

# The Schrödinger equation

## Quantum Mechanics Foundation Course: Sheet 2.

### 1 TIME-INDEPENDENT SCHRÖDINGER EQUATION

The Schrödinger equation governs the time-evolution of quantum mechanical systems. As we saw in the previous lecture, the wavefunction encodes all physical information about a quantum system, and is obtained by solving the corresponding Schrödinger equation. The Schrödinger equation is a second-order partial differential equation in space and time. In 1D, it is given by:

$$\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x, t) \right] \Psi(x, t) = i\hbar \frac{\partial}{\partial t} \Psi(x, t).$$

This is compactly written as  $\hat{H}\Psi(x, t) = i\hbar \frac{\partial}{\partial t} \Psi(x, t)$ , where  $\hat{H}$  is called the Hamiltonian operator. This operator is one of the most important objects in quantum mechanics, and it provides a full description of a given system.

The Schrödinger equation can be simplified when the Hamiltonian is time-independent. In these cases, the time- and space-dependence can be separated into two different equations: this technique is known as **separation of variables**. Let us assume a factorized form for the wavefunction,  $\Psi(x, t) = \psi(x)f(t)$ . Substituting this form into the Schrödinger equation and dividing through by  $\Psi(x, t)$ , we find that the left-hand-side only depends on space, whereas the right-hand-side only depends on time:

$$\frac{1}{\psi(x)} \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) + V(x) \right] = \frac{i\hbar}{f(t)} \frac{\partial}{\partial t} f(t). \quad (1)$$

This is only possible if both sides are separately equal to the same constant,  $E$ :

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

The first of these equations is readily solved to give  $f(t) = e^{-\frac{i}{\hbar} E t}$ . Comparing to a free-particle solution, this shows that the constant  $E$  can be interpreted as the energy of the system. The second equation is known as the **time-independent Schrödinger equation (TISE)**, and is determined by the specific form of the potential  $V(x)$ . The key features of any particular system are fully encoded in the TISE: the time-dependence can always be reinstated by multiplying by  $f(t)$ . Hence, from now on we will focus on solving this equation, calculating  $\psi(x)$  for some model systems.

A solution  $\psi(x)$  to the TISE must satisfy certain **boundary conditions**. In order for the probability density  $|\Psi(x, t)|^2$  to be single-valued, the wavefunction  $\psi(x)$  needs to be continuous everywhere. Furthermore, for any finite potential  $V(x)$ ,  $d\psi(x)/dx$  must also be continuous to prevent  $d^2\psi(x)/dx^2$ , appearing in the TISE, from taking an infinite value. The only exception to this is when  $V(x) = \infty$ , as we will see in Section 4,

### 2 EIGENVALUES AND EIGENFUNCTIONS

We are interested in solving  $\hat{H}\psi(x) = E\psi(x)$ . This equation is reminiscent of **eigenvalue** problems in linear algebra,  $A v = \lambda v$ ,

where  $A$  is a square matrix and  $v$  a vector. Here, the operator  $\hat{H}$  corresponds to the matrix and the function  $\psi(x)$  corresponds to the vector.  $E$  is said to be the eigenvalue associated to the eigenfunction  $\psi(x)$ . Each  $\hat{H}$  will allow a certain number of eigenfunctions which correspond to the **quantum states** of the system. The associated eigenvalues  $E$  are the **energy levels** of the system.

### 3 PARTICLE IN A CONSTANT POTENTIAL

One of the simplest examples in which the Schrödinger equation can be solved analytically is the case where a uniform potential  $V(x) = V_0$  acts on a particle in 1-Dimensional space. In this case, the time-independent Schrödinger equation reduces to:

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V_0 \psi(x) = E \psi(x). \quad (3)$$

The equation can be written in the form  $\frac{d^2 \psi(x)}{dx^2} = -k^2 \psi(x)$ , where  $k = \sqrt{\frac{2m(E - V_0)}{\hbar^2}}$ . This equation is familiar from the theory of the classical harmonic oscillator, and the general solution is given by:

$$\psi(x) = A e^{ikx} + B e^{-ikx}, \quad (4)$$

where  $A$  and  $B$  are constants. When  $V_0 < E$ , these solution describes left- and right- traveling waves in free space. However, if  $V_0 > E$ , we see that  $k$  becomes imaginary and the general solution (4) consists of exponential growth and decay. Thus, when the energy is greater than the potential we get oscillating solutions, whereas when the energy is smaller than the potential we get a decaying wavefunction (the exponential growth is not a physical solution).

### 4 PARTICLE IN A BOX

We consider a free particle confined to move along a line segment in one dimension with two impenetrable barriers at each end. This model is described with the potential:

$$V(x) = \begin{cases} 0, & \text{for } 0 \leq x \leq L \\ \infty, & \text{for } x < 0 \text{ and } x > L, \end{cases}$$

and is visualised in Figure (1).

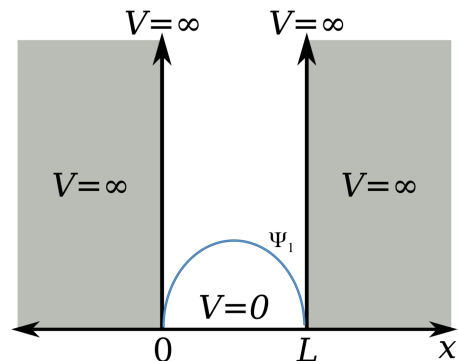


Figure 1: The infinite square well. Source: wiki

We wish to evaluate the allowed energies and wavefunctions of the particle confined to this box. To do this, we have to solve the Schrödinger equation inside and outside the box separately. A physically meaningful wavefunction is required to be continuous at the boundaries (where  $x = 0$  and  $x = L$ ). Since the potential outside the box is infinite, to satisfy the Schrödinger equation we must impose that the wavefunction is zero everywhere outside the box and at the boundaries ( $\psi = 0$  for  $0 \geq x \geq L$ ). This requirement and the boundary conditions constrain the allowed wavefunctions and energy levels to be:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \quad E_n = \frac{n^2 h^2}{8mL^2}. \quad (5)$$

These are labelled by an integer  $n$ , a **quantum number**. We consider a particle described by the wavefunction  $\psi_n(x)$  to have energy  $E_n$ . Where  $n = 1$ , we describe the **ground state** i.e. the lowest allowed energy state of a particle confined inside this box. Again, the Schrödinger equation for this system produces a set of discrete (quantised) allowed energies.

Notice that decreasing the size of the box leads to a higher energy. This can be interpreted as a consequence of the uncertainty principle, as the particle is being confined to a smaller region.

## 5 THE FINITE POTENTIAL WELL

If the potential confining the particle is finite, the wavefunction is no longer zero outside the box as this condition is no longer required by the Schrödinger equation. Consider the potential:

$$V(x) = \begin{cases} 0, & \text{for } 0 \leq x \leq L \\ V, & \text{for } x < 0 \text{ and } x > L. \end{cases} \quad (6)$$

The procedure for solving this Schrödinger equation is analogous to the previous case, however the boundary conditions are different. The wavefunction still needs to be continuous at the interface, but in addition the first derivative also must be continuous. This enforces that the second derivative, appearing in the Schrödinger equation, is well defined.

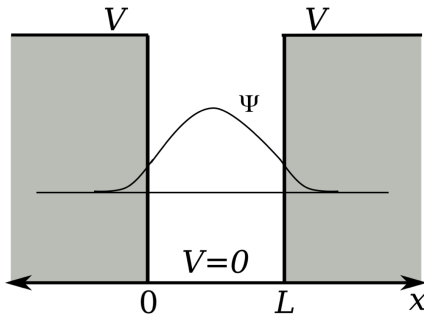


Figure 2: The finite potential well and the ground state wavefunction.

From the solution for a particle in a constant potential (Section 3), we see that the solution decays exponentially in the region where  $V(x) = V$ , whereas in the region where  $V(x) = 0$ , the solution is oscillatory. Matching these wavefunctions leads to solutions of the form displayed in Fig. (5). Remarkably, there is a non-zero

probability for the particle to be in the classically forbidden region outside the box even when  $E < V$ .

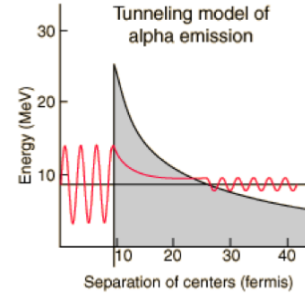


Figure 2: Illustration of quantum tunnelling: emission of an alpha particle from an atomic nucleus.

A quantum particle can thus **tunnel** through a classically forbidden region ( $E < V$ ) and escape from a finite potential: for example, this occurs when an **alpha particle** is emitted from an atomic nucleus (Fig. (5)). Quantum tunnelling can also drastically affect the rate of chemical reactions, as illustrated by the **kinetic isotope effect**. Moreover, quantum tunnelling has important technological applications, such as scanning tunnelling microscopy.

## 6 QUANTUM HARMONIC OSCILLATOR

Another canonical physical system for which we can solve the Schrödinger equation is the quantum harmonic oscillator, defined by the potential  $V(x) = \frac{1}{2}m\omega^2 x^2$ . Explicitly, the Schrödinger equation reads:

$$-\frac{\hbar}{2m} \frac{d^2\psi}{dx^2} + \frac{\omega^2 x^2}{2} \psi = E\psi \quad (7)$$

The procedure to solve this equation is a little more complicated than for the previous examples, but it can be solved using use of series solutions for differential equations. The solutions turn out to be given in terms of a set of functions, known as Hermite polynomials, multiplied by a Gaussian. For illustration, we give the form of the ground state:

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-m\omega x^2/2\hbar}, \quad E_0 = \frac{\hbar\omega}{2}, \quad (8)$$

and the first excited state:

$$\psi_1(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \sqrt{\frac{2m\omega}{\hbar}} x e^{-m\omega x^2/2\hbar}, \quad E_1 = \frac{3\hbar\omega}{2}. \quad (9)$$

It can be verified by substitution that these solve the Schrödinger equation. The general energy levels are given by:

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega. \quad (10)$$

We find that energy levels are separated by  $\hbar\omega$  and that the lowest energy state, given by  $n = 0$  is non-zero. The latter is called **zero-point energy** and is an intrinsically quantum phenomenon.

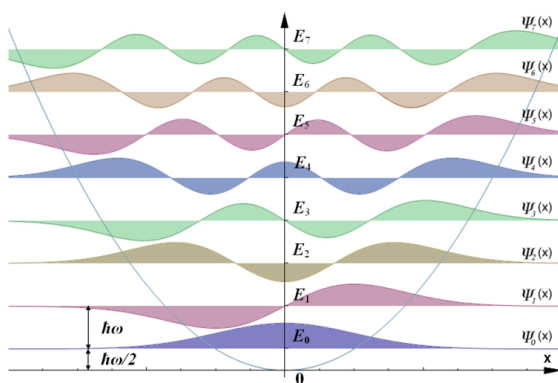


Figure 3: The first 8 allowed eigenstates of the quantum harmonic oscillator. Source: wiki

## 7 KEY POINTS

- The main aim of solving the Schrödinger equation is to find the allowed wavefunctions and their energies for a given Hamiltonian.
- If the Hamiltonian is time-independent, we can separate variables in the Schrödinger equation and consider just the time-independent part, the time dependence is trivial.
- Quantum states obtained from the Schrödinger equation can show properties that differ to classical expectations.

## 8 EXTRA: THE HYDROGEN ATOM

In a similar fashion to the quantum harmonic oscillator, the Schrödinger equation for the hydrogen atom can be solved. This requires more mathematical techniques, including the use of spherical harmonics and Legendre polynomials. A key step is the separation of variables, considering the radial and angular dependence,

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi), \quad (11)$$

where  $\psi$  is the time-independent wavefunction as a function of **spherical coordinates**. This produces two differential equations, one for the radial component  $R(r)$  and another for the spherical component  $Y(\theta, \phi)$ .

It is found that the eigenstates are no longer labeled by a single number  $n$ , but by a triplet of **quantum numbers**  $n, l, m$ . The energies of the eigenstates are solved to be,

$$E_n = -\frac{\mu Z e^2 r}{8\epsilon_0^2 h^2 n^2} \quad (12)$$

which is a function of  $n$  only. Here,  $Z$  is the atomic number and  $\mu$  is the reduced mass  $\mu = \left(\frac{m_1 m_2}{m_1 + m_2}\right)$ . The  $l$  quantum numbers are sometimes labelled with letters,  $0 = s, 1 = p, 2 = d, 3 = f$  and so on, these correspond to orbitals in chemistry.