Chapter 5

Schrödinger equation

Figure 5.1: Erwin Schrödinger

In the autumn of 1925 Erwin Schrödinger was invited by Professor Peter Debye to give a talk at a seminar in Zurich on de Broglie's thesis. During the discussion that followed, Professor Debye commented that the thought this approach to wave-particle duality to be somewhat 'childish'. After all, said Debye, 'to deal properly with waves one had to have a wave equation...'

Perhaps stimulated by this comment, Schrödinger left for holiday in the Swiss Alps just before Christmas 1925, and when he returned on 9 January 1926, he had discovered wave mechanics and the equation that governs the evolution of de Broglie waves.

For non-relativistic quantum physics the basic equation to be solved is the Schrödinger equation. Like Newton's laws, the Schrödinger equation must be written down for a given situation of a quantum particle moving under the influence of some external forces, although it turns out to be easier to frame this in terms of potential energies instead of forces. However, unlike Newton's laws, the Schrödinger equation does not give the trajectory of a particle, but rather the wave function of the quantum system, which carries information about the wave nature of the particle, which allows us to only discuss the probability of finding the particle in different regions of space at a given moment in time. In this chapter, we introduce the Schrödinger equation, obtain solutions in a few situations, and learn how to interpret these solutions.

5.1 Motivation and derivation

It is not possible to derive the Schrödinger equation in any rigorous fashion from classical physics. However, it had to come from somewhere, and it is indeed possible to 'derive' the Schrödinger equation using somewhat less rigorous means. If we first start by considering a particle in one dimension with mass m, momentum p_x moving in a potential $U(x)$ we can express the total energy as

$$E = \frac{p_x^2}{2m} + U(x), \tag{5.1}$$

where we assume non-relativistic energy. (Note: Schrödinger initially used the relativistic form of energy, and arrived at the correct quantum description for relativistic particles of spin zero, but did not realize this at the time and did not publish these results. Later in 1926, Oskar Klein and Walter Gordon published the equation that now bears there name - the Klein-Gordon equation - that was exactly the same as Schrödinger's first equation.) Multiplying both sides of Eq. (5.1) by the wave function $\psi(x,t)$ should not change the equality

$$E\psi(x,t) = \left(\frac{p_x^2}{2m} + U(x)\right)\psi(x,t). \tag{5.2}$$

Now recall the Planck and de Broglie relations between energy and frequency and momentum and wave vector

$$E = h\nu = \hbar\omega, \tag{5.3}$$ $$p_x = h/\lambda = \hbar k_x. \tag{5.4}$$

Suppose the wave function in Eq. (5.2) is a plane wave traveling in the x direction with a well defined energy and momentum, that is,

$$\psi(x,t) = A_0 e^{i(k_x x - \omega t)}, \tag{5.5}$$

where $p_x = \hbar k_x$ and $E = \hbar\omega$. Combining Eqs. (5.2) - (5.5), we have

$$\hbar\omega A_0 e^{i(k_x x - \omega t)} = E A_0 e^{i(k_x x - \omega t)}, \tag{5.6}$$

and

$$\left(\frac{\hbar^2 k_x^2}{2m} + U(x)\right) A_0 e^{i(k_x x - \omega t)} = \left(\frac{p_x^2}{2m} + U(x)\right) A_0 e^{i(k_x x - \omega t)}. \tag{5.7}$$

From Eq. (5.87) we see that for the equality to hold, the product of energy times the wave function $E\psi(x,t)$ must be equal to the first derivative of the wave function with respect to time multiplied by $i\hbar$, that is

$$E\psi(x,t) = i\hbar\frac{\partial}{\partial t}\psi(x,t). \tag{5.8}$$

Similarly, by examining Eq. (5.86), we see that the product of momentum times the wave function $p_x\psi(x,t)$ must be equal to the first derivative of the wave function with respect to position x multiplied by $-i\hbar$, that is

$$p_x\psi(x,t) = -i\hbar\frac{\partial}{\partial x}\psi(x,t). \tag{5.9}$$

Combining Eqs. (5.2), (5.8) and (5.9), we arrive at the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\psi(x,t) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)\right)\psi(x,t). \tag{5.10}$$

Equation (5.10) is known as the **time-dependent Schrödinger equation** or **TDSE** for short. This is a second-order linear differential equation. The term on the left-hand side of Eq. (5.10) represents the total energy of the particle. The first term on the right-hand side represents the kinetic energy of the particle, while the second term represents the potential energy of the particle. The TDSE has three important properties

1. The TDSE is consistent with energy conservation.
2. The TDSE is linear and singular value, which implies that solutions can be constructed by superposition of two or more independent solutions.
3. The free-particle solution ($U(x) = 0$) is consistent with a single de Broglie wave.

If the potential energy is independent of time, as we have written above, we can separate Eq. (5.10) into a time-independent form using the mathematical technique known as separation of variables. Here, we assume that our wave function can be written as a product of a temporal and spatial function

$$\psi(x,t) = \phi(x)\chi(t). \tag{5.11}$$

Substituting Eq. (5.11) into the TDSE we find two equations that must be equal

$$i\hbar\frac{\partial}{\partial t}\chi(t) = E = \hbar\omega \tag{5.12}$$

and

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)\right)\phi(x) = E\phi(x). \tag{5.13}$$

The latter equation, Eq. (5.13) is called the **Time-Independent Schrödinger equation** or **TISE** for short. The solution to Eq. (5.12) can be easily verified to be an oscillating complex exponential

$$\chi(t) = e^{-iEt/\hbar} = e^{-i\omega t}. \tag{5.14}$$

The next steps involve solving the TISE for a given potential energy $U(x)$. The techniques involved in solving this equation are similar regardless of the functional form of the potential and can thus be summarized in a set of steps. We assume that the potential $U(x)$ is known and we wish to determine the wave function $\phi(x)$ and its corresponding energy E for that potential. This differential equations problem known as an eigenvalue problem, and there are only particular values of E that satisfy the differential equation, which are called eigenvalues. We will not go into the general theory of solving such equations, but simply go through a few examples. However, before moving on to that, we note three further properties of the solutions of the TISE.

1. **Continuity**: The solutions to the TISE $\phi(x)$ and its first derivative $\phi'(x)$ must be continuous for all values of x (the latter holds for finite potential $U(x)$).

2. **Normalizable**: The solutions to the TISE must be square integrable, i.e. the integral of the modulus squared of the wave function over all space must be a finite constant so that the wave function can be normalized to give $\int |\psi(x)|^2 \mathrm{d}x = 1$.

3. **Linearity**: Owing to the linearity of the TISE, given two independent solutions $\phi_1(x)$ and $\phi_2(x)$, we can construct other solutions by taking an appropriate superposition of these $\phi(x) = \alpha_1\phi_1(x)+\alpha_2\phi_2(x)$, where $|\alpha_1|^2 + |\alpha_2|^2 = 1$ to ensure normalization.

5.2 Probability, normalization, and expectation value

In the previous chapter, we discussed the interpretation of the wave function as prescribed by Born. There we noted that the modulus squared of the wave function gives the probability density (probability per unit length in one dimension)

$$P(x)\mathrm{d}x = |\phi(x)|^2\mathrm{d}x. \tag{5.15}$$

This interpretation helps us understand the continuity constraint on the wave function. We do not want the probability of the particle to be zero at a point x and jump to a non-zero value infinitessimally close by. (Note: We sometimes say (imprecisely) that $|\phi(x)|^2$ is the probability to find the particle at x. However one should take care to remember the correct definition.) From this interpretation, we see that we can calculate the probability to find the particle between two points x_1 and x_2 from the wave function $\phi(x)$

$$P(x_1 < x < x_2) = \int_{x_1}^{x_2} |\phi(x)|^2 \mathrm{d}x. \tag{5.16}$$

Related to this is the concept of normalization of the wave function. We require that the particle must be found somewhere in space, and thus the probability to find the particle between $-\infty$ and ∞ should be 1, i.e.

$$\int_{-\infty}^{\infty} |\phi(x)|^2 \mathrm{d}x = 1. \tag{5.17}$$

This is known as the normalization of the wave function, and shows us how to find the constant scale factor for solutions of the TISE.

Since we can no longer speak with certainty about the position of the particle, we can no longer guarantee the outcome of a single measurement of *any* physical quantity that depends on position. However, we can calculate the most probable outcome for a single measurement (also known as the *expectation value*), which is equivalent to the average outcome for many measurements. For example, suppose we wish to determine the expected location of a particle by measuring its x coordinate. Performing a large number of measurements, we find the value x_1 a certain number of times n_1, x_2 a number of times n_2, etc..., and in the usual way, we can calculate the average position

$$\begin{aligned} \langle x \rangle &= \frac{n_1 x_1 + n_2 x_2 + \cdots}{n_1 + n_2 + \cdots} \\ &= \frac{\sum n_i x_i}{\sum n_i}. \end{aligned} \tag{5.18}$$

Here we use the notation $\langle x \rangle$ to represent the average value of the quantity within brackets. The number of times n_i that we measure each position x_i is proportional to the probability $P(x_i)\mathrm{d}x$ to find the particle in the interval $\mathrm{d}x$ at x_i. Making this substitution and changing sums to integrals, we have

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} P(x) x \mathrm{d}x}{\int_{-\infty}^{\infty} P(x) \mathrm{d}x}, \tag{5.19}$$

and thus

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\phi(x)|^2 \mathrm{d}x, \tag{5.20}$$

where in the last step we assume that the wave function is normalized so that the integral in the denominator of Eq. (5.19) is equal to 1. The expectation value of any function of x can be found in a similar way, by replacing x with $f(x)$ in Eq. (5.20)

$$\langle f(x)\rangle = \int_{-\infty}^{\infty} f(x)|\phi(x)|^2 \mathrm{d}x. \tag{5.21}$$

A common application of Eq. (5.21) is used to calculate the variance, denoted Δx^2 (or equivalently the standard deviation, which is the square root of the variance $\Delta x = \sqrt{\Delta x^2}$) in the position of a particle. The variance in position is given by

$$\Delta x^2 = \langle (x - \langle x\rangle)^2\rangle = \langle (x^2 - 2x\langle x\rangle + \langle x\rangle^2)\rangle = \langle x^2\rangle - \langle x\rangle^2, \tag{5.22}$$

where we used the fact that $\langle x\langle x\rangle\rangle = \langle x\rangle^2$. Thus, we see that we can express the variance as

$$\Delta x^2 = \int_{-\infty}^{\infty} x^2|\phi(x)|^2 \mathrm{d}x - \left(\int_{-\infty}^{\infty} x|\phi(x)|^2 \mathrm{d}x\right)^2. \tag{5.23}$$

5.3 Free particle solution

A "free" particle refers to a particle that has no external forces acting upon it, in other words the potential energy is constant U_0. The state of such a free particle is represented by its wave function $\phi(x)$. Starting with the TISE Eq. (5.13), and proposing a solution of the form (this is known as an "ansatz" or an educated-guess)

$$\phi(x) = Ae^{ikx} \tag{5.24}$$

we find four possible solutions of the Schrödinger equation that satisfy

$$\begin{aligned} \frac{2m}{\hbar^2}(E - U_0)\phi(x) &= -\frac{\partial^2}{\partial x^2}\phi(x) \\ &= k^2\phi(x). \end{aligned} \tag{5.25}$$

The values $\pm k$ can take on real or imaginary values depending on the particle energy and the potential

$$k = \pm\frac{1}{\hbar}\sqrt{2m(E - U_0)}, \qquad (E > U_0), \tag{5.26}$$

with corresponding wave functions of the form

$$\phi(x) = Ae^{ikx} + Be^{-ikx}, \tag{5.27}$$

which represent traveling wave solutions, and

$$i\kappa = \pm i\frac{1}{\hbar}\sqrt{2m(U_0 - E)}, \qquad (E < U_0), \tag{5.28}$$

with corresponding wave functions of the form

$$\phi(x) = Ae^{\kappa x} + Be^{-\kappa x}, \tag{5.29}$$

which represent exponentially decaying solutions. The allowed energies are given by

$$E = \frac{\hbar^2 k^2}{2m} + U_0. \tag{5.30}$$

The case in which $E > U_0$ is classically allowed, whereas the situation in which $E < U_0$ is classically forbidden. To understand this, imagine our particle rolling on a potential surface described by $U(x)$. If it has total energy E, it can only exist in a region of space in which $U(x) < E$, and once $U(x) \geq E$, the particle must turnaround (this is the classical turning point). However, in quantum physics, the particle has a non-zero probability to be found in this classically forbidden region. We will see how this manifests itself in another section to allow quantum tunneling, in which a particle can penetrate a barrier and emerge on the other side of the barrier.

For the traveling wave solutions, consider the time evolution of the probability density, $P(x,t)$, given by

$$P(x,t) = \psi(x,t)^*\psi(x,t) = \phi(x)^* e^{i\omega t}\phi(x)e^{-i\omega t} = \phi(x)^*\phi(x). \tag{5.31}$$

This is independent of time! If we consider a particle traveling in only one direction, say the $+x$ direction, then the probability density is

$$P(x,t) = \phi(x)^*\phi(x) = A^* e^{-ikx} A e^{ikx} = A^* A, \tag{5.32}$$

which is independent of position! This implies that the particle is equally likely to be anywhere in space! It is completely delocalized! For a superposition of both positive and negative going waves, we have

$$\begin{aligned} P(x,t) &= (Ae^{ikx} + Be^{-ikx})^*(Ae^{ikx} + Be^{-ikx}) \\ &= A^*A + B^*B + 2\Re\{A^*Be^{-2ikx} + B^*Ae^{2ikx}\}, \end{aligned} \tag{5.33}$$

where $\Re\{z\}$ gives the real value of z. For real-valued coefficients A and B, this simplifies to

$$P(x,t) = A^2 + B^2 + 2AB\cos(2kx). \tag{5.34}$$

This is the equation for a standing wave.

5.4 Step potential

In this section we examine the behavior of a particle initially traveling in a region of space of constant potential suddenly moves into a region of

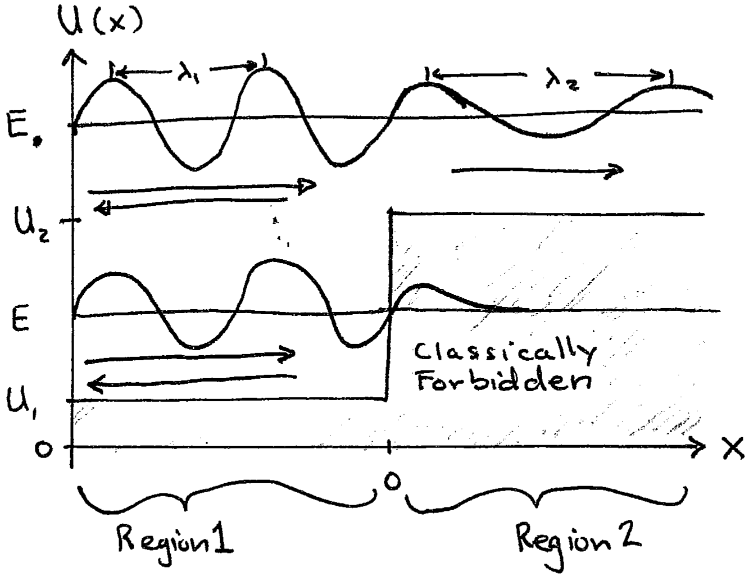

Figure 5.2: Simple step potential for a particle moving from $-x$ to $+x$, going from potential energy U_1 to U_2 at the origin. For a particle with energy greater than the step, $E > U_2$, it can continue propagate arbitrarily far to the right, with an increased wavelength (and thus decreased wave vector and momentum), as shown across the step. When the particle has energy below the step, it is classically forbidden to be found in the region where $x \geq 0$. However, the wave-nature of quantum systems allows it to tunnel into this region and thus have a non-zero probability to be found in the region $x \geq 0$, as depicted by the decaying exponential. In both cases, there is a finite reflectivity, which is 1 for $E < U_2$. To simplify the calculations, we break up the wave function into two regions (Regions 1 and 2).

different, but also constant potential. At $x = 0$, we have the transition between potential U_1 and U_2 as depicted in Fig. 5.2.

The potential can thus be expressed as a piecewise function

$$U(x) = \begin{cases} U_1 & \text{for } x < 0 \\ U_2 & \text{for } x \geq 0. \end{cases} \tag{5.35}$$

The particle has fixed energy E. There are two situations of interest, first when $E > U_1$ and $E > U_2$ and second when $E > U_1$ and $E < U_2$.

Case 1: $E > U_1$ and $E > U_2$

Here we break the problem down into two sections and consider a piecewise wave function defined on either side of the step. For region 1, $x < 0$, the wave function is given by

$$\phi_1(x) = Ae^{ik_1x} + Be^{-ik_1x}, \tag{5.36}$$

where A and B are coefficients to be determined, and the wave vector for region 1 is

$$k_1 = \sqrt{2m(E - U_1)}/\hbar. \tag{5.37}$$

Similarly, in region 2 the wave function is given by

$$\phi_2(x) = Ce^{ik_2x} + De^{-ik_2x}, \tag{5.38}$$

where C and D are coefficients to be determined, and the wave vector for region 2 is

$$k_2 = \sqrt{2m(E - U_2)}/\hbar. \tag{5.39}$$

The ratio of wave vectors is thus given by

$$\frac{k_2}{k_1} = \sqrt{\frac{1 - U_2/E}{1 - U_1/E}}. \tag{5.40}$$

We can set $D = 0$ since we assume the particle initially comes from the $-x$ direction. The A coefficient corresponds to the incident wave, while the B is related to the reflected wave. Now, to determine the remaining coefficients, we use the continuity of the wave function and its first derivative at the origin to give

$$\begin{aligned} \phi_1(0) &= \phi_2(0), \\ A + B &= C, \end{aligned} \tag{5.41}$$

and

$$\begin{aligned} \phi_1'(0) &= \phi_2'(0), \\ ik_1(A + B) &= ik_2C, \end{aligned} \tag{5.42}$$

where the prime implies the first derivative with respect to x. Combining these and eliminating C, we find the ratio of B/A

$$\frac{B}{A} = \frac{k_1 - k_2}{k_1 + k_2} = \frac{1 - k_2/k_1}{1 + k_2/k_1}, \tag{5.43}$$

which is the reflection coefficient of the barrier (the "coefficient" corresponds to the ratio of amplitudes). The reflectivity of the barrier, corresponding to the ratio of probabilities, or flux, is thus given by

$$R = \left|\frac{B}{A}\right|^2 = \left|\frac{1 - k_2/k_1}{1 + k_2/k_1}\right|^2. \tag{5.44}$$

Due to the conservation of particle number (or probability depending on how you want to think about the wave function), the transmissivity is simply given by

$$T = 1 - R = 1 - \left| \frac{1 - k_2/k_1}{1 + k_2/k_1} \right|^2 . \qquad (5.45)$$

Note that in going from region 1 to region 2, the de Broglie wavelength of the particle with energy E changes and becomes longer for an increased potential step as depicted in Fig. 5.2. The specific values of A and B are typically determined by considering the normalization of the wave function. However, since plane wave solutions are infinite in extent, they are not normalizable.

Case 2: $E > U_1$ **and** $E < U_2$

In this case, we follow a similar approach to above. However, in region 2, we now have decaying solutions since $E < U_2$. Again we have the following wave function in region 1

$$\phi_1(x) = Ae^{ik_1x} + Be^{-ik_1x}, \qquad (5.46)$$

where A and B are coefficients to be determined, and the wave vector for region 1 is

$$k_1 = \sqrt{2m(E - U_1)}/\hbar. \qquad (5.47)$$

In region 2 the wave function is now given by exponentials

$$\phi_2(x) = Ce^{\kappa_2 x} + De^{-\kappa_2 x}, \qquad (5.48)$$

where C and D are coefficients to be determined, and κ_2 is given by

$$\kappa_2 = \sqrt{2m(U_2 - E)}/\hbar. \qquad (5.49)$$

We can set $C = 0$ since we cannot have the probability amplitude growing infinitely large as $x \to +\infty$. The A coefficient corresponds to the incident wave, while the B is related to the reflected wave. Now, to determine the remaining coefficients, we use the continuity of the wave function and its first derivative at the origin to give

$$\begin{aligned} \phi_1(0) &= \phi_2(0) \\ A + B &= D, \end{aligned} \qquad (5.50)$$

and

$$\begin{aligned} \phi_1'(0) &= \phi_2'(0) \\ ik_1(A + B) &= \kappa_2 D. \end{aligned} \qquad (5.51)$$

Combining these and eliminating D, we find the ratio of B/A

$$\frac{B}{A} = \frac{k_1 - i\kappa_2}{k_1 + i\kappa_2}, \tag{5.52}$$

which is the reflection coefficient of the barrier. The reflectivity of the barrier is thus given by

$$R = \left|\frac{B}{A}\right|^2 = \left(\frac{k_1 - i\kappa_2}{k_1 + i\kappa_2}\right)\left(\frac{k_1 + i\kappa_2}{k_1 - i\kappa_2}\right) = 1. \tag{5.53}$$

Thus, we see that even though the particle has non-zero probability to penetrate into the classically forbidden region, it will always be reflected (eventually). We could have also obtained the same result in Eq. (5.52) from Eq. (5.44) by allowing $k_2 = -i\kappa$. By allowing k_1 and k_2 to take on complex values, we do not have to consider multiple cases.

Note that the depth at which the particle penetrates into the classically forbidden region is given by the distance from $x = 0$ at which the probability drops by $1/e$,

$$P(\Delta x) = e^{-2\kappa_2 \Delta x} = e^{-1}, \tag{5.54}$$

which gives

$$\Delta x = \frac{1}{2\kappa_2} = \frac{1}{2}\frac{\hbar}{\sqrt{2m(U_2 - E)}}. \tag{5.55}$$

5.5 Potential barrier and tunneling

Another useful example is the scattering of a particle from a potential barrier of width L and height U_0 as depicted in Fig. 5.3. The functional form of the potential can be expressed as a piecewise function

$$U(x) = \begin{cases} U_0 & \text{for } -L/2 < x < L/2 \\ 0 & \text{otherwise.} \end{cases} \tag{5.56}$$

Again, there are two types of behavior that occur. The first, in which the particle energy is greater than the barrier $E > U_0$, in which the particle will have some reflection and some transmission as expected classically. The second situation, in which the particle energy is less than the barrier, is of more interest. Here, the classical prediction would be that the particle should be reflected completely and there is no transmission. There should be zero probability to find the particle on the right hand side of the barrier. However, due to the wave nature of quantum systems, there is a finite, non-zero probability to find the particle on the right-hand side of the barrier, and it will continue to propagate to $+\infty$! This simple model is the precursor to discussing the decay of atomic nuclei as well as other quantum tunneling

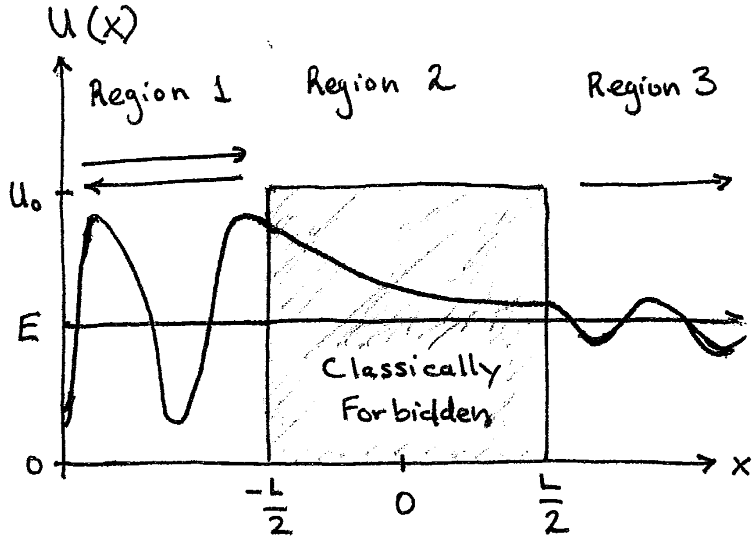

Figure 5.3: Simple step barrier for a particle moving from $-x$ to $+x$ with magnitude U_0 and width L centered on the origin. When the particle has energy below the barrier $E \leq U_0$, it is classically forbidden to be found in the region where $x \geq -L/2$, i.e. anywhere to the right of the first barrier wall. However, the wave-nature of quantum systems allows it to tunnel into and through this region. This leads to a non-zero probability to be found in the region $x \geq -L/2$, as depicted by the decaying exponential through the barrier and the propagating wave (with decreased amplitude, but the same wavelength) to the right of the barrier. To simplify the calculations, we break up the wave function into three regions (Regions 1, 2 and 3).

effects such as those associated with a scanning electron microscope.

On the left-hand and right-hand sides of the barrier, regions 1 and 3, the wave vector is given by

$$k = \sqrt{2mE}/\hbar, \tag{5.57}$$

while within the barrier, the decay is governed by

$$\kappa = \sqrt{2m(U_0 - E)}/\hbar. \tag{5.58}$$

The we can thus express the wave function in each region in terms of either plane waves or decaying exponentials with unknown coefficients to be determined

$$\phi_1(x) = Ae^{ikx} + Be^{-ikx}, \tag{5.59}$$

$$\phi_2(x) = Ce^{\kappa x} + De^{-\kappa x}, \tag{5.60}$$

$$\phi_3(x) = Fe^{ikx} + Ge^{-ikx}. \tag{5.61}$$

Assuming that the particle initially starts on the left-hand side of the barrier (i.e. $x \leq -L/2$), then we can set $G = 0$, since there is no way to obtain a solution on the right-hand side propagating in the negative x direction. Next we apply the boundary conditions on the wave function at the edges of the barrier, which leads to the following four equations

$$e^{-ikL/2} + \frac{B}{A} e^{ikL/2} = \frac{C}{A} e^{-\kappa L/2} + \frac{D}{A} e^{\kappa L/2}, \tag{5.62}$$

$$ik \left(e^{-ikL/2} - \frac{B}{A} e^{ikL/2} \right) = \kappa \left(\frac{C}{A} e^{-\kappa L/2} - \frac{D}{A} e^{\kappa L/2} \right), \tag{5.63}$$

$$\frac{F}{A} e^{ikL/2} = \frac{C}{A} e^{\kappa L/2} + \frac{D}{A} e^{-\kappa L/2}, \tag{5.64}$$

$$ik \left(\frac{F}{A} e^{ikL/2} \right) = \kappa \left(\frac{C}{A} e^{\kappa L/2} - \frac{D}{A} e^{-\kappa L/2} \right), \tag{5.65}$$

where we have divided through by A, since we want to solve for the transmission and reflection coefficients given by the ratios of F/A and B/A respectively. By combining Eqs. (5.64) and (5.65), we can solve for C/A and D/A in terms of F/A. For example, $1/\kappa$ times Eq. (5.65) added to Eq. (5.64) gives

$$\frac{C}{A} = \frac{F}{A} \frac{e^{ikL/2} e^{-\kappa L/2}}{2\kappa} (\kappa + ik) \tag{5.66}$$

and subtracting $1/\kappa$ times Eq. (5.65) from Eq. (5.64) gives

$$\frac{D}{A} = \frac{F}{A} \frac{e^{ikL/2} e^{\kappa L/2}}{2\kappa} (\kappa - ik) \tag{5.67}$$

We can now solve for the transmission and reflection coefficients by combining Eqs. (5.62) and (5.63) and substituting in for C/A and D/A to give

$$\frac{F}{A} = 4ik\kappa e^{-ikL} \left[(\kappa + ik)^2 e^{-\kappa L} - (\kappa - ik)^2 e^{\kappa L} \right]^{-1}, \tag{5.68}$$

$$\frac{B}{A} = \frac{F}{A} \frac{\kappa^2 + k^2}{2ik\kappa} \cosh(\kappa L), \tag{5.69}$$

The transmittance $T = |F/A|^2$ is thus given by

$$T = \left| \frac{F}{A} \right|^2 = 8k^2\kappa^2 \left[(k^2 + \kappa^2)^2 \cosh(2\kappa L) - (k^4 - \kappa^4 - 6k^2\kappa^2) \right]^{-1}, \tag{5.70}$$

In the limit of weak transmission, i.e. $\kappa L \ll 1$, the transmittance can be approximated by setting $\cosh(2\kappa L) \approx e^{2\kappa L}/2$, and dropping the smaller terms in the denominator, leading to

$$T \approx \frac{16k^2\kappa^2}{(k^2 + \kappa^2)^2} e^{-2\kappa L}. \tag{5.71}$$

In the last few sections we found the allowed solutions to the Schrödinger equation for a particle of mass m traveling in free space, and through different potentials - a step and a barrier. We found that the allowed energy and momentum the particle may take on have a continuous range of values, which is in line with our classical notions of energy and momentum for a particle. A key signature of non-classical behavior is the non-zero probability to find the particle in a region of space where it is classically forbidden to go, in which its total energy is less than the potential in that region, i.e. $E < U_0$. This quantum penetration is due to the wave nature of quantum objects and can be shown to be consistent with the uncertainty principle, in which the particle is allowed to penetrate the potential for a finite period of time Δt, which is on the order of $\hbar/\Delta E$, where $\Delta E = U_0 - E$ is the difference between the total particle energy and the potential energy of the barrier. The depth into the barrier can be approximated by multiplying the this allowed time by the "particle velocity" which we approximate as $v = p/m = \sqrt{2m(U_0 - E)}/m$. The reason to take $p = \sqrt{2m(U_0 - E)}$ as the value of the momentum is that $K = U_0 - E$ is the maximum value of kinetic energy the particle could have and still not propagate in the potential barrier region, it is also the only relevant energy quantity by dimensional analysis. This gives us a penetration depth from the uncertainty principle of

$$\Delta x = \frac{1}{2} v \Delta t = \frac{1}{2} \frac{\hbar}{U_0 - E} \frac{\sqrt{2m(U_0 - E)}}{m} = \frac{\hbar}{\sqrt{2m(U_0 - E)}}, \tag{5.72}$$

where the factor of 1/2 arises from the fact that the particle must travel into the forbidden region and return in the time Δt. This is consistent with the result we obtained above in Eq. (5.55) (to within a factor of two), and thus in good agreement.

5.6 Particle in a box

The final example that we will look at is that of a particle confined to an infinite potential well, as depicted in Fig. 5.4. Here a particle of mass m is trapped (or bound) to the well that has a width L, and finite potential U_0 inside the infinite walls. We want to determine what the allowed energies and wave functions that the particle can have. We choose to center the well (or potential "box") on the origin of our coordinate axes, so that the walls of the well are located at $x = -L/2$ and $x = +L/2$. The potential can thus be written as

$$U(x) = \begin{cases} \infty & \text{for } x < -L/2 \\ U_0 & \text{for } -L/2 \leq x \leq L/2 \\ \infty & \text{for } x > L/2 \end{cases} \tag{5.73}$$

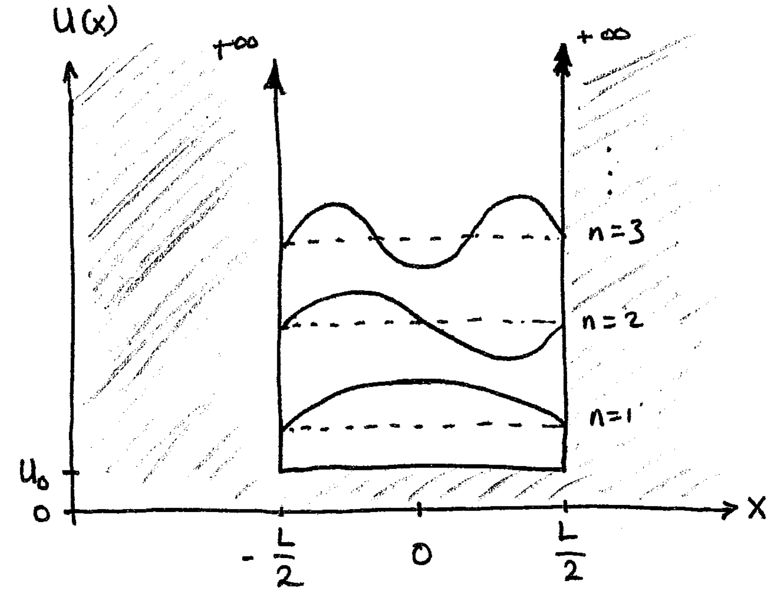

Figure 5.4: Infinite potential well of magnitude U_0 and width L centered on the origin. Particles are only allowed to take on certain discrete energy eigenvalues, labelled by the quantum number n. The first three eigenstates are shown.

We again break up the problem into different regions of space as dictated by the boundaries of the potential. In regions 1 and 3 outside the box where the potential is infinite, we must have

$$\phi(x) = 0, \qquad x < -L/2,\ x > L/2, \tag{5.74}$$

so that the Schrödinger equation can be satisfied (otherwise the term $U(x)\phi(x)$ would be infinite, which makes no sense). Inside the box, we have a 1D plane wave again, similar to the situation of the finite potential in Sec. 5.4

$$\phi(x) = Ae^{ikx} + Be^{-ikx}, \qquad -L/2 \leq x \leq L/2, \tag{5.75}$$

where the magnitude of the wave vector comes from the Schrödinger equation, in which the energy is

$$E = \frac{\hbar^2 k^2}{2m} + U_0, \tag{5.76}$$

which gives the square of the wave vector

$$k^2 = \frac{2m(E - U_0)}{\hbar^2}, \tag{5.77}$$

while the expansion coefficients A and B, and the allowed energy values E are still to be determined. These unknown values of A, B and E are set by the initial conditions of the system and the boundary conditions on the wave function respectively. The boundary conditions for the wave function at the left-hand side of the box, $x = -L/2$ implies that

$$\phi(-L/2) = Ae^{-ikL/2} + Be^{ikL/2} = 0, \tag{5.78}$$

and similarly on the right hand side of the box $x = L/2$

$$\phi(L/2) = Ae^{ikL/2} + Be^{-ikL/2} = 0. \tag{5.79}$$

Adding Eq. (5.78) to Eq. (5.79) gives

$$2(A+B)\cos\left(\frac{kL}{2}\right) = 0, \tag{5.80}$$

while subtracting Eq. (5.78) from Eq. (5.79) gives

$$2i(A-B)\sin\left(\frac{kL}{2}\right) = 0. \tag{5.81}$$

Both conditions in Eqs. (5.80) and (5.81) must be met. There are two cases we can consider. First, when $A = B$ Eq. (5.81) is met, and to satisfy Eq. (5.80), we see that the wave vector can only take on discrete values

$$k = \frac{2\pi n_1}{L} + \frac{\pi}{L}, \tag{5.82}$$

where $n_1 = 0, 1, 2, 3, ...$ The second case is when $A = -B$ in which Eq. (5.80) is met, and to satisfy Eq. (5.81) the wave vector can only take on discrete values

$$k = \frac{2\pi n_2}{L}, \tag{5.83}$$

where $n_2 = 1, 2, 3, ...$ We can consolidate these conditions and rewrite the solutions by noting that both Eqs. (5.82) and (5.84) are satisfied by

$$k = \frac{\pi n}{L}, \tag{5.84}$$

where $n = 1, 2, 3, ...$ and the solution to the TISE is

$$\begin{aligned} \phi_n(x) &= A\begin{cases} \cos\left(n\frac{\pi}{L}x\right) & \text{for } n \text{ odd} \\ \sin\left(n\frac{\pi}{L}x\right) & \text{for } n \text{ even} \end{cases} \\ &= A\sin\left(n\frac{\pi}{L}\left(x + \frac{L}{2}\right)\right). \end{aligned} \tag{5.85}$$

Note that this implies that not only is the wave vector quantized, but also the particle momentum and energy

$$p = \hbar k = \frac{\hbar \pi n}{L}, \tag{5.86}$$

and

$$E = U_0 + \frac{\hbar^2 k^2}{2m} = U_0 + \frac{\hbar^2 \pi^2 n^2}{2mL^2}. \tag{5.87}$$

The amplitude A can be found by considering the normalization condition of the wave function

$$\int_{-\infty}^{\infty} |\phi_n(x)|^2 \mathrm{d}x = \int_{-L/2}^{L/2} |A \sin\left(n\frac{\pi}{L}\left(x + \frac{L}{2}\right)\right)|^2 \mathrm{d}x = |A|^2 \frac{L}{2}, \tag{5.88}$$

where we have made use of the fact that the wave function is zero outside the box, and the following definite integral

$$\int_{-L/2}^{L/2} |\sin\left(n\frac{\pi}{L}\left(x + \frac{L}{2}\right)\right)|^2 \mathrm{d}x = \frac{L}{2}. \tag{5.89}$$

For the normalization integral in Eq. (5.88) to equal unity, we see that the normalization amplitude must be

$$A = \sqrt{\frac{2}{L}}, \tag{5.90}$$

since we require $|A|^2 L/2 = 1$. The solutions for the TISE can thus be expressed as

$$\phi_n(x) = \sqrt{\frac{2}{L}} \sin\left(n\frac{\pi}{L}\left(x + \frac{L}{2}\right)\right). \tag{5.91}$$

Note that the normalization in Eq. (5.90) can be met for a range of complex amplitudes

$$A = e^{i\theta}\sqrt{\frac{2}{L}}, \tag{5.92}$$

in which the phase θ is arbitrary. This implies that the outcome of a measurement about the particle position, which is proportional to $|\phi(x)|^2$ is invariant under a *global* phase factor. However, as we will see shortly, if there are two or more amplitudes that contribute to a measurement outcome, it is important to keep track of the relative phase between amplitudes, as in the double slit experiment, where the fringe pattern arises from the interference of two probability amplitudes with different phases.

Each solution to the TISE $\phi_n(x)$, labelled by the quantum number n, has quantized wave number, momentum, and energy. The wave function $\phi_n(x)$ is often referred to as an *energy eigenstate* with corresponding *eigenvalue* (or *eigen-energy* E_n, because it satisfies the TISE, which is an *eigenvalue equation* (in differential equations speak)

$$\hat{H}\phi_n(x) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)\right)\phi_n(x) = E_n\phi_n(x), \tag{5.93}$$

where we have introduced the Hamiltonian operator,

$$\hat{H} = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x) \right), \tag{5.94}$$

which in this case is the sum of kinetic energy and potential energy operators. You will discuss more about differential operators in your second year. The wave vector and momentum scale linearly with the quantum number ($k_n = k_1 n$ and $p_n = p_1 n$), while the energy scales quadratically ($E_n = E_1 n^2$). The ground state, labelled by $n = 1$ has the lowest allowed energy, followed by the first excited state $n = 2$, which has four times the energy. (NOTE: We often speak of the *state* of the system, which implies specification of the wave function at some initial time, although this is not always explicitly written.) Furthermore, the solutions are orthogonal to one another, that is, they have zero overlap across the entire box

$$\int_{-L/2}^{L/2} \phi_m(x)^* \phi_n(x) \mathrm{d}x = \delta_{mn} \tag{5.95}$$

where δ_{mn} is the Kronecker delta, which is one for $m = n$ and 0 otherwise

$$\delta_{mn} = \begin{cases} 1 & \text{for } m = n \\ 0 & \text{otherwise.} \end{cases} \tag{5.96}$$

The orthogonality relation can be quite useful when trying to determine expectation values as we will see shortly.

5.7 Superposition and time dependence

The time dependence of quantum states is governed by the TDSE, Eq. (5.10). We can separate out the time and spatial degrees of freedom if the potential energy is time-independent ($U(x)$ is independent of time) by using the method of separation of variables, as described in Sec. 5.1. In this case temporal evolution of the wave function is described by an oscillating exponential phase factor

$$\psi_n(x,t) = \phi_n(x) e^{-iE_n t/\hbar}, \tag{5.97}$$

where $\phi_n(x)$ is the solution to the TISE with quantum number n and E_n is its corresponding energy eigenvalue. The states, $\phi_n(x)$ are called energy eigenstates and have special properties in terms of their temporal evolution. Owing to the linearity of the Schrödinger equation, a general solution for the "particle in a box" can be expressed as a sum of different solutions

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x,t), \tag{5.98}$$

where the amplitudes c_n that weight the superposition can be complex, and must obey the normalization condition

$$\sum_{n=1}^{\infty} |c_n|^2 = 1. \tag{5.99}$$

This follows from considering the normalization condition, and the orthogonality of the states as in Eq. (5.95). The set of amplitudes $\{c_n\}$, are determined by the specific initial conditions of the problem. The modulus squared of each coefficient gives the probability to find the particle in that state

$$p_n = |c_n|^2 \tag{5.100}$$

For example, we can consider a particle initially prepared in the symmetric superposition of the ground and first excited states, i.e. an equally weighted superposition of the ground and first excited states, at time $t = 0$

$$\Psi^{(+)}(x, t = 0) = \frac{1}{\sqrt{2}} \left(\phi_1(x) + \phi_2(x)\right). \tag{5.101}$$

The probability to find the particle in state 1 or 2 is 1/2. The state will then evolve in time, with each amplitude having a different time-dependent phase

$$\begin{aligned} \Psi^{(+)}(x, t) &= \frac{1}{\sqrt{2}} \left(\phi_1(x)e^{-i\omega_1 t} + \phi_2(x)e^{-i\omega_2 t}\right) &(5.102)\\ &= e^{-i\omega_1 t}\frac{1}{\sqrt{2}} \left(\phi_1(x) + \phi_2(x)e^{-i\Delta\omega t}\right), &(5.103)\end{aligned}$$

where we have introduced the angular frequency associated with the energy eigenvalues $\omega_n = E_n/\hbar$, and the frequency difference $\Delta\omega = \omega_2 - \omega_1$. The probability to find the particle in state 1, is given by the modulus squared of the corresponding amplitude coefficient, which for the state in Eq. (5.103) is just 1/2. The same holds true for the probability to find the particle in state 2. However, the probability to find the particle in the initial superposition state is not time independent.

Probability overlap

Suppose we know that a state is initially prepared in the symmetric superposition state of Eq. (5.105). We know the time evolution of the state, given by Eq. (5.103). Now as time evolves, the phase factor on the second term in Eq. (5.103) will eventually become $e^{-i\Delta\omega t} = -1$, which first occurs when

$$\tau = \frac{\pi}{\Delta\omega}. \tag{5.104}$$

The state at this point in time is equal to the antisymmetric superposition state (up to an overall, unobservable global phase factor $e^{-i\omega_1\tau}$)

$$\Psi^{(-)}(x,t=0) = \frac{1}{\sqrt{2}}\left(\phi_1(x) - \phi_2(x)\right). \tag{5.105}$$

Thus, we should expect that the probability to find the particle in the symmetric superposition at this point in time should be zero. To calculate the probability to find a particle in a particular state $\Phi(x)$ at time t given the time dependent state $\psi(x,t)$, we calculate the amplitude overlap between the two states

$$\langle\Phi|\psi(t)\rangle = \int_{-\infty}^{\infty} \Phi^*(x)\psi(x,t)\mathrm{d}x, \tag{5.106}$$

which gives the overlap between the probability amplitudes of the two states. The probability to find the particle in state $\Phi(x)$ at time t is then give by the modulus squared of this overlap

$$P_\Phi(t) = |\langle\Phi|\psi(t)\rangle|^2 = \left|\int_{-\infty}^{\infty} \Phi^*(x)\psi(x,t)\mathrm{d}x\right|^2 \tag{5.107}$$

From this, we can calculate the probability to find the particle initially prepared in the symmetric superposition state, with time evolution given by Eq. (5.103), in the antisymmetric superposition state by first calculating the amplitude (or state) overlap

$$\begin{aligned}
\langle\Psi^{(-)}|\Psi^{(+)}(t)\rangle &= \int_{-\infty}^{\infty} \Psi^{(-)*}(x)\Psi^{(+)}(x,t)\mathrm{d}x \\
&= \frac{1}{2}\int_{-\infty}^{\infty} \left(\phi_1^*(x) - \phi_2^*(x)\right)\left(\phi_1(x) + \phi_2(x)e^{-i\Delta\omega t}\right)\mathrm{d}x \\
&= \frac{1}{2}\int_{-\infty}^{\infty} (|\phi_1(x)|^2 - |\phi_2(x)|^2 e^{-i\Delta\omega t} \\
&+ \phi_1^*(x)\phi_2(x)e^{-i\Delta\omega t} - \phi_2^*(x)\phi_1(x))\mathrm{d}x \\
&= \frac{1}{2}\left(1 - e^{-i\Delta\omega t}\right),
\end{aligned} \tag{5.108}$$

where I have used the orthogonality between the states to eliminate the cross terms, and the normality of the wave functions to evaluate the integrals on the second to last line. Thus the probability to find the particle in the antisymmetric superposition state is just the modulus squared of this amplitude

$$\begin{aligned} P_{\Psi^{(-)}}(t) &= \left|\frac{1}{2}\left(1 - e^{-i\Delta\omega t}\right)\right|^2 \\ &= \frac{1}{4}\left(2 - 2\Re\left\{e^{-i\Delta\omega t}\right\}\right) \\ &= \frac{1}{2}\left(1 - \cos(\Delta\omega t)\right) \\ &= \sin^2\left(\frac{\Delta\omega t}{2}\right). \end{aligned} \tag{5.109}$$

So we see that the probability to find the particle in the antisymmetric superposition state oscillates in time with a frequency proportional to the energy difference between the two states of the superposition

$$\begin{aligned} \Delta\omega &= \frac{E_2 - E_1}{\hbar} \\ &= \frac{1}{\hbar}\left(\frac{\hbar^2\pi^2}{2m}(2^2 - 1^2) + U_0 - U_0\right) \\ &= 3\frac{\hbar\pi^2}{2m}. \end{aligned} \tag{5.110}$$

The frequency is independent of the potential value inside the well! Thus, we see that the system dynamics do not depend on the actual value of the potential within the box. This should be clear considering that the walls of the potential are infinite.

Expectation values

Now, we may want to ask a few questions about the expected values of position or energy of the particle. For example, what is the expected (or average) position of the particle inside the box as a function of time when prepared in this superposition state? We may also want to know the uncertainty in the particle position as a function of time. Similarly, we could ask these questions about the energy. We may also ask about the probability to find the particle in certain regions of space. Let us tackle each of these in turn.

We start by calculating the probability to find the particle in some region of the box. For example, the probability to find the particle in the left-hand side of the box ($-L/2 \leq x \leq 0$) as a function of time is given by

$$P_{\mathrm{LHS}}(t) = \int_{-L/2}^{0} |\psi(x,t)|^2 \mathrm{d}x, \tag{5.111}$$

where we evaluate the integral over the region of space we are interested in looking for the particle. For a particle initially prepared in one of the energy eigenstates, $\phi_n(x)$, the probability to find the particle in the left-hand side of the box is

$$\begin{aligned} P_{\rm LHS}(t) &= \int_{-L/2}^{0} |\psi(x,t)|^2 \mathrm{d}x \\ &= \int_{-L/2}^{0} |\phi_n(x,t) e^{-i\omega_n t}|^2 \mathrm{d}x \\ &= \int_{-L/2}^{0} |\phi_n(x,t)|^2 \mathrm{d}x \\ &= \frac{1}{2}, \end{aligned} \tag{5.112}$$

where I have made use of the integral

$$\int_{-L/2}^{0} |\phi_n(x)|^2 \mathrm{d}x = \frac{1}{2}. \tag{5.113}$$

Note that this is independent of time. This time independence stems from the fact that the energy eigenstates are stationary and only evolve in time by gathering an unobservable phase factor $e^{i\omega_n t}$. For this reason energy eigenstates are often called stationary states, which not-so-coincidentally, match the stationary states that Bohr postulated for the electron in the hydrogen atom (albeit with a different potential than we are considering here).

Now let us repeat the calculation for a particle prepared in the equal symmetric superposition of the ground and first excited state in Eq. (5.103). The probability to find the particle on the left-hand side of the box as a function of time is

$$\begin{aligned} P_{\rm LHS}(t) &= \int_{-L/2}^{0} |\psi(x,t)|^2 \mathrm{d}x \\ &= \frac{1}{2}\int_{-L/2}^{0} \left[|\phi_1(x)|^2 + |\phi_2(x)|^2 + 2\Re\left\{\phi_2^*(x)\phi_1(x)e^{i\Delta\omega t}\right\}\right] \mathrm{d}x \\ &= \frac{1}{2}\left(\frac{1}{2} + \frac{1}{2} + 2\frac{4}{3\pi}\cos(\Delta\omega t)\right) \\ &= \frac{1}{2}\left(1 + \frac{8}{3\pi}\cos(\Delta\omega t)\right). \end{aligned} \tag{5.114}$$

Here I have made use of Eq. (5.113) and the following integral

$$\int_{-L/2}^{0} \phi_1^*(x)\phi_2(x) \mathrm{d}x = \frac{4}{3\pi}, \tag{5.115}$$

which can be found by evaluating the corresponding sinusoidal integral. The probability to find the particle on the right-hand side of the box can be found either by evaluating the appropriate integrals, or using the fact that since the probability to find the particle in the box must be unity

$$P_{\rm RHS}(t) + P_{\rm LHS}(t) = 1, \tag{5.116}$$

we have

$$P_{\rm RHS}(t) = 1 - P_{\rm LHS}(t) = \frac{1}{2}\left(1 - \frac{8}{3\pi}\cos(\Delta\omega t)\right). \tag{5.117}$$

Note that the probability to find the particle in the left-hand side of the box is no longer constant! The probability oscillates at a frequency $\Delta\omega = \omega_2 - \omega_1$ proportional to the energy difference between the two states. This time evolution arises from the superposition of energy eigenstates and their corresponding phase evolution. Another way to say this is that the superposition of energy eigenstates leads to dynamics in quantum mechanics.

Next we consider the expected position of the particle, which is simply given by the average

$$\langle x(t)\rangle = \int_{-\infty}^{\infty} x|\psi(x,t)|^2 {\rm d}x. \tag{5.118}$$

To determine the uncertainty in the particle position, we need to calculate the the expectation value of x^2, given by

$$\langle x^2(t)\rangle = \int_{-\infty}^{\infty} x^2|\psi(x,t)|^2 {\rm d}x. \tag{5.119}$$

Using the state in Eq. (5.103) gives the following average position

$$\begin{aligned}\langle x(t)\rangle &= \frac{1}{2}\int_{-\infty}^{\infty} x\left[|\phi_1(x)|^2 + |\phi_2(x)|^2 + 2\Re\left\{\phi_2^*(x)\phi_1(x)e^{i\Delta\omega t}\right\}\right]{\rm d}x \\ &= -\frac{16L}{9\pi^2}\cos(\Delta\omega t),\end{aligned} \tag{5.120}$$

where the following integrals become quite useful

$$\int_{-L/2}^{L/2} x|\phi_n(x)|^2 {\rm d}x = 0, \qquad \forall\ n \in \{1,2,3...\}, \tag{5.121}$$

which arises from the fact that $x|\phi_n(x)|^2$ is an odd function integrated over even limits, and

$$\int_{-L/2}^{L/2} x\phi_n(x)\phi_m^*(x){\rm d}x = \begin{cases} 0 & \text{for } m \text{ and } n \text{ both even or both odd} \\ -\frac{8mnL}{(m^2-n^2)^2\pi^2} & \text{otherwise.}\end{cases} \tag{5.122}$$

The variance in the position can be calculated in a similar manner with the help of the following integrals

$$\int_{-L/2}^{L/2} x^2|\phi_n(x)|^2 \mathrm{d}x = \frac{L^2}{12}\left(1-\frac{6}{n^2\pi^2}\right), \qquad \forall\, n \in \{1,2,3...\}, \tag{5.123}$$

and

$$\int_{-L/2}^{L/2} x^2\phi_n(x)\phi_m^*(x)\mathrm{d}x = \begin{cases} \frac{8mnL^2}{(m^2-n^2)^2\pi^2} & \text{for } m \text{ and } n \text{ both odd or both even} \\ 0 & \text{otherwise.} \end{cases} \tag{5.124}$$

This gives

$$\begin{aligned}
\langle x^2(t)\rangle &= \frac{1}{2}\int_{-\infty}^{\infty} x^2\left[|\phi_m(x)|^2 + |\phi_n(x)|^2 + 2\Re\left\{\phi_m^*(x)\phi_m(x)e^{i\Delta\omega_{mn}t}\right\}\right]\mathrm{d}x \\
&= \frac{L^2}{12}\left(1-\frac{3}{m^2\pi^2}-\frac{3}{n^2\pi^2}+\frac{96mn}{(m^2-n^2)^2\pi^2}\cos(\Delta\omega_{m,n}t)\right) \\
&= \left(\frac{L}{12}\right)^2\left(12\pi^2 - 45 + 256\cos(\Delta\omega_{1,2}t)\right).
\end{aligned} \tag{5.125}$$

where I have included the general case for the case of an arbitrary initial equal two state superposition $\Psi(x, t = 0) = \phi_m(x) + \phi_n(x)$ in the second line of Eq. (5.125), used the fact that $\Re\{e^{i\theta}\} = \cos(\theta)$, and defined the frequency difference $\Delta\omega_{m,n} = \omega_m - \omega_n$. Thus the variance in the position is given by

$$\begin{aligned}
\Delta x^2(t) &= \langle x^2(t)\rangle - \langle x(t)\rangle^2 \\
&= \left(\frac{L}{12}\right)^2\left(12\pi^2 - 45 + 256\cos(\Delta\omega_{1,2}t)\right) - \left(\frac{16L}{9\pi^2}\cos(\Delta\omega_{1,2}t)\right)^2 \\
&= \frac{L^2}{1296\pi^4}\left(9\pi^2(12\pi^2 - 45 + 256\cos(\Delta\omega_{1,2}t)) - 4096\cos^2(\Delta\omega_{1,2}t)\right),
\end{aligned} \tag{5.126}$$

This example shows that even a seemingly simple situation in which the particle is prepared in a superposition state of only two energy eigenstates can lead to nontrivial evolution.

The average energy for a state can be calculated by noting that since this is an isolated system, and the potential is time independent, the total energy must be invariant in time as well. Thus, the average energy can be determine from the initial state superposition. If we consider an equal superposition of two states labelled by m and n

$$\psi(x, t = 0) = \frac{1}{\sqrt{2}}\left(\phi_m(x) + \phi_n(x)\right), \tag{5.127}$$

the initial energy of the state is

$$E\psi(x,t=0) = \frac{1}{\sqrt{2}}\left(E_m\phi_m(x) + E_n\phi_n(x)\right), \tag{5.128}$$

according to the TISE. The average energy is thus calculated by multiplying by $\psi^*(x,t=0)$ and integrating over all x, as in Eq. (5.21)

$$\begin{aligned}
\langle E\rangle &= \int_{-\infty}^{\infty}\psi^*(x,t=0)E\psi(x,t=0)\mathrm{d}x \\
&= \frac{1}{2}\int_{-\infty}^{\infty}\left(\phi_m^*(x)+\phi_n^*(x)\right)\left(E_m\phi_m(x)+E_n\phi_n(x)\right)\mathrm{d}x \\
&= \frac{1}{2}\int_{-\infty}^{\infty}\left(E_m|\phi_m(x)|^2 + E_m|\phi_m(x)|^2 + 2E_mE_n\Re\{\phi_m^*(x)\phi_n(x)\}\right)\mathrm{d}x \\
&= \frac{1}{2}(E_m+E_n).
\end{aligned} \tag{5.129}$$

Here I have made use of the orthogonality, Eq. (5.95), and normalization of the wave function, so that the first two terms on the third line are proportional to the energy multiplied by the weight $E_m/2$ and $E_n/2$ in this case, while the final term on the third line is zero since the two wave functions are orthogonal. This can be generalized to an arbitrary superposition, as in Eq. (5.98), and the average energy can be expressed as

$$\langle E\rangle = \sum_{n=1}^{\infty}|c_n|^2E_n, \tag{5.130}$$

where the same recipe as above follows. Each energy E_n is weighted by the probability $p_n = |c_n|^2$ that the particle is found in the corresponding state $\phi_n(x)$.

5.8 Insight: Why steps and boxes?

The above examples may seem somewhat abstract and not directly related to any realistic problems that one finds in the real world. However, you should try not to think of these as useless simplified cases of the Schrödinger equation, but rather first-order approximations to scenarios that are encountered in the real world. The solutions of these simplified models can give us insight into the behavior (both qualitative and quantitative) of actual physical systems. For example, the quantum tunneling model through the step barrier gives reasonable approximations for quantum tunneling effects in a variety of real-world situations, such as the scanning electron microscope. Similarly, the bound states for the infinite potential well discussed in the previous section demonstrate the concept of bound states, quantized energy levels, and temporal evolution of energy eigenstate superpositions, all of which are intimately linked to numerous real-world scenarios such as the hydrogen atom.

Furthermore, I would like to note that the examples of the propagation of a free particle in Sec. 5.3, propagation of a particle across a potential step in Sec. 5.4 tunneling in Sec. 5.5 are all analogous to the propagation of light through various media with varying refractive indices. In the case of light propagation, the refractive index profile $n(x)$ takes on the role played by the potential $U(x)$ in the Schrödinger equation. Aside from this and a rescaling of the equations, the differential equations solved are exactly the same. Thus, I want to stress the importance in recognizing this "analogy". Not only can one gain insight into the propagation of quantum systems through understanding optical systems, but it also helps to solve problems. This line of thinking also holds true for the particle in a box, where the box now becomes an optical cavity, the same as we discussed for the derivation of the Planck equation. Thus, you have already done some work on a particle in a 3D box by looking at the solutions for a photon inside a 3D cavity.