \end{aligned} \quad (6)$$

Substituting these expressions into the Schrödinger equation for Ψ , we obtain

$$i\hbar \left(a \frac{\partial \Psi_1}{\partial t} + b \frac{\partial \Psi_2}{\partial t} \right) = -\frac{\hbar^2}{2m} \left(a \frac{\partial^2 \Psi_1}{\partial x^2} + b \frac{\partial^2 \Psi_2}{\partial x^2} \right) + V(a\Psi_1 + b\Psi_2). \quad (7)$$

Rearranging this expression yields

$$a \left(i\hbar \frac{\partial \Psi_1}{\partial t} + \frac{\hbar^2}{2m} \frac{\partial^2 \Psi_1}{\partial x^2} - V \Psi_1 \right) = b \left(i\hbar \frac{\partial \Psi_2}{\partial t} + \frac{\hbar^2}{2m} \frac{\partial^2 \Psi_2}{\partial x^2} - V \Psi_2 \right). \quad (8)$$

As Ψ_1 and Ψ_2 are valid solutions to the Schrödinger equation, then the terms within the parentheses are exactly zero, the equation makes sense and Ψ must also be a valid solution to the wave equation. Given the Schrödinger equation is linear we know that the principle of superposition is valid and we can confidently create wave packets from linear wave superposition that are themselves valid solutions of the Schrödinger equation. Recall from Lecture 3 that wave superposition, demonstrated as interference fringes, is required to describe the results of the two-slit experiment.

T–Rex Example 6.2: Investigating valid solutions to the Schrödinger equation

In Lecture 3 we investigated solutions to the classical wave equation of the form

$$\Psi(x, t) = A \sin(kx - \omega t + \phi) \quad (9)$$

where k is the wave number, ω is the angular frequency and ϕ is a phase constant. The wave is moving in the positive x -direction. This “classical” wave is not a valid solution to the time-dependent Schrödinger equation.

We start by considering the three derivative terms

$$\begin{aligned} \frac{\partial \Psi}{\partial t} &= -\omega A \cos(kx - \omega t) \\ \frac{\partial \Psi}{\partial x} &= kA \cos(kx - \omega t) \\ \frac{\partial^2 \Psi}{\partial x^2} &= -k^2 A \sin(kx - \omega t) = -k^2 \Psi. \end{aligned} \quad (10)$$

Inserting these relations into the time-dependent Schrödinger equation we obtain

$$\begin{aligned} -i\hbar\omega \cos(kx - \omega t) &= \left(\frac{\hbar^2 k^2}{2m} + V \right) \Psi \\ &= \left(\frac{\hbar^2 k^2}{2m} + V \right) A \sin(kx - \omega t), \end{aligned} \quad (11)$$

which is never satisfied ($\cos x \neq \sin x$).

We now consider a more general wave function

$$\Psi(x, t) = A e^{i(kx - \omega t)} = A[\cos(kx - \omega t) + i \sin(kx - \omega t)]. \quad (12)$$

We note that this general wave solution is complex yet still represents a wave moving in the positive x -direction. In general, the amplitude A can also be complex. In order to demonstrate that this

wave function is a valid solution to the time-dependent Schrödinger equation, we follow the same approach as before, i.e.

$$\begin{aligned}\frac{\partial \Psi}{\partial t} &= -i\omega A e^{i(kx - \omega t)} = -i\omega \Psi \\ \frac{\partial \Psi}{\partial x} &= ik \Psi \\ \frac{\partial^2 \Psi}{\partial x^2} &= i^2 k^2 \Psi = -k^2 \Psi.\end{aligned}\tag{13}$$

Inserting these relations into the time-dependent Schrödinger equation we obtain

$$\begin{aligned}i\hbar(-i\omega \Psi) &= -\frac{\hbar^2}{2m}(-k^2 \Psi) + V \Psi \\ \left(\hbar\omega - \frac{\hbar^2 k^2}{2m} + V\right) \Psi &= 0.\end{aligned}\tag{14}$$

We can understand this equation by noting that $E = hf = \hbar\omega$ and $p = \hbar k$ to obtain

$$\left(E - \frac{p^2}{2m} - V\right) \Psi = 0.\tag{15}$$

The term in parentheses represents the conservation of energy (i.e. $E - KE - V = 0$) and therefore $Ae^{i(kx - \omega t)}$ represents a valid solution to the time-dependent Schrödinger equation.

4.2 Probability and normalisation

In the previous lecture we introduced the idea of probabilities based upon the wave function. The probability $P(x) dx$ of observing a particle between x and $x + dx$ is

$$P(x) dx = \Psi^*(x, t) \Psi(x, t) dx.\tag{16}$$

The probability of observing the particle between x_1 and x_2 is

$$P = \int_{x_1}^{x_2} \Psi^* \Psi dx.\tag{17}$$

The particle must exist somewhere; this condition is imposed by **normalising** the wave function according to

$$\int_{-\infty}^{\infty} \Psi^*(x, t) \Psi(x, t) dx = 1.\tag{18}$$

T–Rex Example 6.4 Normalising the wave function

Consider the wave function $\Psi(x, t) = Ae^{-\alpha|x|}$. Normalise the wave function and determine the probability of observing the particle between $0 < x < 1/\alpha$, and between $1/\alpha < x < 2/\alpha$.

The wave function is normalised as follows

$$\int_{-\infty}^{\infty} A^2 e^{-2\alpha|x|} dx = 1. \quad (19)$$

As the wave function is symmetric about zero we may re-write it as

$$\begin{aligned} 2 \int_0^{\infty} A^2 e^{-2\alpha|x|} dx = 1 &= \frac{2A^2}{-2\alpha} [e^{-2\alpha x}]_0^{\infty} \\ 1 &= \frac{-A^2}{\alpha} (0 - 1) = \frac{A^2}{\alpha}. \end{aligned} \quad (20)$$

The coefficient $A = \sqrt{\alpha}$ and the wave function may be written as

$$\Psi = \sqrt{\alpha} e^{-\alpha|x|}. \quad (21)$$

The probability of locating the particle between $0 < x < 1/\alpha$ may be written as

$$\begin{aligned} P &= \int_0^{1/\alpha} \alpha e^{-2\alpha x} \\ &= \frac{\alpha}{-2\alpha} [e^{-2\alpha x}]_0^{1/\alpha} \\ &= -\frac{1}{2} (e^{-2} - 1) = 0.432. \end{aligned} \quad (22)$$

Compute the value of the probability of localising the particle between $1/\alpha < x < 2/\alpha$ as an exercise.

4.3 Properties of valid wave functions

In order that the wave function corresponds to physical (i.e. real) situations, it must satisfy a number of extra conditions in addition to the Schrödinger equation - these are sometimes referred to as **boundary conditions**:

1. In order to avoid infinite probabilities, Ψ must be finite everywhere.
2. In order to avoid multiple probability values, Ψ must take a single value at each position and time.
3. For finite potentials, $\partial\Psi/\partial x$ must also be continuous (things are different when V is infinite).
4. In order to normalise the wave function one must have $\lim_{x \rightarrow \pm\infty} \Psi \rightarrow 0$.

4.3.1 The free wave function

The wave function $\Psi(x, t) = Ae^{i(kx - \omega t)}$ represents a valid solution to the Schrödinger equation. The wave function is referred to as the free wave function as it represents a particle experiencing zero net force (constant V). However, the free wave function cannot be normalised as it is a continuous (not localised) wave, i.e.

$$\begin{aligned} \int_{-\infty}^{\infty} \Psi^*(x, t) \Psi(x, t) dx &= \int_{-\infty}^{\infty} A^2 dx \\ &= \infty. \end{aligned} \quad (23)$$

One can understand this result via the uncertainty principle: the free wave function possesses a definite value k and ω ($\Delta k = \Delta \omega = 0$). Therefore we must have $\Delta x = \Delta t = \infty$. Despite this condition, the free wave function remains a useful basic solution to the Schrödinger equation as all valid wave functions can be constructed from a sum or integral of free wave functions, for example

$$\Psi_{TOT} = \int_{-\infty}^{\infty} e^{-x^2/2\sigma} e^{i(kx - \omega t)} dx, \quad (24)$$

represents a Gaussian wave packet.

4.4 The time independent Schrödinger equation

We have so far considered the time dependent Schrödinger equation. However, in the case where the potential term is constant, i.e. $V(x, t) = V(x)$, the Schrödinger equation can be separated into position and time dependent components

$$\Psi(x, t) = \psi(x)f(t). \quad (25)$$

Inserting this wave function into the time dependent Schrödinger equation, we obtain

$$i\hbar\psi(x)\frac{\partial f(t)}{\partial t} = -\frac{\hbar^2 f(t)}{2m}\frac{\partial^2 \psi(x)}{\partial x^2} + V(x)\psi(x)f(t). \quad (26)$$

Dividing by $\psi(x)f(t)$ yields

$$i\hbar\frac{1}{f(t)}\frac{df(t)}{dt} = -\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2} + V(x). \quad (27)$$

The lhs of this equation is a function of time only, the rhs is a function of position only; therefore each must be equal to a constant value, named B . To determine the value of B , we consider the

lhs only

$$\begin{aligned}
 i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} &= B \\
 i\hbar \int \frac{df}{f} &= \int B dt \\
 i\hbar \ln f &= Bt + C,
 \end{aligned} \tag{28}$$

where C is an integration constant which can be set to zero by specifying $f(t=0) = 0$. Therefore

$$\begin{aligned}
 \ln f &= \frac{Bt}{i\hbar} \\
 f(t) &= e^{Bt/i\hbar} = e^{-iEt/\hbar}.
 \end{aligned} \tag{29}$$

If we compare this result to the free particle wave function we note that $f(t) = e^{-i\omega t}$ and that $B = \hbar\omega = E$, the total energy. Note that this can also be seen from a dimensional analysis of the term $f(t) = e^{-iEt/\hbar}$; t has units of seconds and \hbar has units of energy times time – therefore B must have units of energy. This is a general result. We may now write

$$i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} = E, \tag{30}$$

and we can now form the **time independent Schrödinger equation** as

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x). \tag{31}$$

Returning to the general form of the wave function we may write

$$\Psi(x, t) = \psi(x)e^{-i\omega t} \tag{32}$$

The probability density of this wave function is

$$\begin{aligned}
 \Psi^*\Psi &= \psi^2(x)(e^{i\omega t}e^{-i\omega t}) \\
 &= \psi^2(x).
 \end{aligned} \tag{33}$$

The probability distribution is constant in time. In classical physics this phenomena is referred to as a *standing wave*. In quantum mechanics, we refer to this as a **stationary state**. Therefore we can use the time independent Schrödinger equation to study stationary or stable states in quantum systems.

4.5 Expectation values

If the wave function represents localised particles, we require a method for computing the predicted values of observable quantities (e.g. position, momentum, total energy) from the wave function.

The determination of observable quantities from the wave function is based upon **expectation values**. The idea of an expectation value is based upon the statistical interpretation of the wave function. If we make many measurements of a particle described by a given wave function, the average of many measurements will converge upon the expectation value.

Any observable quantity for which we can compute an expectation value from the wave function is referred to as a **physical observable**. Physical observables must be represented by real – not imaginary – numbers.

Imagine that we observe the position of a particle constrained to move along the x -axis. We observe the particle at x_1 , N_1 times, at x_2 , N_2 times, and so on. The average position of the particle is

$$\bar{x} = \frac{x_1 N_1 + x_2 N_2 + x_3 N_3 + x_4 N_4 + \dots}{N_1 + N_2 + N_3 + N_4 + \dots} = \frac{\sum_i x_i N_i}{\sum_i N_i}. \quad (34)$$

If $P(x)$ describes the probability of observing the particle at some x (distributed continuously) we may re-write the above equation in integral form

$$\bar{x} = \frac{\int_{-\infty}^{\infty} x P(x) dx}{\int_{-\infty}^{\infty} P(x) dx}. \quad (35)$$

Within our quantum mechanical formalism $P(x) = \Psi^*(x, t)\Psi(x, t)$ and the expectation value of x is now

$$\begin{aligned} \langle x \rangle &= \frac{\int_{-\infty}^{\infty} \Psi^*(x, t) x \Psi(x, t) dx}{\int_{-\infty}^{\infty} \Psi^*(x, t) \Psi(x, t) dx} \\ &= \int_{-\infty}^{\infty} \Psi^*(x, t) x \Psi(x, t) dx, \end{aligned} \quad (36)$$

for a normalised wave function. the expectation value of a general function $g(x)$ for a normalised wave function is

$$\langle g(x) \rangle = \int_{-\infty}^{\infty} \Psi^*(x, t) g(x) \Psi(x, t) dx. \quad (37)$$

The expectation value of a stationary state may be written as

$$\begin{aligned} \langle x \rangle &= \int_{-\infty}^{\infty} \psi^*(x) e^{i\omega t} x \psi(x) e^{-i\omega t} dx \\ &= \int_{-\infty}^{\infty} \psi^*(x) x \psi(x) dx. \end{aligned} \quad (38)$$

When we state that the wave function provides a complete description of a physical system, we mean that the expectation value of physical observables (real quantities) can be computed using the wave function. The wave function cannot provide the value of individual measurements.

4.5.1 The momentum operator

How do we compute the expectation value of the momentum? Any knowledge of the momentum must also be consistent with the uncertainty principle. Consider the free particle wave function, $\Psi(x, t) = e^{i(kx - \omega t)}$. Taking the derivative w.r.t. x , we have

$$\frac{\partial \Psi}{\partial x} = \frac{\partial}{\partial x} [e^{i(kx - \omega t)}] = ik e^{i(kx - \omega t)} = ik \Psi. \quad (39)$$

The wave number $k = p/\hbar$, such that

$$\frac{\partial \Psi}{\partial x} = i \frac{p}{\hbar} \Psi, \quad (40)$$

and rearranging the equation yields

$$p[\Psi(x, t)] = -i\hbar \frac{\partial}{\partial x} [\Psi(x, t)]. \quad (41)$$

We therefore define the **momentum operator** as

$$\hat{p} = -i\hbar \frac{\partial}{\partial x}. \quad (42)$$

In mathematical language, an **operator** transforms one function into another, e.g. the operator \hat{A} operates on $f(x)$ such that $\hat{A}f(x) = g(x)$. Every physical observable has an associated operator that is used to determine the expectation value of the observable. The general formalism is

$$\langle A \rangle = \int_{-\infty}^{\infty} \Psi^*(x, t) \hat{A} \Psi(x, t) dx. \quad (43)$$

The expectation value of the momentum is therefore

$$\langle p \rangle = -i\hbar \int_{-\infty}^{\infty} \Psi^*(x, t) \frac{\partial \Psi(x, t)}{\partial x} dx. \quad (44)$$

As we have seen earlier, position x is its own operator.

4.5.2 The energy operator

We next consider the total energy of the wave function. Take the time derivative of the free particle wave function

$$\frac{\partial \Psi}{\partial t} = \frac{\partial}{\partial t} e^{i(kx - \omega t)} = -i\omega e^{i(kx - \omega t)} = -i\omega \Psi. \quad (45)$$

Substituting $\omega = E/\hbar$ we have

$$E[\Psi(x, t)] = i\hbar \frac{\partial}{\partial t} [\Psi(x, t)], \quad (46)$$

and we define the energy operator as

$$\hat{E} = i\hbar \frac{\partial}{\partial t}. \quad (47)$$

The expectation value of the energy is then

$$\langle E \rangle = i\hbar \int_{-\infty}^{\infty} \Psi^*(x, t) \frac{\partial \Psi(x, t)}{\partial t} dx. \quad (48)$$

Though the above results have been generated using the free particle wave function, they are valid in general as well.

T–Rex example 6.6: Use energy conservation to generate the Schrödinger equation

The total energy of a particle may be written as

$$E = K + V = \frac{p^2}{2m} + V. \quad (49)$$

We now permit the operators associated with each observable to act upon the wave function. Considering the lhs of the above equation

$$\hat{E} \Psi = i\hbar \frac{\partial \Psi}{\partial t}. \quad (50)$$

The rhs of the equation becomes

$$\begin{aligned} \left[\frac{1}{2m} (\hat{p})^2 + V \right] \Psi &= \frac{1}{2m} \left(-i\hbar \frac{\partial}{\partial x} \right)^2 \Psi + V \Psi \\ &= -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V \Psi. \end{aligned} \quad (51)$$

Equating the lhs with the rhs of the original energy conservation equation we obtain the time dependent Schrödinger equation.

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V \Psi. \quad (52)$$

It is important to note that this is not a derivation of the Schrödinger equation. Instead it shows the consistency of the energy and momentum terms just defined.

4.6 The infinite square well potential

We now wish to solve the time independent Schrödinger equation for several simple potentials. In doing so we will investigate the behaviour of the quantum wave function and the expected value of

physical observables. The infinite square well potential is essentially a particle in a box. However, on this occasion our analysis will be more rigorous.

The *infinite square well* describes the potential term

$$\begin{aligned} V(x) &= \infty & x \leq 0, x \geq L \\ &= 0 & 0 < x < L, \end{aligned} \quad (53)$$

and the particle is restricted to the interval $0 < x < L$. This can be seen clearly by considering the time independent Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x). \quad (54)$$

When $V(x) = \infty$ we must have $\psi(x) = 0$ (to avoid an infinity in the equation) and therefore $\psi^*\psi = 0$ with the consequence that the particle cannot exist in this region. When $V(x) = 0$, $\psi(x)$ now represents the free particle wave function and we re-write the time independent Schrödinger equation as

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) &= E\psi(x) \\ \frac{d^2\psi(x)}{dx^2} &= -\frac{2mE}{\hbar^2} \psi(x). \end{aligned} \quad (55)$$

We note that $p = \hbar k$ and $E = p^2/2m$. Therefore, $p^2 = 2mE$ and $k^2 = (2mE)/\hbar^2$ and we may re-write the above equation as

$$\frac{d^2\psi(x)}{dx^2} = -k^2\psi(x). \quad (56)$$

A general solution to this equations takes the form

$$\psi(x) = A \sin kx + B \cos kx. \quad (57)$$

However, does such a solution match the boundary conditions for an acceptable wave function? As the potential term is discontinuous in x , $d\psi(x)/dx$ need not be a continuous function. However, $\psi(x)$ must be a continuous function, i.e. $\psi(x=0) = 0$ and $\psi(x=L) = 0$. Taking the first condition we see that

$$\psi(x=0) = A \sin(0) + B \cos(0) = 0 \Rightarrow B = 0. \quad (58)$$

At $x = L$ we have

$$\psi(x=L) = A \sin(kL) = 0 \Rightarrow kL = n\pi. \quad (59)$$

The wave function is therefore

$$\psi(x) = A \sin\left(\frac{n\pi x}{L}\right) \quad \text{for } n = 1, 2, 3, \dots \text{ and } 0 < x < L. \quad (60)$$

The important point to note here is that the range of permitted wavefunctions is quantised. We next have to normalise the wave function over all space, i.e.

$$\begin{aligned} \int_{-\infty}^{\infty} \psi^* \psi dx &= 1 \\ \int_{-\infty}^0 \psi^* \psi dx + \int_0^L \psi^* \psi dx + \int_L^{\infty} \psi^* \psi dx &= 1 \\ 0 + \int_0^L A^2 \sin^2\left(\frac{n\pi x}{L}\right) dx + 0 &= 1 \end{aligned} \quad (61)$$

We solve this integral by applying the change of variable $u = n\pi x/L$ and writing

$$\int_0^L A^2 \sin^2\left(\frac{n\pi x}{L}\right) dx = \int_0^{n\pi} A^2 \sin^2 u \frac{dx}{du} du. \quad (62)$$

The integral in Equation 61 then reduces to

$$\begin{aligned} A^2 \frac{L}{n\pi} \left[-\frac{1}{2} \cos u \sin u + \frac{u}{2} \right]_0^{n\pi} &= 1 \\ A^2 \frac{L}{n\pi} \left[-\frac{1}{2} \cos(n\pi) \sin(n\pi) + \frac{n\pi}{2} \right] &= 1 \\ A &= \sqrt{\frac{2}{L}}. \end{aligned} \quad (63)$$

Hence the normalised wave function may be written

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad \text{for } n = 1, 2, 3, \dots \text{ and } 0 < x < L. \quad (64)$$

The wave function is exactly the same as a classical time independent standing wave and the particle in a box therefore corresponds to a stationary state.

T–Rex Example 6.7: Show that the wave function $\Psi_n(x, t)$ for a particle in an infinite square well corresponds to a standing wave in a box.

To generate the time dependent wave function we form the quantity

$$\begin{aligned} \Psi_n(x, t) &= \psi(x) e^{i\omega_n t} \\ &= \sqrt{\frac{2}{L}} \sin(k_n x) e^{i\omega_n t}. \end{aligned} \quad (65)$$

However, $\sin(k_n x)$ can be written as

$$\sin(k_n x) = \frac{e^{ik_n x} - e^{-ik_n x}}{2i}, \quad (66)$$

so that the wave function becomes

$$\Psi_n(x, t) = \sqrt{\frac{2}{L}} \left(\frac{e^{i(k_n x - \omega_n t)} - e^{-i(k_n x + \omega_n t)}}{2i} \right). \quad (67)$$

This is simply the superposition of two waves, one travelling in the positive x -direction and one travelling in the negative direction. A standing wave will result with an angular frequency ω_n .

End of Example 6.7

The energy associated with each stationary state comes from a consideration of the wave number

$$k_n = \frac{n\pi}{L} = \sqrt{\frac{2mE_n}{\hbar^2}} \quad n = 1, 2, 3, \dots, \quad (68)$$

where the subscript n indicates that k_n and E_n depend upon the value of n – **the principal quantum number**. We may write the energy of each quantum state as

$$E_n = n^2 \frac{\pi^2 \hbar^2}{2mL^2} = n^2 \frac{\pi^2 (\hbar c)^2}{2(mc^2)L^2} = \frac{(\text{eV nm})^2}{\text{eV nm}^2} = \text{eV}. \quad (69)$$

Once again, we note that the possible energy values of the particle are quantised. In this case, energy quantisation arises solely from the boundary conditions. Each state available to the wave function $\psi_n(x)$, is characterised by a unique energy state E_n , and probability density $|\psi_n|^2$ (see T-Rex Figure 6.3). A number of additional points should be emphasized

- The particle cannot have $E = 0$ (or at least only in the case where the particle does not exist but this is not an interesting possibility). The lowest available energy state is E_1 corresponding to $n = 1$. This is referred to as the **ground state**. Though this effect is only noticeable for quantum situations, the same rules holds in the macroscopic world. A tennis ball constrained to lie within a court cannot have $E = 0$. However, in this case, E_1 is so small as to be unmeasurable in most practical circumstances. Once again, this view agrees with the principle that macroscopic objects possess very large quantum numbers.
- In general we see that the energy of the confined particle is inversely proportional to both the mass m and the square of the confinement scale L . Therefore, confining a given particle to a smaller region imposes a greater minimum energy. Taking the case of an electron we can write

$$E_1 = \frac{\pi^2 (\hbar c)^2}{2(mc^2)L^2} = \frac{(\pi^2)(197.3 \text{ eV nm})^2}{(2)(511,000 \text{ eV})(L^2)} \approx \frac{0.4}{(L/\text{nm})^2} \text{ eV}. \quad (70)$$

Therefore, if we confine an electron in a one dimensional box of length 0.1 nm we obtain a ground state energy $E_1 \approx 40 \text{ eV}$, a reasonable approximation to atomic electron energies.

- The probability density $P(x)$ to observe the particle at a given x is

$$P(x) = \psi^* \psi = \frac{2}{L} \sin^2 \left(\frac{n\pi x}{L} \right). \quad (71)$$

In the classical limit this probability is $P(x) = 1/L$ for $0 < x < L$. For large values of n there will be many wave oscillations within the box. As the average value of $\sin^2 \theta$ over one cycle is $1/2$. Therefore, in the limit of large quantum numbers we obtain the classical result.

T–Rex Example 6.8: Calculate the expected values of x , x^2 , p and p^2 for a particle in an infinite square well existing in the first excited state.

The first excited state corresponds to $n = 2$. The wave function for this case is

$$\psi_2(x) = \sqrt{\frac{2}{L}} \sin \left(\frac{2\pi x}{L} \right) \quad (72)$$

1. The expectation value of $\langle x \rangle_2$ is

$$\langle x \rangle_2 = \frac{2}{L} \int_0^L x \sin^2 \left(\frac{2\pi x}{L} \right) dx. \quad (73)$$

Once again, we solve this using a change of variable $u = 2\pi x/L$ and noting that $dx/du = L/2\pi$. The integral then becomes

$$\begin{aligned} \langle x \rangle_2 &= \frac{2}{L} \left(\frac{L}{2\pi} \right)^2 \int_0^{2\pi} u \sin^2 u \, du \\ &= \frac{2}{L} \left(\frac{L}{2\pi} \right)^2 \left[\frac{u^2}{4} - u \frac{\sin 2u}{4} - \frac{\cos 2u}{8} \right]_0^{2\pi} \\ &= \frac{2}{L} \left(\frac{L}{2\pi} \right)^2 \left[\pi^2 - \frac{1}{8} + \frac{1}{8} \right] \\ &= \frac{L}{2}. \end{aligned} \quad (74)$$

Note that the expected position of the particle is in the middle of the box although the value of the wave function is zero at this point.

2. The expectation value of $\langle x^2 \rangle_2$ is

$$\begin{aligned} \langle x^2 \rangle_2 &= \frac{2}{L} \int_0^L x^2 \sin^2 \left(\frac{2\pi x}{L} \right) dx \\ &= \left(\frac{1}{3} - \frac{1}{8\pi^2} \right) L^2 = 0.32L^2, \end{aligned} \quad (75)$$

Note that the integral is solved with a change of variable to convert the integrand to a standard form and is then worked in a straightforward (if lengthy) manner.

3. The expectation of the momentum $\langle p \rangle_2$ is given by

$$\begin{aligned}\langle p \rangle_2 &= (-i\hbar) \frac{2}{L} \int_0^L \sin\left(\frac{2\pi x}{L}\right) \left[\frac{d}{dx} \sin\left(\frac{2\pi x}{L}\right) \right] dx \\ &= -\frac{4\pi i\hbar}{L} \int_0^L \sin\left(\frac{2\pi x}{L}\right) \cos\left(\frac{2\pi x}{L}\right) dx \\ &= 0.\end{aligned}\tag{76}$$

The average, or expected value of the momentum is zero – as the particle is moving left as often as it is moving right.

4. However, the expectation value of $\langle p^2 \rangle_2$ behaves in a different manner and is given by

$$\begin{aligned}\langle p^2 \rangle_2 &= \frac{2}{L} \int_0^L \sin\left(\frac{2\pi x}{L}\right) \left(-i\hbar \frac{d}{dx}\right) \left(-i\hbar \frac{d}{dx}\right) \sin\left(\frac{2\pi x}{L}\right) dx \\ &= (-i\hbar)^2 \frac{2}{L} \int_0^L \sin\left(\frac{2\pi x}{L}\right) \left(\frac{2\pi}{L} \frac{d}{dx}\right) \cos\left(\frac{2\pi x}{L}\right) dx \\ &= -(\hbar^2) \frac{8\pi^2}{L^3} \int_0^L \sin\left(\frac{2\pi x}{L}\right) \sin\left(\frac{2\pi x}{L}\right) dx \\ &= \frac{4\pi^2 \hbar^2}{L^2}.\end{aligned}\tag{77}$$

This value can be compared to the value of E_2 , i.e.

$$E_2 = \frac{4\pi^2 \hbar^2}{2mL^2} = \frac{\langle p^2 \rangle_2}{2m},\tag{78}$$

which is simply the statement $E = p^2/2m + V$, for which in this case we have $V = 0$.

Finally, what happens if we consider the uncertainty relation for this wave function? We can form the uncertainty relation by noting that $\Delta x = (\langle x^2 \rangle - \langle x \rangle^2)^{1/2}$ and $\Delta p = (\langle p^2 \rangle - \langle p \rangle^2)^{1/2}$. In this case, we find that

$$\Delta p \Delta x = \frac{2\pi\hbar}{L} \left(\frac{L^2}{3} - \frac{L^2}{4} \right)^{1/2} = \frac{2\pi\hbar}{L} \frac{L}{2\sqrt{3}} = \hbar \frac{\pi}{\sqrt{3}} > \frac{\hbar}{2}.\tag{79}$$

4.7 The finite square well potential

The infinite square well provides a useful first example of how to manipulate the time independent Schrödinger equation. However, infinite potentials are not very realistic. A more reasonable example of the potentials encountered in nature is the finite square well potential where we observe the following

$$\begin{aligned} &= V_0 & x \leq 0 & \text{region I} \\ V(x) &= 0 & 0 < x < L & \text{region II} \\ &= V_0 & x \geq L & \text{region III} \end{aligned}$$

We consider a particle of energy $E < V_0$. In classical physics the particle is completely bound within the potential. However, within quantum theory we will see that there exists a possibility that the particle can exist outside the potential well.

We begin by considering the time independent Schrödinger equation for regions I and III outside the square well

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = (E - V_0)\psi. \quad (80)$$

We can re-write this equation using $\alpha^2 = 2m(V_0 - E)/\hbar^2$, as positive constant, as

$$\frac{d^2\psi}{dx^2} = \alpha^2\psi. \quad (81)$$

Solutions to this equation take the form $e^{\alpha x}$ and $e^{-\alpha x}$, i.e. exponential terms rather than sinusoidal. We can use the boundary condition $\psi(x) \rightarrow 0$ as $x \rightarrow \pm\infty$ to select physically reasonable wave functions. In the region $x > L$ we can reject the positive exponential term as otherwise we would have $\psi(x) \rightarrow \infty$ as $x \rightarrow \pm\infty$. Similarly we can reject the negative exponential term at $x < 0$. Therefore we can write

$$\begin{aligned} \psi_I(x) &= Ae^{\alpha x} & x < 0 \\ \psi_{III}(x) &= Be^{-\alpha x} & x > L. \end{aligned}$$

The constants A and B represent probability amplitudes that we must solve for using the boundary conditions.

Within the potential well, in region II, the time independent Schrödinger equation takes the form

$$\frac{d^2\psi}{dx^2} = -k^2\psi, \quad (82)$$

where $k = \sqrt{(2mE)/\hbar^2}$. The general sinusoidal wave function that satisfies this equation can be written as

$$\psi_{II}(x) = Ce^{ikx} + De^{-ikx} \quad 0 < x < L. \quad (83)$$

Note that when we looked at the infinite square well, we were able to use the boundary conditions to simplify this oscillatory solution to a sine term. However, with the finite square well, we no longer have $\psi(x) = 0$ for $x = 0$ or $x = L$.

We now use the boundary conditions to solve for the probability amplitudes A, B, C and D . We will not solve for them in detail but rather illustrate the overall method. We require the wave function $\psi(x)$ and its derivative $d\psi/dx$ be continuous functions of x . There are two “boundaries” in the finite square well (between regions I and II and between II and III). Therefore we can generate a total of four equations to solve for four unknown probability amplitudes. We examine each condition in turn

- $\psi(x)$ must be continuous. Therefore

$$\begin{aligned}\psi_I(x=0) &= \psi_{II}(x=0) \\ A &= C + D,\end{aligned}\tag{84}$$

and

$$\begin{aligned}\psi_{II}(x=L) &= \psi_{III}(x=L) \\ Ce^{ikL} + De^{-ikL} &= Be^{-\alpha L}.\end{aligned}\tag{85}$$

- $\psi'(x) = d\psi/dx$ must be continuous. Therefore

$$\begin{aligned}\psi'_I(x=0) &= \psi'_{II}(x=0) \\ \alpha Ae^{\alpha x}|_{x=0} &= ikC^{ikx}|_{x=0} - ikDe^{-ikx}|_{x=0} \\ \alpha A &= ikC - ikD,\end{aligned}\tag{86}$$

and

$$\begin{aligned}\psi'_{II}(x=L) &= \psi'_{III}(x=L) \\ ikC^{ikL} - ikDe^{-ikL} &= \alpha Be^{-\alpha L}.\end{aligned}\tag{87}$$

We will not work further through the maths here. Instead, we emphasize a number of qualitative points.

- The form of the total wave function (I+II+III) for the finite square well is shown in T-Rex Figure 6.5. The most important result is that where there exists a finite potential, there exists a finite possibility to observe the particle outside the well. The greater the energy of the particle, the greater the probability of existing outside the potential well (see below). This is in contrast to the results derived for the infinite square well and for any classical analysis of a particle trapped in a box.
- Once again we note that the energy levels are quantized and that $E = 0$ is not permitted.
- If we compare wave solutions for the finite and infinite square wells, we see that the De Broglie wavelength of a given solution ($n = 1, 2, 3, \dots$) is longer in the finite well compared to the infinite well. This in turn implies that the momenta and energy of each state are smaller for the finite potential. In addition, the number of energy levels is curtailed to $E < V_0$.
- The finite probability for the particle to exist outside the well is linked to the idea of **quantum tunneling** (more later). The extent to which the particle will be observed outside the well is given by the probability $P(x)dx = \psi^*(x)\psi(x)dx$. In regions III we can write

$$\psi^2(x) = B^2 e^{-2\alpha x} \propto e^{-2\alpha} = e^{-2\sqrt{2m(V_0-E)\hbar^2}}. \quad (88)$$

With a similar expression for region I. We see that the probability to observe the particle outside the well is smaller for larger potentials and also that the probability is larger for higher energy states. The interval of distance δx over which the probability drops by a factor e is equal to $1/2\alpha$, i.e.

$$\delta x = \frac{1}{2\alpha} = \frac{\hbar}{2\sqrt{2m(V_0 - E)}}. \quad (89)$$

We call δx the penetration depth. In general, the presence of \hbar in the numerator ensures that δx corresponds to a very small distance.

Worked problem: consider a particle with an energy E bound within a finite square well of height V_0 and width $2L$ such that $-L \leq x \leq +L$. As the potential energy is symmetric about the mid-point of the well, the permitted stationary states will be either symmetric or anti-symmetric about the mid-point.

1. Show that for $E < V_0$ the boundary conditions restrict the permitted energies of symmetric waves to be

$$k \tan kL = \alpha, \quad (90)$$

where $\alpha = \sqrt{(2m/\hbar^2)(V_0 - E)}$, and $k = \sqrt{2mE/\hbar^2}$ is the wave number of the oscillation interior to the well.

Solution: The time independent Schrödinger equation reduces to

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}(V(x) - E)\psi. \quad (91)$$

Within the potential $V(x) = 0$ and we obtain solutions of the form $\sin kx$ and $\cos kx$ where $k^2 = 2mE/\hbar^2$. Waves that are symmetric about the mid-point of the well take the form

$$\psi(x) = A \cos kx, \quad (92)$$

for $-L \leq x \leq +L$. Outside the well, we have $V(x) = V_0$ and solutions to the wave equation take the form $\exp(\pm\alpha x)$. Boundary conditions force us to reject growing exponentials. In addition, the condition that the total wave function be symmetric about the mid-point of the well restricts us to

$$\psi(x) = Ce^{-\alpha|x|}, \quad (93)$$

where $\alpha = 2m(V_0 - E)/\hbar^2$ and for $x < -L$ and $x > L$. We next apply the boundary conditions at $x = L$. Continuity of ψ provides

$$A \cos kL = Ce^{-\alpha L}. \quad (94)$$

Continuity of $d\psi/dx$ provides

$$-Ak \sin kL = -C\alpha e^{-\alpha L}. \quad (95)$$

Dividing these two expressions leads to the desired expression for the permitted energies

$$k \tan kL = \alpha. \quad (96)$$

2. Show that the energy condition above can be written as

$$k \sec kL = \frac{\sqrt{2mV_0}}{\hbar}. \quad (97)$$

Solution: Inspection of k and α indicates that

$$k^2 + \alpha^2 = \frac{2mV_0}{\hbar^2} \quad (98)$$

We can therefore re-write the answer to part (1) as

$$k \tan kL = \sqrt{\frac{2mV_0}{\hbar^2} - k^2}. \quad (99)$$

We multiply this expression by L and square both sides. We note that $\tan^2 \theta + 1 = \sec^2 \theta$ and take the square root of the resulting expression to obtain

$$k \sec kL = \frac{\sqrt{2mV_0}}{\hbar}, \quad (100)$$

as required.

3. Apply this result to compute the ground state energy of an electron trapped with a defect in a crystal that displays an effective potential of 5eV and a width of 0.2nm.

Solution: Multiplying each side of the answer to part (2) by L generates

$$kL \sec kL = \frac{\sqrt{2mV_0L}}{\hbar}. \quad (101)$$

We calculate the quantity

$$\frac{2mV_0L}{\hbar^2} = \frac{2mc^2V_0L}{\hbar^2c^2} = (2)(511 \text{ keV})(5 \text{ eV})(0.1 \text{ nm})/(197.3 \text{ eV nm})^2 = 1.3127, \quad (102)$$

and note that we now have an equation of the form

$$kL \sec kL = \sqrt{1.3127} = 1.1457. \quad (103)$$

Expressions of this form can be solved numerically. A simple trial and error approach yields $kL = 0.799$ from which we deduce that $k = 7.99 \text{ nm}^{-1}$. The energy of a non-relativistic electron possessing this wave number is

$$E = \frac{\hbar^2k^2}{2m} = \frac{(\hbar c)^2k^2}{2mc^2} = \frac{(197 \text{ eV nm})^2(7.99 \text{ nm}^{-1})^2}{(2)(511 \text{ keV})} = 2.432 \text{ eV}. \quad (104)$$

4.8 The three dimensional infinite square well

We are steadily improving our understanding of the Schrödinger equation to the point where we can tackle realistic atomic physics problems. The next stage is to understand the application of the Schrödinger equation in three dimensions. We return to the three dimensional infinite square well as a simple case.

Assuming that there will exist stationary states in three dimensions, we consider the time independent Schrödinger equation. However, the spatial component of the wave function is a function of three spatial coordinates, i.e. $\psi = \psi(x, y, z)$. Applying the conservation of energy to the time independent Schrödinger equation and using our knowledge of operators, we can arrive at an expression of for the Schrödinger equation in three dimensions. Starting with the conservation of energy we write

$$E = K + V = \frac{p^2}{2m} + V. \quad (105)$$

Multiplying by the wave function ψ we obtain

$$E\psi = \frac{p^2}{2m}\psi + V\psi. \quad (106)$$

To write p^2 as an operator, we note that $p^2 = p_x^2 + p_y^2 + p_z^2$ and therefore apply the momentum operator in three dimensions. i.e.

$$\begin{aligned}\hat{p}_x &= -i\hbar \frac{\partial \psi}{\partial x} \\ \hat{p}_x^2 &= -\hbar^2 \frac{\partial^2 \psi}{\partial x^2},\end{aligned}\tag{107}$$

with similar expressions for y and z . Therefore,

$$\hat{p}^2 \psi = -\hbar^2 \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi = -\hbar^2 \nabla^2 \psi,\tag{108}$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2},\tag{109}$$

is the Laplacian operator. Therefore, we may re-write our conservation of energy equation as

$$E\psi = -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi,\tag{110}$$

which corresponds to the time independent Schrödinger equation in three dimensions.

Turning to the three dimensional infinite square well, we consider a box of sides equal to L_1, L_2, L_3 . The sides of the box are infinitely rigid such that $V = 0$ inside the box and $V = \infty$ outside. The additional point that guides us to a valid wave function is the fact that the box is free to move in any dimension within the box – the x, y, z components of the wave function must be independent of each other. Within the box the Schrödinger equation takes the form

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E\psi,\tag{111}$$

and we guess a solution of the form

$$\psi(x, y, z) = A \sin(k_1 x) \sin(k_2 y) \sin(k_3 z),\tag{112}$$

where A is a normalisation constant and the wave numbers k_1, k_2, k_3 are determined by applying the boundary conditions of the infinite well. In each dimension we have can apply the boundary condition of the form $\psi(x) = 0$ for $x = 0$ and $x = L_1$ such that

$$k_1 L_1 = n_1 \pi \Rightarrow k_1 = \frac{n_1 \pi}{L_1},\tag{113}$$

with similar expressions in the y and z dimensions. We calculate the permitted energy levels directly from the Schrödinger equation. To do this we must first compute the spatial derivatives of the wave function (we show this explicitly for x only), i.e.

$$\begin{aligned}
 \frac{\partial\psi}{\partial x} &= \frac{\partial}{\partial x}[A \sin(k_1x) \sin(k_2y) \sin(k_3z)] \\
 &= k_1 A \cos(k_1x) \sin(k_2y) \sin(k_3z) \\
 \frac{\partial^2\psi}{\partial x^2} &= \frac{\partial}{\partial x}[k_1 A \cos(k_1x) \sin(k_2y) \sin(k_3z)] \\
 &= -k_1^2 A \sin(k_1x) \sin(k_2y) \sin(k_3z) \\
 &= -k_1^2 \psi.
 \end{aligned} \tag{114}$$

As the derivatives for y and z are similar, the Schrödinger equation within the box becomes

$$\frac{\hbar^2}{2m}(k_1^2 + k_2^2 + k_3^2)\psi = E\psi, \tag{115}$$

which indicates that

$$E = \frac{\hbar^2}{2m}(k_1^2 + k_2^2 + k_3^2). \tag{116}$$

Inserting the values of k_1, k_2, k_3 derived from the boundary conditions, we obtain the following expression for the permitted energy levels

$$E_{n_1n_2n_3} = \frac{\pi^2\hbar^2}{2m} \left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2} \right). \tag{117}$$

Unsurprisingly, we now require three quantum numbers to describe the possible energy states of a three dimensional system.

In the case where we have a cubic well, i.e. $L = L_1 = L_2 = L_3$, the energy states can be written as

$$E_{n_1n_2n_3} = \frac{\pi^2\hbar^2}{2mL^2}(n_1^2 + n_2^2 + n_3^2). \tag{118}$$

The ground state energy occurs when $n_1 = n_2 = n_3 = 1$,

$$E_{gs} = \frac{3\pi^2\hbar^2}{2mL^2}. \tag{119}$$

There is only one combination of n_1, n_2, n_3 that generates the ground state. What about the first excited state? The first excited state can be achieved with the following configurations

$$\begin{array}{ccc} n_1 & n_2 & n_3 \\ 1 & 1 & 2 \\ 1 & 2 & 1 \\ 2 & 1 & 1 \end{array} \tag{120}$$

Therefore, three different quantum states generate the same energy level – they are said to be **degenerate states**. In this case the three dimensional symmetry of the potential box creates the degeneracy. The degeneracy can be broken if the symmetry of the system is broken. Symmetry can be broken in a number of ways: if the lengths of the side of the potential are unequal then the degenerate energy states will take different values. Symmetry can also be broken by external factors – an electric or a magnetic field say. As the electric /magnetic field is a vector, it introduces a preferred axis into the system such that wave terms aligned with the field will respond differently to wave terms aligned perpendicular. This is exactly what happens to the energy levels of an atom when subjected to an electric (Stark effect) or magnetic (Zeeman effect) field – the addition of a vector force/potential breaks the degeneracy between the energy states.

Worked problem: Consider an electron trapped in a crystal defect modelled as a three dimensional infinite square well of length $L = L_1 = L_2 = L_3 = 0.5 \text{ nm}$.

1. Compute the probability of observing the ground state electron within $\bar{x} \pm L/4$, $\bar{y} \pm L/4$, $\bar{z} \pm L/4$.

Solution: To compute any probability based upon the wave function, we must first determine the value of the normalisation constant, i.e.

$$\int_0^L \int_0^L \int_0^L \psi^*(x, y, z) \psi(x, y, z) dx dy dz = 1. \quad (121)$$

As the wave function involves no cross terms of the form $\sin(xy)$ etc., we can separate the three dimensional wave function into three one dimensional functions, i.e. $\psi(x, y, z) = f(x)g(y)h(z)$. This permits us to write the above normalisation expression into a more convenient form

$$A^2 \left[\int_0^L \sin^2 k_1 x dx \right] \left[\int_0^L \sin^2 k_2 y dy \right] \left[\int_0^L \sin^2 k_3 z dz \right] = 1. \quad (122)$$

This equation is very similar to the case where we normalised the wave function for a one dimensional infinite square well. In this case, each integral contained within the square brackets contributes $(L/2)$ such that

$$A^2 \left(\frac{L}{2} \right) \left(\frac{L}{2} \right) \left(\frac{L}{2} \right) = 1 \quad (123)$$

and

$$A = \left(\frac{2}{L} \right)^{3/2}, \quad (124)$$

which is simply the cube of the normalisation constant determined for the one dimensional case. The average position of the particle in each dimension is simply $L/2$, once again, the same result as for the one dimensional case. To compute the probability of observing the electron within $\bar{x} \pm L/4$, $\bar{y} \pm L/4$, $\bar{z} \pm L/4$, we therefore form the quantity

$$\begin{aligned} P(\bar{x} \pm L/4, \bar{y} \pm L/4, \bar{z} \pm L/4) &= \int_{L/4}^{3L/4} \int_{L/4}^{3L/4} \int_{L/4}^{3L/4} \psi^*(x, y, z) \psi(x, y, z) dx dy dz \\ &= \left(\frac{2}{L} \right)^3 \left[\int_{L/4}^{3L/4} \sin^2 k_1 x dx \right] [\text{plus similar terms for } y \text{ and } z]. \end{aligned}$$

We note that for the ground state electron $k_1 = \pi/L$ and we concentrate upon the form of the x integral, i.e.

$$\int_{L/4}^{3L/4} \sin^2 k_1 x dx = \frac{L}{\pi} \left[\frac{x}{2} - \frac{1}{4} \sin 2x \right]_{L/4}^{3L/4}$$

$$\begin{aligned}
&= \frac{L}{\pi} \left(\left[\frac{3\pi}{8} - \frac{1}{4} \sin \left(\frac{3\pi}{2} \right) \right] - \left[\frac{\pi}{8} - \frac{1}{4} \sin \left(\frac{\pi}{2} \right) \right] \right) \\
&= \frac{L}{4}.
\end{aligned} \tag{125}$$

Therefore, the probability integral over each dimension contributes a term $L/4$ and we may re-write the three dimensional probability integral as

$$P(\bar{x} \pm L/4, \bar{y} \pm L/4, \bar{z} \pm L/4) = \left(\frac{2}{L} \right)^3 \left(\frac{L}{4} \right)^3 = \frac{1}{8}. \tag{126}$$

2. Compute the ground state energy of the electron.

Solution: The ground state of a three dimensional well is described by the quantum numbers $n_1 = n_2 = n_3 = 1$. Inserting these values into the expression for the energy levels of a particle in a three dimensional infinite square well, we obtain

$$E_{111} = \frac{3\pi^2\hbar^2}{2mL^2} = \frac{3\pi^2(\hbar c)^2}{2(mc^2)L^2} = \frac{3\pi^2}{2} \frac{(197.3 \text{ eV nm})^2}{(511 \text{ keV})(0.5 \text{ nm})^2} = 4.51 \text{ eV}. \tag{127}$$

3. What wavelength of photon will cause the ground state electron to make a transition to the first excited state?

Solution: The first excited state corresponds to an energy

$$E_{211} = \frac{\pi^2\hbar^2}{2mL^2} [2^2 + 1^2 + 1^2] = 2E_{111}. \tag{128}$$

Note that any one of the three possible first excited states would give the same answer. In order to cause the electron to change from the ground state to the first excited state the photon energy must be

$$E_{\text{photon}} = \frac{hc}{\lambda} = E_{211} - E_{111} = E_{111}, \tag{129}$$

Therefore,

$$\lambda = \frac{hc}{E_{111}} = \frac{1240 \text{ eV nm}}{\times 4.51 \text{ eV}} = 273 \text{ nm}. \tag{130}$$