Abstract

In this research group project we discussed the role of differential equations in quantum mechanics. We introduced the time-independent Schrödinger equation and studied it as a Sturm-Liouville problem for some examples of the potential. We started with the infinite square well problem and looked into the asymptotic special case of the free particle.
We studied the quantum harmonic oscillator using both analytical techniques and operator algebra; we put emphasis on the general nature of the solution of this problem which can be used to approximate the minimum of any potential. We compared classical and quantum approach while underlining the behaviour of particles as waves.
Throughout this process, we discussed some general properties of the wave function such as the probabilistic interpretation of its square module and the orthonormality of its eigenstates. This brought us to consider the space of square-integrable functions, some limited aspects of measure theory as well as general vector space theory. We made use of elements of Fourier theory, the theory of Hermite polynomials, statistics and linear algebra. We applied the superposition principle in concrete examples to underline the probabilistic interpretation but also more in general through the inverse of the Fourier transform.
Our main goal was to make this project as applied as possible, so we included several examples and a chapter dedicated to numerical methods in which we solved the problem of the infinite square well and of the quantum harmonic oscillator. Using Matlab and Python, we implemented the diagonalisation method as well as the shooting method via the Runge-Kutta. We also introduced the mathematics behind these methods while briefly discussing their effectiveness.

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CHAPTER 1

Introduction

Differential equations are widely used in several fields such as Physics, Engineering, Finance and Biology. Let's just think at models used to predict the spread of viruses or at option pricing with the famous Black-Scholes equation or at Newton's Law of Cooling: the implications that differential equations have in our lives are profound! In Physics, differential equations are like buildings blocks which can be used to analyse phenomena, from atoms up to black-holes. In this project we looked at the former; in particular, we analysed within some limited cases the law of mechanics that hold for *very small* particles. With this goal in mind, we introduced the Schrödinger equation, named after Erwin Schrödinger who was a Nobel prize winning physicist. More in general we call *quantum mechanics* the mechanics that governs small entities such as atoms, electrons and other subatomic particles.

However, here comes the first subtlety: small particles do not behave just like small particles, but they also behave as waves. Intuitively, we could motivate this by thinking at an astronaut approaching the Earth from the Space: from her perspective, our planet will appear like a small particle when she's far away. As she moves closer, more details will begin to emerge. Hence, in order to model the behaviour of the particle when you are far away you use a simplified version of the model that you need when you want to measure the interactions between entities at the atomic level.

Historically, the theory of quantum mechanics was gradually developed throughout the last 150 years by various physicists. Other than Schrödinger, among them we have Max Planck, Albert Einstein, Niels Bohr, Louis de Broglie, Max Born, Johann Von Neumann, Paul Dirac, Werner Heisenberg, Wolfgang Pauli and Richard Feynman. An important milestone in the development of quantum mechanics was the concept of black-body, which is an idealised physical object that absorbs (and emits) *all* incident electromagnetic radiation, independently from factors such as frequency or angle of incidence. This object was at the center of the so called *ultraviolet catastrophe*. In fact, around 1900 Rayleigh and Jeans developed a law to approximate the spectral radiance of electromagnetic radiation from a black body using a classical approach. However, this law diverges from empirical evidence as we reach the ultraviolet region of the electromagnetic spectrum.

By analysing this problem, Max Plank was able to realise that radiation was given in the form of discrete packets of energy which are known as quanta. The concept of *discrete energy* was further developed by Einstein who in 1905 explained the photoelectric effect discovered by Heinrich Hertz. Einstein theorised that all electromagnetic radiation is shared into quanta, which take the form of photons (later named by Gilbert N. Lewis in 1926). Einstein was able to show that electrons are released when specific frequencies that are equal to multiples of Planck's constant are reached. More recent experiments demonstrated how a beam of electrons forms an interference pattern, something which implies that electrons collectively behave like a wave.

In 1926, Born argued that the wave function used to describe the behaviour of particles does not have a specific physical meaning while its square module can be interpreted as a probability distribution. This gives birth to what we refer to as the probabilistic interpretation of quantum mechanics and it can be considered another extremely significant milestone,

together with the concept of discretisation of energy and wave-particle duality. Johann Von Neumann [Rod19] further developed Born's approach by defining among other things the concept of probability of possible measurement outcomes. In fact, he introduced what we call today "operator algebra" which is a fundamental tool used to solve very complicated problems. Both the probabilistic interpretation and the operator algebra represent a crucial juncture between Mathematics and Physics.
Another important physicist, Schrödinger, showed great interest in the philosophical aspects of science and came up with the "Schrödinger's cat paradox" - a theoretical experiment to show the paradox of quantum superposition. The cat is imagined to be left in a steel box with a Geiger counter which detects radioactivity, a flask of poison, a hammer and a radioactive substance. Once the radioactive substance is decayed, the Geiger is able to detect it and the hammer drops and breaks the flask causing the poison to kill the cat. Until the box is opened, no one knows whether the cat is alive or dead because this depends on the random process of decay of the radioactive substance inside the box and there is truly *no way* to find out when the radioactive substance will decay. This is why, unless the box is opened to observe the cat, it is assumed that the the cat is in some superposition state of being *both* dead and alive. Once the cat is observed, there is a definite answer of the cat being alive, or the cat being dead, but not both. Similarly, a wave function for a particle has a probability of being in any position, but unless you observe it you don't really know where it's placed. This is why its position could be *anywhere* with maybe the tiniest probability.
Over the past years, one of the fundamental question has been whether quantum physics is deterministic or stochastic. Determinism is the view that all events, including human actions, occur due to previous causes and it excludes the choice of free will. Stochastic is the opposite and suggests that events occur in a random manner. It makes us wonder, what part of quantum physics is real and which parts are measured and so, in a way, "manipulated" by experiments.
While our dissertation only focuses on part of the mathematics underlying the topic, discussions on the interpretation of quantum mechanics seem to be endless [EPR35; t H20]. This is part of the everlasting fascination of this subject, and we further comment on this in our **Conclusions**.

1.1 Outline

The rest of the text is organised as follows:

Chapter 2 This chapter gives an overview of the Schrödinger equation and the associated wave function: key concepts of Mathematics and Physics such as the statistical interpretation of quantum mechanics or the normalisation process of a wave function are introduced. All the topics treated in this chapter will become very handy later in Chapter 3. An expert reader might choose to skip this chapter and go directly to Chapter 3.

Chapter 3 This chapter forms the main skeleton of this project. We introduce the time independent Schrödinger equation and immediately consider different concrete scenarios. We start with the infinite square well followed by its asymptotic counterpart, the free particle. We generalise some properties of the wave function and consider different case studies and applications.
In the second part of this chapter we move our attention to the quantum harmonic oscillator. We approach this problem using two methods. This section should be read while carefully considering Appendix C where we motivate some analytical results and some of the mathematical theory behind operators and L^p functions. We conclude the chapter with an application on the comparison between classical and harmonic oscillator.

Chapter 4 Chapter four is fully dedicated to the practical resolution of problems analysed in the previous chapter using numerical techniques. We start by solving the infinite square well problem with the help of the diagonalisation method and give particular attention to the normalisation process of the wave function. Thereafter, we apply the shooting method implemented via RK4 recursion. In this chapter, a lot of the concepts previously discussed are condensed and applied directly with the help of various numerical methods. Finally, we look briefly at a modern application of quantum mechanics, quantum computing.

Appendix A In this appendix we comment on Chapter 3 (in particular on the section about the free particle) by looking in more detail into Fourier series and Fourier transform.

Appendix B This appendix supports Chapter 4 as we analyse with more attention matrix diagonalisation and Simpson rule.

Appendix C This appendix gives a theoretical overview of the main definitions and theorems that one has to consider to fully understand the implications of the problems solved in Chapter 3. The focus is on vector spaces, operator algebra and Hermite polynomials.

Appendix D This appendix contains the code developed for Chapter 4.

Note: In this project we followed quite closely [Gri94]. In addition, we consulted various sources such as the lecture notes on quantum mechanics available on MIT OpenCourseWare. The complete bibliography can be found at the end.

CHAPTER 2

The wave function

2.1 The Schrödinger equation

The goal of this chapter is to introduce the Schrödinger equation with the associated wave function: we present fundamental concepts such as the statistical interpretation of quantum mechanics or the normalisation process of a wave function. In this chapter we based our work on [Gri94; Lib02; MIT17c; MIT17d; MITnd; Zwi16c; Zwi16e].
Let's start by looking at a particle of mass m, subject to a force $F(x)$ and constrained to move along the x axis as shown in figure 2.1. The classical approach to solve this problem

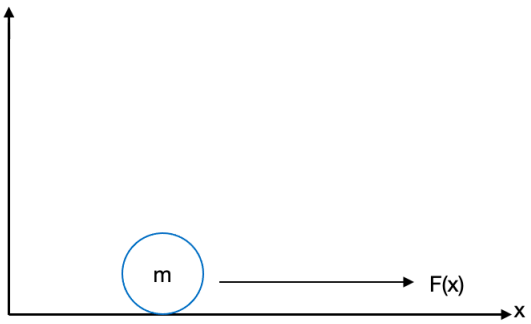


Figure 2.1: Particle moving along the x axis subject to a force $F(x)$

would be to first identify $x(t)$, the position of the particle at any given time. We can derive it by applying Newton's Second Law

$$F = ma, \tag{2.1}$$

where a is the acceleration of the particle, defined by $a = \frac{d^2x}{dt^2}$. This gives us a second order ordinary differential equation

$$F(x) = m\frac{d^2x}{dt^2} \tag{2.2}$$

We can also consider the energy of the system. For conservative systems, the force is defined as the derivative of the potential energy function V:

$$F(x) = -\frac{\partial V}{\partial x} \tag{2.3}$$

Note that the negative sign arises as the potential energy is the work done against the force. Now, by equating equation 2.3 with equation 2.2 we get:

$$m\frac{d^2x}{dt^2} = -\frac{\partial V}{\partial x} \tag{2.4}$$

The next step would be to use the appropriate initial conditions to work out the exact solution: typically, the initial conditions would specify position or velocity $v = \frac{dx}{dt}$ of the particle at time $t = 0$. In the initial value problem described by (2.4), V depends on the problem at hand. Any variables of interest can also be derived, for example momentum $p = m\frac{dx}{dt}$ or kinetic energy $E_{kin} = \frac{p^2}{2m}$.

Quantum Mechanics approaches the problem of describing the dynamics of a particle by using the concept of wave-particle duality. This means that every quantum entity may be viewed as a particle *or* as a wave. In optic, the light diffracts if we try to pass it through a small hole: that light which is split up and travels along different paths, interferes when it is recombined. This behaviour is typical of waves. On the other hand, other phenomena such as the discrete clicks from the photo-multiplier tube suggest that light behaves in the same way as a particle.

Therefore, in quantum mechanics in order to describe the behaviour of a particle with respect to any observer, we introduce the concept of wave function $\Psi(x,t)$ which represents an observer's subjective knowledge of the system. In other words, $\Psi(x,t)$ is the analogous of $x(t)$ in the classical world.

Although all the information about a particle can be described by a wave function, it's not possible to extract it through measurements as this would alter the state of the quantum system. This principle is summarised by the Schrödinger cat paradox, which we introduced earlier: any attempts to interact with the system (opening the box where the cat lies) would kill the cat. This is formalised by the fact that any physical observable is expressed by an operator, while the value obtained with a measurement of the physical observable will be an eigenvalue for that operator. This marks a first strong difference between classical and quantum physics: a wave function that describes a quantum system (or more specifically its square module) is proportional to the probability relative to different measurement results. On the other hand, in classical physics position and momentum of a particle together with knowledge of the external potential predict exactly the behaviour of the particle for all future times. The randomness associated with the dynamics of a particle in a quantum system can also be explained through *Heisenberg's uncertainty principle*:

$$\Delta x \Delta p \geq \frac{h}{4\pi} = \frac{\hbar}{2} \tag{2.5}$$

where Δx and Δp describe the uncertainty of x respectively p while $\hbar = \frac{h}{2\pi} = 1.054573 \cdot 10^{-34}$ J s is the reduced Plank's constant. Heisenberg showed how it's not possible to know the value of all the properties of a quantum system at the same time, since position x and momentum p are inversely proportional. Those properties that are not known with precision must be described by probabilities. To determine how a wave function Ψ evolves in time we use the **Schrödinger equation** given by:

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\Psi(x,t) \tag{2.6}$$

As we will see later, the Schrödinger equation expresses the principle of conservation of energy for the quantum world by equating total energy (LHS) with the sum of kinetic and potential energy (RHS). As we normally do in Classical Physics, we can characterise a system by specifying its potential. In Chapter 3, we will consider different types of potentials and solve the Schrödinger equation for those potentials.

2.2 Probabilistic interpretation

Given the important role of probability theory in quantum mechanics, we will dedicate this section to recall some basic but important concepts of probability and statistics.
Based on Born's statistical interpretation we know that $|\Psi(x,t)|^2 d\mu(x)$ gives the probability of finding a particle at point x, upon measurement at time t. More precisely, the probability of finding a particle between a and b upon measurement at time t is given by

$$\int_a^b |\Psi(x,t)|^2 dx = \int_a^b \Psi^*(x,t)\Psi(x,t)dx \tag{2.7}$$

We should specify that in real life what we normally refer to as a particle is a 3-D object.

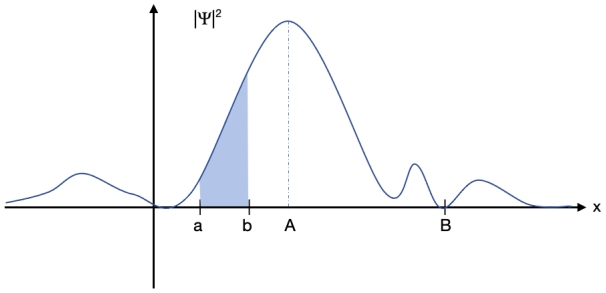


Figure 2.2: Probability of finding a particle between a and b at time t

Therefore, what we stated above for the 1-D case can be expressed more rigorously for the 3-D case as follows: let $A \subset \mathbb{R}^3$, $r \in \mathbb{R}^3$. Then the probability to find a particle in the region A upon measurement at time t can be expressed as

$$\int_A |\Psi(r,t)|^2 dr = \int_A \Psi^*(r,t)\Psi(r,t)dr \tag{2.8}$$

Of course two observations come immediately to mind: first, the expression above has to represent a probability; second, the integral itself needs to be well defined, or more precisely the wave function needs to satisfy certain conditions in order for the integral to exist. In other words, we cannot accept a probability to find a particle in a certain region of 250% or an infinite probability at a certain point. In addition not all functions are integrable. We will come back to these conditions for the wave function once we have introduced other elements. For now we can assume that the expressions above hold provided that the wave function is well defined and it represents a "probability".
Figure 2.2 represents a typical wave function with the shaded area indicating the probability of finding the particle between a and b. It is more likely to find the particle near A while it is unlikely to find the particle near B.
We deduce from equation (2.7) that $|\Psi(x,t)|^2$ can be interpreted as the probability density function for an underlying random variable that describes the position of a particle in a quantum system.
As we said, Max Born first suggested a probabilistic interpretation to describe the dynamic of quantum objects but this wasn't the only interpretation given to the wave function. In fact, Schrödinger thought that the square of the module of the wave function was proportional to the fraction of a particle that could be found at r. We mentioned this to show that the history behind quantum mechanics is not linear and at times multiple interpretations were given to the same phenomena. This suggests that there were also multiple interpretations of the general dynamic of quantum objects. To easily compare them we can consider the question "Where was the particle just before trying to measure its position?". Each answer can be associated with a specific interpretation of quantum mechanics as follows:

- The realist position, that implies that the particle had to be at the same point where it was found by measuring its position.
- The orthodox (or Copenhagen) position, which says that it was the act of measurement that perturbed the system of the particle determining its position. Hence, it's uncertain where the particle was before the measurement.
- The agnostic position, which says that it does not make sense to answer a question whose answer cannot be verified or tested since the measurement happens after "just before the measurement".

The position which collects most of the consensus is the Copenhagen interpretation, which is the one that we will be adopting in this dissertation. To add on to what we mentioned above, we could ask ourselves what happens if we were to make a second measurement immediately following the first one. Well, there is no other answer except that the repeated measurement should gives us back the same value. However, if this is not the case for immediate repeated measurements, the only explanation left is that the first measurement radically alters the wave function, creating a peak in the proximity of point C (Figure 2.3).

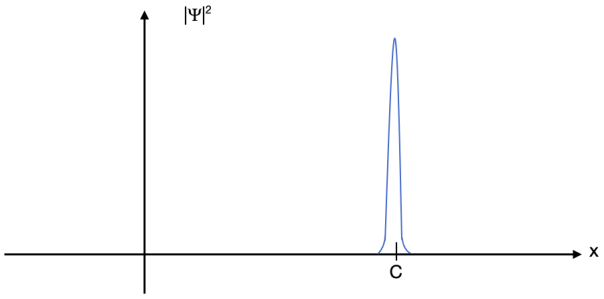


Figure 2.3: The measurement radically alters the wave function

To elaborate on the Copenhagen interpretation, the wave function collapses upon measurement at time t and spikes at point C, which is the point where the particle was measured.

Probability

Let's consider a probability space $(\Omega, \mathcal{A}, P)$. Here Ω denotes the non-empty set of events, $\mathcal{A}$ the corresponding σ-algebra (or "event algebra") while P is the probability measure on Ω (or event space).

Discrete random variables

Using the sigma-additivity property of a general measure and the fact that a probability measure $P: \mathcal{A} \to [0, 1]$, we get that

$$1 = P(\Omega) = P\left(\dot{\bigcup_{j \in \mathcal{J}}} X_j\right) = \sum_{j \in \mathcal{J}} P\left(X_j\right)$$

where $(X_j)_{j \in \mathcal{J}}$ is a disjoint partition, $\mathcal{J}$ is a countable set.
The probability computed at the variable x given the underlying random variable $\mathcal{X}$ is:

$$P(\mathcal{X} = x) = P(w \in \Omega | \mathcal{X}(w) = x) = p_{\mathcal{X}}(x) \tag{2.9}$$

where $p_{\mathcal{X}}$ represents the probability mass function of a given random variable $\mathcal{X}$.
The median is the middle number in a sorted, ascending or descending, list of numbers; the expectation of a discrete random variable $\mathcal{X}$ is given by:

$$< \mathcal{X} >= \sum_{x \in \mathcal{J}} p_{\mathcal{X}}(x)x \tag{2.10}$$

where $\mathcal{J}$ is countable. Within quantum mechanics, we can think at the expected value $< \mathcal{X} >$ as the average of measurements performed on particles which are all in the same state (not necessarily consecutive, since the first measurement will create a spike in the wave function). The variance is given by:

$$Var[\mathcal{X}] = \sum_{x \in \mathcal{J}} (x - < \mathcal{X} >)^2 =< \mathcal{X}^2 > - < \mathcal{X} >^2 \tag{2.11}$$

which is a function of the second and the first statistical moments. The variance is a measure of volatility or uncertainty. The standard deviation $\sigma_{\mathcal{X}}$ is given by the square root of the variance:

$$\sigma_{\mathcal{X}} = \sqrt{\sum_{x \in \mathcal{J}} (x - < \mathcal{X} >)^2} = \sqrt{< \mathcal{X}^2 > - < \mathcal{X} >^2} \tag{2.12}$$

Continuous random variables

Our previous considerations can be generalized to the continuous distribution. Thus, the probability that an event in Ω lies between x and $x + dx$ is given by $\rho(x)dx$ where $\rho(x)$ is the probability density. Hence, the probability that x lies between a and b is given by:

$$P(a \leq \mathcal{X}(w) \leq b) = \int_a^b \rho(x)dx \tag{2.13}$$

The relations which we deducted for discrete distributions apply for continuous distributions in a very similar way:

$$P(\Omega) = \int_{-\infty}^{+\infty} \rho(x)dx = 1 \tag{2.14}$$

$$< \mathcal{X} > = \int_{\mathbb{R}} x\rho(x)dx \tag{2.15}$$

$$Var[\mathcal{X}] = \sigma^2 = \int_{\mathbb{R}} (x - < \mathcal{X} >)^2 dx = < \mathcal{X}^2 > - < \mathcal{X} >^2 \tag{2.16}$$

$$< f(\mathcal{X}) > = \int_{\mathbb{R}} f(x)\rho(x)dx \tag{2.17}$$

for some measurable function f.
We can now go back to equation (2.7) to consider when that expression makes mathematical sense. The wave function $\Psi(x,t)$ in order to be well-defined needs to be an element of the Hilbert space $L^2(\mathbb{R})$ (or square integrable functions) as this assures that the integral in (2.7) is finite; implicitly, we are considering only integrable (or more in general measurable) functions as possible candidates for the $L^2(\mathbb{R})$ space. Since we introduced the notion of probabilistic interpretation we need to operate on a probability space as well. In other words, the probability to find a particle somewhere in all space must be one, i.e. $P(\Omega) = 1$ which implies that for all elements Ψ in $L^2(\mathbb{R})$ holds:

$$\|\Psi\|^2_{L^2(\mathbb{R})} =< \Psi, \Psi >_{L^2(\mathbb{R})} = 1 \tag{2.18}$$

where $< \cdot, \cdot >_{L^2(\mathbb{R})}$ indicates the inner product on L^2, while $\|\cdot\|$ is the induced norm. We explored more in detail concepts such as Hilbert and L^2 spaces in Appendix C.

2.3 Normalisation

As motivated previously, a well-defined wave function needs to be normalised and in this section we will discuss the motivations behind this process which we call normalisation of the wave function. As we will see, this in not only important for applied theoretical problems but also for numerical applications (see Chapter 4).
In any probabilistic space,

$$P(\Omega) = 1 \tag{2.19}$$

For a wave function $\Psi(x,t) \in L^2(\mathbb{R})$, this can be rewritten as

$$\int_{-\infty}^{+\infty} \mid \Psi(x,t) \mid^2 dx = 1 \tag{2.20}$$

Of course, equation (2.20) does not hold for all elements in $L^2(\mathbb{R})$, but we need an extra-condition. Suppose then that we obtain a solution to the Schrödinger equation, say $\Phi(x,t)$. Suppose that the wave function $\Phi(x,t)$ is an element of $L^2(\mathbb{R})$. Then due to the superposition principle we have that $C\Phi(x,t)$ must be a solution as well for any (complex) constant C. If we apply condition (2.20) we obtain

$$1 = \int_{-\infty}^{+\infty} |C|^2 \mid \Phi(x,t) \mid^2 dx = |C|^2 \int_{-\infty}^{+\infty} \mid \Phi(x,t) \mid^2 dx = |C|^2 K \tag{2.21}$$

Note that $K < \infty$ since we took $\Phi \in L^2(\mathbb{R})$. Of course the trivial solution is not an interesting one and we can assume $K \neq 0$. We can then rewrite the equation above as

$$C = +\sqrt{\frac{1}{K}} \tag{2.22}$$

where we take only the positive square root. Note also that K is by construction a positive constant due to the positive definit property of any norm. We can then conclude that C is a real constant as well. In addition, in physics we are looking for real solutions to the Schrödinger equation so we can also assume for $\Phi(x,t)$ to be a real valued function. We can rewrite the (unitary) wave function $\Psi(x,t)$ as

$$\Psi(x,t) = +\sqrt{\frac{1}{K}}\Phi(x,t) \tag{2.23}$$

As we shall see in the next chapters, this process of normalisation will become fundamental to identify the correct set of solutions to the Schrödinger equation.
Another observation is that $\Psi(x,t)$ will tend to zero faster than $\frac{1}{\sqrt{x}}$. This is due to the fact that $\int_{-\infty}^{+\infty} \Psi\Psi^* dx$ must be equal to 1 (to normalise the wave function), and in order for this to happen $\Psi(x,t)$ must be in $L^2(\mathbb{R})$. This is not the case for $\frac{1}{\sqrt{x}}$ since $\int_{-\infty}^{+\infty} \frac{1}{\sqrt{x}} \frac{1}{\sqrt{x}} dx$ diverges. Therefore, the wave function Ψ must go to zero faster than $\frac{1}{\sqrt{x}}$ in order for the integral of the square of its module to converge.
An additional property of the wave equation is that it will stay normalised as time moves on. This can be shown by taking the derivative of (2.20) with respect to t on both sides. Let's start by considering

$$\frac{d}{dt} \int_{-\infty}^{+\infty} \mid \Psi(x,t) \mid^2 \ dx = \int_{-\infty}^{+\infty} \frac{\partial}{\partial t} \mid \Psi(x,t) \mid^2 \ dx \tag{2.24}$$

A couple of (trivial) observations: first, note how $\frac{d}{dt}\int_{-\infty}^{+\infty} \mid \Psi(x,t) \mid^2 \, dx$ is independent on x; second, since the wave function is in $L^2(\mathbb{R})$ and we assume its square module to be also differentiable, we are able to bring the derivative inside the integral; third, once we bring the derivative inside the integral, this becomes a partial derivative in t since $\Psi(x,t)$ depends on both x and t.
If we apply the product rule to the expression inside the integral we get that

$$\frac{\partial}{\partial t} \mid \Psi \mid^2 = \frac{\partial}{\partial t}(\Psi^*\Psi) = \Psi^* \frac{\partial \Psi}{\partial t} + \frac{\partial \Psi^*}{\partial t}\Psi \tag{2.25}$$

So, if we go back to the Schrödinger equation (2.6) and rearrange it, we obtain

$$\frac{\partial \Psi}{\partial t} = \frac{i\hbar}{2m}\frac{\partial^2 \Psi}{\partial x^2} - \frac{i}{\hbar}V\Psi \tag{2.26}$$

By taking the complex conjugate we find:

$$\frac{\partial \Psi^*}{\partial t} = -\frac{i\hbar}{2m}\frac{\partial^2 \Psi^*}{\partial x^2} + \frac{i}{\hbar}V\Psi^* \tag{2.27}$$

Therefore, by substituting equations (2.27),(2.26) into equation (2.25) we get

$$\begin{aligned} \frac{\partial}{\partial t} \mid \Psi \mid^2 &= \Psi^* \frac{\partial \Psi}{\partial t} + \frac{\partial \Psi^*}{\partial t}\Psi \\ &= \Psi^* \left(\frac{i\hbar}{2m}\frac{\partial^2 \Psi}{\partial x^2} - \frac{i}{\hbar}V\Psi \right) + \Psi \left(-\frac{i\hbar}{2m}\frac{\partial^2 \Psi^*}{\partial x^2} + \frac{i}{\hbar}V\Psi^* \right) \\ &= \frac{i\hbar}{2m}\left(\Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \frac{\partial^2 \Psi^*}{\partial x^2}\Psi \right) \end{aligned} \tag{2.28}$$

Hence by adding and subtracting a factor $\frac{\partial \Psi^*}{\partial x}\frac{\partial \Psi}{\partial x}$ we get,

$$\begin{aligned} \frac{\partial}{\partial t} \mid \Psi \mid^2 &= \frac{i\hbar}{2m}\left(\Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \frac{\partial^2 \Psi^*}{\partial x^2}\Psi \right) \\ &= \frac{i\hbar}{2m}\left(\frac{\partial \Psi^*}{\partial x}\frac{\partial \Psi}{\partial x} - \frac{\partial \Psi}{\partial x}\frac{\partial \Psi^*}{\partial x} \right) + \frac{i\hbar}{2m}\left(\Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \frac{\partial^2 \Psi^*}{\partial x^2}\Psi \right) \end{aligned} \tag{2.29}$$

By using the product rule, we can extract the factor $\frac{\partial}{\partial x}$ to obtain:

$$\frac{\partial}{\partial t} \mid \Psi \mid^2 = \frac{\partial}{\partial x}\left[\frac{i\hbar}{2m}\left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x}\Psi \right) \right] \tag{2.30}$$

The integral can then be computed explicitly using equation (2.30):

$$\frac{d}{dt}\int_{-\infty}^{+\infty} \mid \Psi(x,t) \mid^2 dx = \int_{-\infty}^{+\infty} \frac{\partial}{\partial t} \mid \Psi(x,t) \mid^2 dx = \frac{i\hbar}{2m}\left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x}\Psi \right)\Big|_{-\infty}^{+\infty} \tag{2.31}$$

To be normalisable the wave function $\Psi(x,t)$ must tend to zero as x goes to $\pm\infty$ since if we take the derivative to the the LHS of equation 2.20 we get

$$\frac{d}{dt}\int_{-\infty}^{+\infty} \mid \Psi(x,t) \mid^2 \, dx = \frac{d1}{dt} = 0 \tag{2.32}$$

for this to be true, it must be that

$$\frac{d}{dt}\int_{-\infty}^{+\infty} \mid \Psi(x,t) \mid^2 \, dx = 0 \tag{2.33}$$

This shows that this integral is independent of time and therefore constant and confirms that the wave function continues to be normalised even if x evolves with time.

2.4 Momentum

As mentioned before, the expected position of x is described by

$$< x >_\Psi = \int_{-\infty}^{\infty} x|\psi(x,t)|^2 dx \tag{2.34}$$

There can be confusion of what x may mean. It can be misinterpreted which may lead some to believe that x is found by repeating the same measurements of a particle and then obtaining the mean from that. The correct way of defining x is taking the average measurement of various measurements of different particles that are in the same state. Let Ψ be a wave function in $L^2(\mathbb{R})$, then the expected velocity $< v >_\Psi$ with respect to Ψ can be defined as

$$< v >_\Psi = \frac{d\langle x\rangle_\Psi}{dt} = \frac{d}{dt}\int_{-\infty}^{\infty} x|\psi(x,t)|^2 dx = \int_{-\infty}^{\infty} x\frac{\partial}{\partial t}(\Psi^*(x,t)\Psi(x,t))dx \tag{2.35}$$

Using equation (2.30) -and implicitly the Schrödinger equation- we can compute $\frac{\partial}{\partial t}(\Psi^*(x,t)\Psi(x,t))$ that leads to:

$$< v >_\Psi = \frac{d\langle x\rangle_\Psi}{dt} = \frac{i\hbar}{2m}\int_{-\infty}^{\infty} x\frac{\partial}{\partial x}\left(\frac{\partial\Psi}{\partial x}\Psi^* - \Psi\frac{\partial\Psi^*}{\partial x}\right)dx \tag{2.36}$$

Let's define $\beta := (\frac{\partial\Psi}{\partial x}\Psi^* - \Psi\frac{\partial\Psi^*}{\partial x})$. By using integration by part we get:

$$< v >_\Psi = \frac{d\langle x\rangle_\Psi}{dt} = \frac{i\hbar}{2m}\left(\beta\Big|_{-\infty}^{+\infty} x - \int_{\mathbb{R}}\beta dx\right) = -\frac{i\hbar}{2m}\int_{\mathbb{R}}\beta(\Psi)dx \tag{2.37}$$

since we can assume that β goes to 0 at $\pm\infty$. By integrating by part the term $\Psi\frac{\partial\Psi^*}{\partial x}$ in β, and by the linearity of the integral we get:

$$\begin{aligned} < v >_\Psi &= -\frac{i\hbar}{2m}\int_{\mathbb{R}}\beta(\Psi)dx = -\frac{i\hbar}{2m}\int_{\mathbb{R}}\left(\frac{\partial\Psi}{\partial x}\Psi^* - \Psi\frac{\partial\Psi^*}{\partial x}\right)dx \\ &= -\frac{i\hbar}{2m}\left(\int_{\mathbb{R}}\Psi^*\frac{\partial\Psi}{\partial x}dx - \Psi(\Psi^*\Big|_{\mathbb{R}}\right) + \int_{\mathbb{R}}\Psi^*\frac{\partial\Psi}{\partial x}dx \end{aligned} \tag{2.38}$$

Assuming that $\Psi\left(\Psi^*\Big|_{\mathbb{R}}\right)$ goes to 0 we obtain:

$$< v >_\Psi = \frac{d\langle x\rangle}{dt} = -\frac{i\hbar}{m}\int_{\mathbb{R}}\Psi^*\frac{\partial\Psi}{\partial x}dx \tag{2.39}$$

The expected momentum $< p >_\Psi$ defined as $m < v >_\Psi$ is then:

$$< p >_\Psi = m < v >_\Psi = -i\hbar\int_{\mathbb{R}}\Psi^*\frac{\partial\Psi}{\partial x}dx \tag{2.40}$$

Notice how the expected position $< x >_\Psi$ can be written as

$$< x >_\Psi = \int_{\mathbb{R}}\Psi^* x\Psi dx \tag{2.41}$$

which implies that the expected momentum becomes

$$< p >_\Psi = \int_{\mathbb{R}} \Psi^* \left(-i\hbar \frac{\partial}{\partial x} \right) \Psi dx = -i\hbar \left\langle \frac{\partial}{\partial x} \right\rangle_\Psi \tag{2.42}$$

Notice that this relation holds for any operators, and not just for the expectation operator. This implies that given the position operator $\hat{x}$, we have that the momentum operator is defined by

$$\hat{p} := -i\hbar \frac{\partial}{\partial \hat{x}} \tag{2.43}$$

For simplicity, we can leave out the *hat* from the position operator. Using the identity $E_{kin} = \frac{p^2}{2m}$ we get that the expected kinetic energy is:

$$< E_{kin} >_\Psi = \frac{< p >_\Psi^2}{2m} = -\frac{\hbar^2}{2m} \int_{\mathbb{R}} \Psi^* \frac{\partial^2 \Psi}{\partial x^2} dx = -\frac{\hbar^2}{2m} \left\langle \frac{\partial^2}{\partial x^2} \right\rangle_\Psi \tag{2.44}$$

CHAPTER 3

Time-independent Schrödinger equation

In this chapter we introduce the time independent Schrödinger equation and consider different applications, namely the infinite square well, the free particle and the quantum harmonic oscillator. This chapter is based on [Ada13; Gri94; Lib02; Sch16b; Zwi16a; Zwi16f; Zwi16g].

Let's start by considering the Schrödinger equation for the wave function $\Psi(r,t)\ \forall r \in \mathbb{R}^3$:

$$i\hbar\frac{\partial}{\partial t}\Psi(r,t) = \hat{H}\Psi(r,t) \tag{3.1}$$

where $\hat{H} := -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + V(r)$ is the Hamiltonian operator that describes the sum over operators for kinetic[1] and potential energy V. The equation above describes how the wave function $\Psi(r,t)$ evolves in time. The potential $V(r)$ is time independent since by definition it depends only on the position r of a certain particle in the system. The eigenstates of the Hamiltonian $\hat{H}$ contain information about the total energy that each state can take. Similarly, the eigenvalues of the Hamiltonian describe the energy levels for the system.
Often in physics we analyse a wave by taking a snapshot of it at a certain time. In this case, the goal is to find a solution of the Schrödinger equation that is independent of time t. Hence, let's focus on waves for which position and time are "independent" from each other, meaning that they factorise. Define:

$$\Psi(r,t) = g(t)\psi(r) \tag{3.2}$$

for some g,$\psi(r)$. By substituting back in the Schrödinger equation we get:

$$\left(i\hbar\frac{\partial g(t)}{\partial t}\right)\psi(r) = g(t)\hat{H}\psi(r) \tag{3.3}$$

Assuming that $g(t)$ and $\psi(t)$ are not zero $\forall\ t, r$, we can divide by $\Psi(r,t) = \psi(r)g(t)$ on both sides:

$$i\hbar\frac{1}{g(t)}\frac{\partial g(t)}{\partial t} = \frac{1}{\psi(r)}\hat{H}\psi(r) \tag{3.4}$$

Since the left hand side depends only on t, while the right hand side[2] only on r, we can conclude that there exists a constant level of energy E -an eigenvalue- such that:

$$\begin{cases} i\hbar\frac{1}{g(t)}\frac{\partial g(t)}{\partial t} = E \\ \frac{\hat{H}\psi(r)}{\psi(r)} = E \end{cases} \tag{3.5}$$

[1] The momentum is defined via the equation $\hat{p}\Psi = i\hbar\frac{\partial}{\partial r}\Psi$. Hence, $\hat{E}_{kin}\Psi = \frac{\hat{p}^2}{2m}\Psi = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}\Psi$

[2] For this to be true the potential V needs to be time independent

$$\begin{cases} i\hbar\frac{\partial g(t)}{\partial t} = Eg(t) \\ \hat{H}\psi(r) = E\psi(r) \end{cases} \tag{3.6}$$

The equations above show that E is in fact an eigenvalue for the operators $\hat{H}$ and $\frac{d}{dt}$ respectively. By solving for t using separation of variables we get

$$g(t) = e^{-i\frac{Et}{\hbar}} \tag{3.7}$$

This means that the eigenstate of the system $\Psi(r,t)$ acquires a phase $g(t) = e^{-i\frac{Et}{\hbar}}$ for some eigenvalue E. On the other hand, the time-independent Schrödinger equation (TISE) is given, $\forall r \in \mathbb{R}^3$, by:

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + V(r)\right)\psi(r) = E\psi(r) \tag{3.8}$$

It follows that the final solution to equation (3.1) is given by

$$\Psi(r,t) = e^{-i\frac{Et}{\hbar}}\psi(r) \tag{3.9}$$

such that

$$\hat{H}\psi(r) = E\psi(r) \quad \text{for some eigenvalues } E \tag{3.10}$$

As mentioned before, E is an eigenvalue of the TISE and this means it is also an eigenvalue of

$$\hat{H}\Psi(r) = E\Psi(r) \tag{3.11}$$

since we just multiply by $g(t)$ on both sides of equation (3.8). In order for $\Psi(r,t) = e^{-i\frac{Et}{\hbar}}\psi(r)$ to be a well defined solution we need to verify that its norm over $L^2(\mathbb{R})$ is 1. Hence,

$$\begin{aligned} 1 &\overset{!}{=} \int_{\mathbb{R}^3} \Psi^*(r,t)\Psi(r,t)dr \\ &= \int_{\mathbb{R}^3} \psi^*(r)\psi(r)e^{i\frac{E^*t}{\hbar}}e^{-i\frac{Et}{\hbar}}dr \\ &= e^{i\frac{(E^*-E)t}{\hbar}}\int_{\mathbb{R}^3} \psi^*(r)\psi(r)dr \end{aligned} \tag{3.12}$$

Therefore $E^* = E \Leftrightarrow E \in \mathbb{R}$. This is consistent with the interpretation of the eigenvalue E as a constant energy level for the Hamiltonian. If we apply the expectation operator $<>_\Psi$ to the Hamiltonian $\hat{H}$ we get:

$$< \hat{H} >_\Psi = \int_{\mathbb{R}^3} \Psi^*(r,t)\hat{H}\Psi(r,t)dr = \int_{\mathbb{R}^3} \Psi^*(r,t)E\Psi(r,t)dr = E \tag{3.13}$$

This is equivalent to say that the eigenstate E of the operator $\hat{H}$ coincides with the expected value of the Hamiltonian. Similarly,

$$\begin{aligned} < \hat{H}^2 >_\Psi &= \int_{\mathbb{R}^3} \Psi^*(r,t)\hat{H}^2\Psi(r,t)dr = \int_{\mathbb{R}^3} \Psi^*(r,t)\hat{H}(E\Psi(r,t))dr \\ &= E\int_{\mathbb{R}^3} \Psi^*(r,t)E\Psi(r,t)dr = E^2 \end{aligned} \tag{3.14}$$

This means that the variance operator $Var[]_\Psi$ applied to the Hamiltonian $\hat{H}$ gives

$$Var[\hat{H}]_\Psi = < \hat{H}^2 >_\Psi - < \hat{H} >_\Psi^2 = E^2 - E^2 = 0 \tag{3.15}$$

In other words, the volatility of this state with eigenvalue E is 0. The probability to find a particle between a,b $\in \mathbb{R}^3$ becomes then:

$$\iiint_a^b \Psi^*(r,t)\Psi(r,t)dr = \iiint_a^b e^{i\frac{E^*t}{\hbar}}\psi^*(r)e^{-i\frac{E^*t}{\hbar}}\psi(r)dr = \iiint_a^b \psi^*(r)\psi(r)dr \tag{3.16}$$

This implies again that the probability of finding a particle in a given state does not change with the time. Finding the energy eigenstates and eigenvalues by solving the time-independent Schrödinger equation allows us to identify the state of the system for all times. Therefore, what can vary is the potential $V(r)$ which becomes a sort of "boundary condition[3]" for different types of systems.

3.1 Infinite square well

As mentioned previously, in order to obtain an explicit solution from the Schrödinger equation it's necessary to impose some conditions to (3.8) by specifying the potential $V(r)$ for $r \in \mathbb{R}^3$. One of the simplest potentials we can consider $\forall x \in \mathbb{R}$ and real parameters a and b, is given by

$$V(x) = \begin{cases} 0, & \text{if } a \leq x \leq b \\ \infty, & \text{if } x > b,\ x < a \end{cases} \tag{3.17}$$

This problem, named infinite square well, describes the motion of a particle that cannot penetrate the *infinite* walls of the well. It is a very well known problem in quantum mechanics as it can be solved exactly. The broader idea of particles in a box can be applied to electrons in atoms and to their behaviour.

For the potential described above, we can distinguish three states in our system: outside

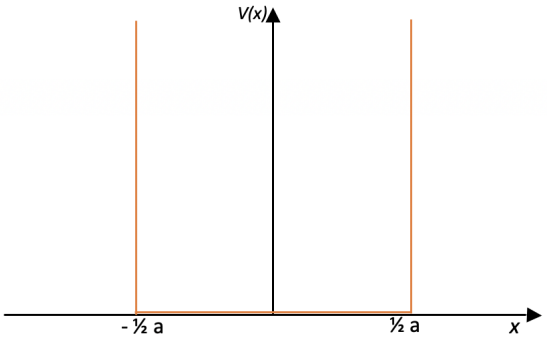


Figure 3.1: Symmetric potential of the infinite square well with infinite potential walls

the well walls, inside the walls and at the points of the walls themselves. Outside the walls the potential energy is infinite and the probability of finding the particle is 0, therefore the wave function must vanish $\forall x \in [a,b]^c$.

In addition, the wave function must be continuous in order to be well defined in the Schrödinger equation, so it must also vanish at $x = a$ and at $x = b$. As a side note, $\psi(x)$ is not continuously differentiable on the interval $[a,b]$. In fact, since we are not considering the trivial solution $\psi(x) = 0$, we cannot have that both $\psi(x_0)$ and $\psi'(x_0)$ are equal zero at $x_0 = a$ or at $x_0 = b$. This would imply that $\psi = 0\ \forall\ x$. Therefore $\psi(x)$ is not differentiable in a and b, meaning that we cannot impose boundary conditions on $\psi'(x)$. Notice that, the particle is completely free except outside the two endpoints a and b.

[3]It is not meant as the typical boundary condition of an initial value problem; on the other hand we can derive these typical boundary conditions thanks to the given potential V

Within the walls the potential energy is $V = 0$, so by plugging this into, the time-independent Schrödinger equation (3.8), we get

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} = E\psi(x) \tag{3.18}$$

This is a second order differential equation, which can be rewritten as

$$\frac{\partial^2\psi(x)}{\partial x^2} = -k^2\psi(x), \tag{3.19}$$

where we define

$$k = \frac{\sqrt{2mE}}{\hbar}, \tag{3.20}$$

Notice that we assume the energy E of our system to be positive as negative energy is not defined in physics. In fact, the existence of negative energy would imply the existence of infinite negative energy which is a contradiction since this would cause the collapse of any systems. The characteristic polynomial of (3.18) is then given by

$$t^2 + k^2 = 0 \tag{3.21}$$

If we solve for t we get $t = \pm ik$, so that the wave function ψ takes the form

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \quad A, B \in \mathbb{C} \tag{3.22}$$

To find a specific solution, we apply the boundary conditions defined by (3.17), meaning that the wave function is equal to zero at the endpoints a and b. Hence,

$$\begin{cases} Ae^{ika} + Be^{-ika} = 0 \\ Ae^{ikb} + Be^{-ikb} = 0 \end{cases}. \tag{3.23}$$

By multiplying each side in (3.23) by e^{-ika} and e^{-ikb}, and by substituting for A, we obtain

$$B(e^{-2ika} - e^{-2ikb}) = 0 \tag{3.24}$$

Since we are not interested in the trivial solution we impose $B \neq 0$, so $e^{2ik(a-b)} = 1 = e^{2i\pi n}$ for $n \in \mathbb{Z}$. By substituting for k we get

$$k := k_n = \frac{\pi n}{a-b} \quad \text{for} \quad a \neq b, \quad n \in \mathbb{Z} \setminus \{0\} \tag{3.25}$$

Since we are not allowing the trivial solution, k_n must be different from 0. Therefore, we can restrict the values of the index n to the positive or negative integers. As $\sin(-x) = -\sin(x)$, $\cos(-x) = \cos(x)$, the negative sign of the sine function can be absorbed by the constant B. In fact, we know that equation (3.23) can be rewritten as a linear combination of *sine* and *cosine*, meaning that final solution will be a linear combination of $\sin$ and $\cos$. By construction b is bigger than a, so we can for instance restrict our choice of n to the negative integers in order to obtain positive eigenvalues. By substituting back k_n into (3.23) we get that

$$A = -Be^{-i\frac{2a\pi n}{a-b}} \quad \text{for} \quad a \neq b \tag{3.26}$$

Therefore, the general solution for ψ_n is

$$\psi_n(x) = -B(e^{\gamma}e^{ik_nx} - e^{-ik_nx}) \quad \text{for} \quad \gamma := -i\frac{2a\pi n}{a-b}, \quad a \neq b \tag{3.27}$$

We can distinguish three important cases:

$$\psi_n(x) = \begin{cases} \bar{B} sin(\frac{\pi n}{b} x), & b > a = 0,\ \bar{B} \in \mathbb{R} \\ Ae^{ik_n x} + Be^{-ik_n x} = \bar{C}\cos\left(\frac{\pi n x}{\tau}\right), & a = -\frac{\tau}{2},\ b = \frac{\tau}{2},\ n \text{ odd},\ \bar{C} \in \mathbb{R} \\ Ae^{ik_n x} - Ae^{-ik_n x} = \bar{D}\sin\left(\frac{\pi n x}{\tau}\right), & a = -\frac{\tau}{2},\ b = \frac{\tau}{2}, \quad n \text{ even},\ \bar{D} \in \mathbb{R} \end{cases} \tag{3.28}$$

Notice that the in the second and third case in equation (3.28) the potential given by

$$V_s(x) = \begin{cases} 0, & \text{if } \mid x \mid < \frac{\tau}{2} \\ \infty, & \text{if } \mid x \mid > \frac{\tau}{2} \end{cases} \tag{3.29}$$

is the same. Here we substitute $a = -\tau/2,\ b = \tau/2$ to get $\gamma = \pi n i$ through equation (3.27). This implies that $e^\gamma = e^{\pi n i} = (-1)^n$. So we can deduce from (3.26) that $A = -Be^\gamma = (-1)^{n+1}B$. This means that $A = B$, if n is odd, while $A = -B$, if n is even. Using equation (3.25) we obtain $k_n = -\frac{\pi n}{\tau}$ for $\mathrm{n} \in \mathbb{Z}^{<0}$.
k_n depends on the energy E according to equation (3.20), so if k_n can only take discrete values it means that also the energy can only take discrete values. Hence, we derive the (discrete) energy eigenvalues

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 \pi^2 n^2}{2m\tau^2} \quad \text{for } n \in \mathbb{N} \tag{3.30}$$

Such a discretisation of the energy does not take place in classical mechanics, where the energy of any moving system varies continuously and this is one of the highlights of a quantum physical system.
The first case in equation (3.28) has potential given by

$$V_c(x) = \begin{cases} 0, & \text{if } 0 \le x \le b \\ \infty, & \text{otherwise} \end{cases} \tag{3.31}$$

Here we set $a = 0,\ b > a$, so we obtain $\gamma = 0$ through equation (3.27). This implies that $e^\gamma = 1$. So we can deduce from (3.27) that $\psi(n) = B(-e^{ixk_n} + e^{-ixk_n}) = \bar{B}\sin(k_n x)$ for some $\bar{B} \in \mathbb{R}$. Thanks to equation (3.25) we obtain $k_n = -\frac{\pi n}{b}$ for $n \in \mathbb{Z}^{<0}$. Hence, we obtain the same energy eigenvalues $E_n = \frac{\hbar^2 \pi^2 n^2}{2mb^2}$ for $n \in \mathbb{N}$.
The final case we haven't considered yet is the one where $a \to -\infty,\ b \to \infty$. In this case the potential $V = 0\ \forall x \in \mathbb{R}$, so technically there is no "potential well". In this scenario the particle is free over all x as there are not boundary conditions determined by the potential. We have already computed a "mathematical" solution to this problem in equation (3.22) as we just need to stop with our computations before imposing any boundary conditions determined by the potential. This partial solution is given by

$$\begin{aligned} &\Psi(x,t) = e^{-\frac{iE}{\hbar}t}\left(Ae^{ikx} + Be^{-ikx}\right) = e^{-\frac{iE}{\hbar}t}\left(\bar{A}\cos(kx) + \bar{B}\sin(kx)\right) \\ &\textit{for some real constants } \bar{A},\ \bar{B} \end{aligned} \tag{3.32}$$

We will discuss further this case in the next section since there are additional considerations to be made. For instance, we will need to verify that the solution above represents a physically realizable state. A free particle is characterised by definition by a non-definite energy state, so we will need to sum up continuously the solutions in equation (3.32) with respect to k, before normalising them. In fact, the notion of discrete energy levels would imply a definite energy state which would lead to a contradiction since the particle is "free".
In order to obtain the final wave functions, we need to normalise the various $\psi(x)$ that we obtained in equation (3.28). Let's start by considering $\psi(x) = \bar{B}\sin(k_n x)$.

$$\begin{aligned} 1 \overset{!}{=} &\int_0^b \mid \bar{B} \mid^2 (\sin(k_n x))^2\, dx = \mid \bar{B} \mid^2 \left(\frac{x}{2} - \frac{\sin(2k_n x)}{4k}\right)\Big|_0^b \\ = &\left(\frac{b}{2} - \frac{\sin(2k_n b)}{4k}\right) = \mid \bar{B} \mid^2 \frac{b}{2} \end{aligned} \tag{3.33}$$

Notice that $\sin(2k_n b) = \sin(\frac{2n\pi b}{b}) = 0$. It follows that $|\bar{B}|^2 = \frac{2}{b}$ which implies that the real constant $\bar{B} = \sqrt{\frac{2}{b}}$ where $b > 0$. It follows that the solution to the Schrödinger equation with boundary conditions given by V_c is

$$\Psi(x,t) = e^{-\frac{iE_n}{\hbar}t}\left(\sqrt{\frac{2}{b}}\sin\left(\frac{n\pi}{b}x\right)\right) \tag{3.34}$$

where $E_n = \frac{\hbar\pi^2 n^2}{2mb^2},\ n \in \mathbb{N},\ 0 \leq x \leq b$

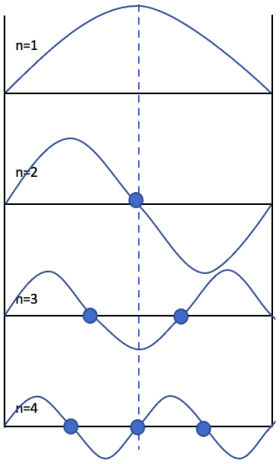


Figure 3.2: Energy eigenstates for the wave function $\psi_n(x) = \sqrt{\frac{2}{b}}\sin\left(\frac{n\pi}{b}x\right)$ with $n-1$ nodes

Similarly, we need to normalise $\psi(x)$ which is bounded by the symmetric potential V_s. Note that the wave function vanishes within the box (i.e. $-\frac{\tau}{2} \leq x \leq \frac{\tau}{2}$).

$$\begin{aligned} 1 &\overset{!}{=} \int_{-\frac{\tau}{2}}^{\frac{\tau}{2}} 4\,|B|^2\cos^2\left(\frac{\pi n x}{\tau}\right)dx = 4 \mid B \mid^2 \int_{-\frac{\tau}{2}}^{\frac{\tau}{2}} \frac{1}{2}\left(1+\cos\left(\frac{2n\pi x}{\tau}\right)\right)dx \\ &= 2 \mid B \mid^2 \left(x\Big|_{-\frac{\tau}{2}}^{\frac{\tau}{2}} + \delta\right) \end{aligned} \tag{3.35}$$

Notice that $\delta = \frac{\tau}{2n\pi}\left[\sin\left(\frac{2\pi n x}{\tau}\right)\right]_{-\frac{\tau}{2}}^{\frac{\tau}{2}} = \frac{\tau}{2n\pi}(0-0) = 0$. By rearranging equation (3.35) we obtain $2 \mid B \mid^2 \tau = 1$. We conclude that $B = \sqrt{\frac{1}{2\tau}}$ which is a real constant since $\tau > 0$. Similarly, $\int_{-\frac{\tau}{2}}^{\frac{\tau}{2}} 4|B|^2\sin^2(k_n x)dx = 2|B|^2\tau = 1$, so the normalisation constant is again $B = \sqrt{\frac{1}{2\tau}}$.
The solution to the Schrödinger equation with boundary conditions given by V_s is finally

$$\Psi(x,t) = \begin{cases} e^{-\frac{iE_n}{\hbar}t}\left(\sqrt{\frac{2}{\tau}}\sin\left(\frac{n\pi}{\tau}x\right)\right) & \text{where} \quad E_n = \frac{\hbar\pi^2 n^2}{2mb^2},\ n \text{ even},\ |x| \leq \frac{\tau}{2} \\ e^{-\frac{iE_n}{\hbar}t}\left(\sqrt{\frac{2}{\tau}}\sin\left(\frac{n\pi}{\tau}x\right)\right) & \text{where} \quad E_n = \frac{\hbar\pi^2 n^2}{2mb^2},\ n \text{ odd},\ |x| \leq \frac{\tau}{2} \end{cases} \tag{3.36}$$

Example 3.1.1. As suggested by the superposition principle, the general solution to the time-dependent Schrödinger equation is a linear combination of its stationary states given by

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \Psi_n(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-\frac{iE_n t}{\hbar}}, \quad c_n \in \mathbb{R} \tag{3.37}$$

The initial wave function $\Psi(x, t = 0)$ gives us the equation

$$\Psi(x,0) = \sum_{n=1}^{\infty} c_n \psi_n(x) \tag{3.38}$$

As the ψs form an orthonormal base on $L^2(\mathbb{R})$, we can express a generic function f as a linear combination

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) \tag{3.39}$$

If we multiply by $\psi_m^*,\ m \in \mathbb{N}$ on both sides and then integrate we get

$$\int_{\mathbb{R}} \psi_m^*(x) f(x) dx = \sum_{n=1}^{\infty} c_n \int_{\mathbb{R}} \psi_n(x) \psi_m^*(x) dx = \sum_{n=1}^{\infty} c_n \delta_{m,n} = c_m \tag{3.40}$$

Going back to the infinity square well problem, we found that a stationary state n can be described by

$$\Psi_n(x,t) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}, \tag{3.41}$$

so that the general solution to the time-dependent Schrödinger equation becomes

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t} \tag{3.42}$$

Thus we set $f(x) = \sqrt{\frac{2}{a}} sin\left(\frac{n\pi}{a} x\right)$ and obtain

$$c_n = \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a} x\right) \psi(x,0) dx \tag{3.43}$$

Let's consider an example where we take the following initial wave function

$$\Psi(x,0) = Ax(a-x), \quad 0 \le x \le a, \quad A, a \in \mathbb{R} \tag{3.44}$$

The potential is ∞ outside the well, where of course, $\psi = 0$. First, we need to normalise $\Psi(x, 0)$ to find A

$$1 \overset{!}{=} \int_0^a |\psi(x,0)|^2 dx = \int_0^a |A|^2 x^2 (a-x)^2 dx = |A|^2 \frac{a^5}{30} \tag{3.45}$$

and so

$$A = \sqrt{\frac{30}{a^5}} \tag{3.46}$$

With the use of (3.42) we obtain

$$\begin{aligned}
c_n =& \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \sqrt{\frac{30}{a^5}} x(a-x)dx \\
=& \frac{2\sqrt{15}}{a^3}\left[a\int_0^a x\sin\left(\frac{n\pi}{a}x\right)dx - \int_0^a x^2\sin\left(\frac{n\pi}{a}x\right)dx\right] \\
=& \frac{2\sqrt{15}}{a^3}\left\{a\left[\left(\frac{a}{n\pi}\right)^2\sin\left(\frac{n\pi}{a}x\right) - \frac{ax}{n\pi}\cos\left(\frac{n\pi}{a}x\right)\right]\Bigg|_0^a\right. \\
&\left. = \left[2\left(\frac{a}{n\pi}\right)^2 x\sin\left(\frac{n\pi}{a}x\right) - \frac{(nx\pi/a)^2-2}{(n\pi/a)^3}\cos\left(\frac{n\pi}{a}x\right)\right]\Bigg|_0^a\right\} \\
=& \frac{2\sqrt{15}}{a^3}\left[-\frac{a^3}{n\pi}\cos(n\pi) + a^3\frac{(n\pi)^2-2}{(n\pi)^3}\cos(n\pi) + a^3\frac{2}{(n\pi)^3}\cos(0)\right] \\
=& \frac{4\sqrt{15}}{(n\pi)^3}[\cos(0)-\cos(n\pi)] = \begin{cases} 0, & \text{if } n \text{ even} \\ \frac{8\sqrt{15}}{(n\pi)^3} & \text{if } n \text{ odd} \end{cases}
\end{aligned} \tag{3.47}$$

and so the result that we get is

$$\Psi(x,t) = \sqrt{\frac{30}{a}}\left(\frac{2}{\pi}\right)^3 \sum_{n=1,3,5..} \frac{1}{n^3}\sin\left(\frac{n\pi}{a}x\right) e^{-in^2\pi^2\hbar t/2ma^2} \tag{3.48}$$

We can now check that the sum over all probabilities of a measurement of the energy E_n returns one.
In the interval $[0,a]$ the wave function looks very similar to the first stationary state of the infinite square well, meaning that $|c_1|^2$ should be close to 1:

$$|c_1|^2 = \left(\frac{8\sqrt{15}}{\pi^3}\right)^2 = 0.998555.... \tag{3.49}$$

The rest of the coefficients make up for the difference

$$\sum_{n=1}^{\infty}|c_1|^2 = \left(\frac{8\sqrt{15}}{\pi^3}\right)^2 \sum_{k=1}^{\infty}\frac{1}{(2k-1)^6} = \left(\frac{8\sqrt{15}}{\pi^3}\right)^2 \frac{\pi^6}{960} = 1 \tag{3.50}$$

Therefore, the outcome that we are most likely to get from an energy measurement is $E_1 = \frac{\pi^2\hbar^2}{2ma^2}$ and so the expectation value of the energy is

$$< H > = \sum_{n=1,3,5..}^{\infty}\left(\frac{8\sqrt{15}}{n^3\pi^3}\right)^2 \frac{n^2\pi^2\hbar^2}{2ma^2} = \frac{480\hbar^2}{\pi^4 ma^2}\sum_{n=1,3,5..}^{\infty}\frac{1}{n^4} = \frac{480\hbar^2}{\pi^4 ma^2}\frac{\pi^4}{96} = \frac{5\hbar^2}{ma^2} \tag{3.51}$$

The expected value is slightly larger than E_1: this is due to the dominance of c_1 and the first state, with the remaining combination of excited states making up for the difference.

Example 3.1.2. The superposition principle holds in quantum mechanics as well. The linear combination of solutions $\psi_n(r)$ is itself a solution to the time independent Schrödinger equation. In general, we can think at the various $\psi_n(r)$s as an infinite dimensional base of the correspondent Hilbert space. As shown for the infinite square well solution, these states form an orthonormal base of $L^2(\mathbb{R})$.

Let's look at another application of what we have seen so far. Assume the potential V to be $0 \quad \forall x \in [0,a] \subset \mathbb{R}$ and ∞ otherwise. Consider the following solution which is a combination of two stationary states m and n for some $n,\ m \in \mathbb{N},\ m \neq n$ in the infinite square well problem.

$$\Psi(x,0) = A\big[\psi_n(x) + \psi_m(x)\big], \quad 0 \leq x \leq a \tag{3.52}$$

We can determine the value of the normalisation constant A by remembering that $\|\Psi(x,t)\|^2_{L^2(\mathbb{R})} = 1$. In addition, since $\Psi(x,t) = e^{-\frac{\hbar\pi^2 n^2}{2Ma^2}it}\psi(x)$ it's enough to impose $\|\psi(x)\|^2_{L^2(\mathbb{R})} = 1$ as $\|e^{-\frac{\hbar\pi^2 n^2}{2Ma^2}it}\|^2_{L^2(\mathbb{R})} = 1\ \forall x \in \mathbb{R}$. Since the solution $\psi(x)$ given in equation (3.34) is real, $\psi(x)\psi(x)^* = \psi(x)^2$. Here M represents the mass. Let $c := \frac{2}{a}$, then

$$\begin{aligned}
A^{-2} &\overset{!}{=} \int_0^a \big[\psi_n(x) + \psi_m(x)\big]^2 dx \\
&= c\int_0^a \big[\sin(k_n x) + \sin(k_m x)\big]^2 dx \\
&= c\int_0^a \big[2\sin(k_n x)\sin(k_m x)\big]dx + c\int_0^a \big[\sin(k_n x)\big]^2 dx + c\int_0^a \big[\sin(k_n x)\big]^2 dx \\
&= c\Big[\frac{x}{2} - \frac{\sin(2k_n x)}{4k_n} + \frac{x}{2} - \frac{\sin(2k_m x)}{4k_m}\Big] + c\Big[\frac{\sin((k_n-k_m)x)}{k_n-k_m} - \frac{\sin((k_n+k_m)x)}{k_n+k_m}\Big]\Big|_0^a \\
&= c\left(a - \frac{\sin(2k_m a)}{4k_m} - \frac{sin(2k_m a)}{4k_m}\right) + c\left(\frac{\sin((k_n-k_m)a)}{k_n-k_m} - \frac{\sin((k_n+k_m)a)}{k_n+k_m}\right)
\end{aligned} \tag{3.53}$$

Notice that $\forall s \in \mathbb{N}:\ sin(k_s a) = sin(\pi s) = 0$, hence we get that all sin terms cancel and

$$A^{-2} = ca = 2 \iff A = \frac{1}{\sqrt{2}} \tag{3.54}$$

Thus, we obtain

$$\Psi(x,0) = \psi(x) = \frac{1}{\sqrt{a}}\left(\sin(k_n x) + \sin(k_m x)\right) \tag{3.55}$$

The general solution of the Schrödinger equation is given by the linear combination over all infinite eigenstates $\psi_s(x),\ s \in \mathbb{N}$. As shown in equation (3.55), the only two states represented in $\psi(x)$ are n and m. This means that $k_s = 0\ \forall s \neq n,m$ for $s \in \mathbb{N}$. Therefore, we deduce that the energy eigenvalue E_s for $s \in \mathbb{N}$ will take eigenvalues $E_n,\ E_m$, while all others term will cancel out. Define $w := \frac{\pi\hbar}{2Ma^2}$. The general solution is then given by

$$\begin{aligned}
\Psi(x,t) &= \frac{1}{\sqrt{a}}\left(\sin(k_n x)e^{-i\frac{k_n^2\hbar}{2M}} + \sin(k_m x)e^{-i\frac{k_n^2\hbar}{2M}}\right) \\
&= \frac{1}{\sqrt{2}}\left(\sqrt{\frac{2}{a}}\sin\left(n\frac{\pi x}{a}\right)e^{-in^2wt}\right) + \frac{1}{\sqrt{2}}\left(\sqrt{\frac{2}{a}}\sin\left(m\frac{\pi x}{a}\right)e^{-im^2wt}\right) \\
&= \frac{1}{\sqrt{2}}\left(\psi_n(x)e^{-in^2wt} + \psi_m(x)e^{-im^2wt}\right)
\end{aligned} \tag{3.56}$$

From equation (3.56) we can determine that the probabilities of measuring the eigenstates $E_n = \frac{n^2\pi^2\hbar^2}{2Ma^2}$ and $E_m = \frac{m^2\pi^2\hbar^2}{2Ma^2}$ are

$$\mathbb{P}(E_n) = \left|\frac{1}{\sqrt{2}}\right|^2 = \frac{1}{2} = \mathbb{P}(E_m) \tag{3.57}$$

Therefore, the expectation value of the energy becomes

$$< H >_\Psi = \mathbb{P}(E_n)E_n + \mathbb{P}(E_m)E_m = \frac{\pi^2\hbar^2}{2Ma^2}\frac{1}{2}\left(n^2+m^2\right) = \frac{\pi^2\hbar^2}{4Ma^2}\left(n^2+m^2\right) \tag{3.58}$$

Let's now compute the probability distribution of the particle at time t which is given by

$$\begin{aligned} |\Psi(x,t)|^2 &= \Psi(x,t)\Psi^*(x,t) \\ &= \left(\frac{1}{\sqrt{2}}\right)^2 \left(\psi_n e^{-in^2wt} + \psi_m e^{-im^2wt}\right)\left(\psi_n^* e^{in^2wt} + \psi_m^* e^{im^2wt}\right) \\ &= \frac{1}{2}\left(|\psi_n|^2 + |\psi_m|^2 + e^{iwt}\left(\psi_m\psi_n^* e^{n^2-m^2} + \psi_n\psi_m^* e^{m^2-n^2}\right)\right) \end{aligned} \tag{3.59}$$

Notice that the norm of the wave function $\Psi(x,t)$ is in fact equal to one

$$\begin{aligned} \int_{\mathbb{R}} |\Psi(x,t)|^2 dx &= \int_0^a \frac{1}{2}\left(|\psi_n|^2 + |\psi_m|^2 + e^{iwt}\left(\psi_m\psi_n^* e^{n^2-m^2} + \psi_n\psi_m^* e^{m^2-n^2}\right)\right) dx \\ &= \frac{1}{2}\left(1+1+0\right) \end{aligned} \tag{3.60}$$

The time dependent integral goes to 0 due to the orthogonality of the wave functions $\psi_m,\ \psi_n$. In order to compute the expectation value of x at time t we first need to acknowledge some results.

$$\begin{aligned} < x >_\psi &= \int_{\mathbb{R}} \psi^*(x) x \psi(x) dx \\ &= \frac{2}{a}\int_0^a x\left(\sin(kx)\right)^2 dx = \frac{2}{a}\left(-\frac{\cos(2kx)}{8k^2} - \frac{x\sin(2kx)}{4k} + \frac{x^2}{4}\right)\Bigg|_0^a \\ &= \frac{2}{a}\frac{2a^2k^2 - 2ak\sin(2ak) - \cos(2ak) + 1}{8k^2} = \frac{2}{a}\frac{2a^2k^2 + 0 - 1 + 1}{8k^2} \\ &= \frac{a}{2} \end{aligned} \tag{3.61}$$

Furthermore,

$$\begin{aligned} \mathcal{L} &:= \int_{\mathbb{R}} \psi_n(x) x \psi_m(x) dx = \frac{2}{a}\int_0^a x\left(\sin(k_n x)\sin(k_m x)\right) dx \\ &= \frac{1}{a}\left(\frac{x\sin\left(x(k_n-k_m)\right)}{k_n-k_m} - \frac{x\sin\left(x(k_n+k_m)\right)}{k_n+k_m}\right)\Bigg|_0^a \\ &+ \frac{1}{a}\left(\frac{\cos\left(x(k_n-k_m)\right)}{\left(k_n-k_m\right)^2} - \frac{\cos\left(x(k_n+k_m)\right)}{\left(k_n+k_m\right)^2}\right)\Bigg|_0^a \\ &= \frac{1}{a}\left(+\frac{\cos\left(\pi(n-m)\right)-1}{\left(k_n-k_m\right)^2} + \frac{-\cos\left(\pi(n+m)\right)+1}{\left(k_n+k_m\right)^2}\right) \end{aligned} \tag{3.62}$$

The sin terms cancel out because the argument of the sine is an integer multiple of π. Suppose that n is even and m is odd or vice-versa, then both their difference and their sum will be odd. This means that the cos term will be equal to minus one in both cases. Assume instead that n and m are both either odd or even, then their sum and difference will be even; this means that both terms in equation (3.62) cancel out. Hence,

$$\mathcal{L} := \int_{\mathbb{R}} \psi_n(x) x \psi_m(x) dx = \begin{cases} 0, & \textit{if both } n \textit{ and } m \textit{ are either even or odd} \\ \frac{a}{\pi^2}\left(\frac{1}{(n+m)^2} - \frac{1}{(n-m)^2}\right), & \textit{otherwise} \end{cases} \tag{3.63}$$

If we apply the expectation operator to x at time t we find that

$$\begin{aligned} < x >_\Psi &= \int_{\mathbb{R}} \Psi^*(x) x \Psi(x) dx \\ &= \int_0^a x \frac{1}{2}\left(|\psi_n|^2 + |\psi_m|^2 + e^{iwt}\left(\psi_m \psi_n^* e^{n^2-m^2} + \psi_n \psi_m^* e^{m^2-n^2}\right)\right) dx \\ &= \frac{1}{2}\left(< x >_{\psi_n} + < x >_{\psi_m} + \int_0^a x e^{iwt}\left(\psi_m \psi_n 2\cosh(n^2-m^2)\right) dx\right) \\ &= \frac{1}{2}\left(\frac{a}{2} + \frac{a}{2} + e^{iwt}\alpha_{n,m}\mathcal{L}\right) \\ &= \frac{a}{2} + \frac{\beta_{n,m}}{2} e^{iwt} \\ &\quad \textit{where } \alpha_{n,m} := 2\cosh(n^2-m^2) \textit{ while } \beta_{n,m} := \alpha_{n,m}\mathcal{L} \end{aligned} \tag{3.64}$$

Note that $< x >_\Psi$ needs to be real so we shall only take the real part of e^{iwt}, hence

$$< x >_\Psi = \frac{a}{2} + \frac{\beta_{n,m}}{2}\cos(wt) \quad \textit{where } \alpha_{n,m} := 2\cosh(n^2-m^2),\ \beta_{n,m} := \alpha_{n,m}\mathcal{L} \tag{3.65}$$

Example 3.1.3. In this example we are going to solve the time-independent Schrödinger equation with appropriate boundary conditions for an infinite square well centred at the origin.

$$V(x) = \begin{cases} 0, & \text{if } \mid x \mid < \frac{a}{2} \\ \infty, & \text{if } \mid x \mid > \frac{a}{2} \end{cases} \tag{3.66}$$

Lets start with the time independent Schrödinger equation.

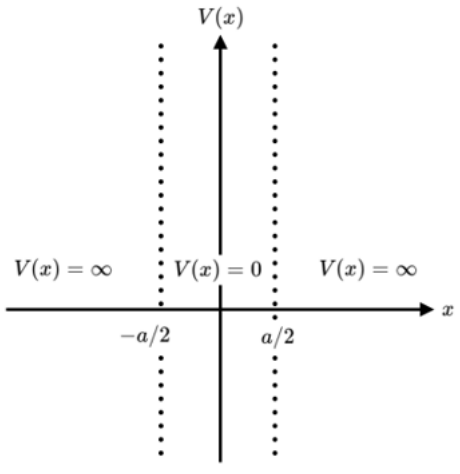


Figure 3.3: Infinite square well diagram

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x) = E\psi(x) \tag{3.67}$$

Collecting all the $\psi(x)$ on to one side, we get

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} = E\psi(x) - V(x)\psi(x) \tag{3.68}$$

$$\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} = (V(x) - E)\psi(x) \tag{3.69}$$

As we have previously already mentioned, $\psi(r) = 0$ outside the well. Inside the well $V(x) = 0$

$$\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} = -E\psi(x) \tag{3.70}$$

$$\frac{\partial^2\psi(x)}{\partial x^2} = -\frac{2m}{\hbar^2}E\psi(x) \tag{3.71}$$

Here we have the second derivative of the function equals a negative of some constant multiplied by the original function. Using the characteristic polynomials $t^2 + k^2 = 0$ derived from equation (3.71) where $k = \frac{\sqrt{2mE}}{\hbar}$ and by taking the solution expressed "in real form", we get

$$\psi(x) = A\sin(kx) + B\cos(kx), \quad A, B \in \mathbb{R} \tag{3.72}$$

Now, using the boundary conditions $\psi(-a/2) = 0$ and $\psi(a/2) = 0$ we get

$$0 = A\sin(k(\pm a/2) + B\cos(k(\pm a/2)) \tag{3.73}$$

We are considering a non trivial solution for ψ, so $A,\ B$ cannot be both 0. Due to the fact that sin is an odd function, while cos is an even function we get

$$0 = \pm A\sin(k(a/2) + B\cos(k(a/2)) \tag{3.74}$$

By solving this system, the sin terms cancel out and we obtain

$$2B\cos(k(a/2)) = 0 \tag{3.75}$$

If we multiply by minus one on both sides of the sin equation in the system (3.74) we get a second equation

$$2A\sin(k(a/2)) = 0 \tag{3.76}$$

Notice that $\cos(kx) = 0$ when $kx = \frac{(2n+1)\pi}{2},\ \forall n \in \mathbb{Z}$. On the other hand, $\sin(kx) = 0$ when $kx = \frac{(2n)\pi}{2},\ \forall\ l \in \mathbb{Z}$ This implies that

$$\frac{ka}{2} = \frac{(2l+1)\pi}{2} \iff k_n = n\frac{\pi}{a}, \quad \text{if } n \text{ is odd} \tag{3.77}$$

and

$$\frac{ka}{2} = \frac{(2l)\pi}{2}, \iff k_n = n\frac{\pi}{a} \quad \text{if } n \text{ is even} \tag{3.78}$$

Therefore, we can write

$$\psi_n(x) = \begin{cases} A\sin(k_n x), & \text{if } n \text{ is even} \\ B\cos(k_n x), & \text{if } n \text{ is odd} \end{cases} \tag{3.79}$$

In order to derive back the solution where the potential V is 0 when x lies between 0 and a, we need to apply a map to $n \in \mathbb{Z}$

$$\mathcal{L}(n) = \begin{cases} \frac{n}{2}, & \text{if } n \text{ is even} \\ \frac{n-1}{2}, & \text{if } n \text{ is odd} \end{cases} \tag{3.80}$$

In fact,

$$\psi_{L(n)}(x) = \begin{cases} A\sin(k_{\mathcal{L}(n)}ax) = A\sin(\mathcal{L}(n)\frac{\pi}{a}x) \\ B\cos(k_{\mathcal{L}(n)}ax) = B\cos(\mathcal{L}(n)\frac{\pi}{a}x) \end{cases} \tag{3.81}$$

$$= \begin{cases} A\sin(\frac{n\pi}{2a}x) = A\sin(\frac{l\pi}{a}x), & \text{if } n \text{ is even, } l \in \mathbb{N} \\ B\cos(\frac{(n-1)\pi}{2a}x) = B\cos(\frac{l\pi}{a}x), & \text{if } n \text{ is odd, } l \in \mathbb{N} \end{cases} \tag{3.82}$$

Notice that if we apply $\mathcal{L}(n)$ to $\psi_n(x)$, the potential well shifts to the right by $a/2$ due to the factor $\frac{1}{2}$ in the image of $\mathcal{L}$

$$V_{x+\frac{a}{2}}(x) = \begin{cases} 0, & 0 \le x \le a \\ \infty, & \text{otherwise} \end{cases} \tag{3.83}$$

By applying the boundary conditions the coefficient B cancels out as expected.
To find the energy eigenvalues E_n with respect to the symmetric potential we use

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2} \tag{3.84}$$

In general, when we apply $\mathcal{L}$ to n we are shifting x to the right by $\frac{a}{2}$. The inverse transformation is therefore $x - \frac{a}{2}$. Now, by the substitution $x \to x - \frac{a}{2}$ in the solution with non symmetric potential $\sqrt{\frac{2}{a}}\sin(\frac{n\pi}{a}x)$, we should obtain back our original solution

$$\sin\left(\frac{n\pi}{a}\left(x - \frac{a}{2}\right)\right) = \sin\left(\frac{n\pi}{a}x - n\frac{\pi}{2}\right) \tag{3.85}$$

Due to the fact that sine is periodic, wlog we can take only some values of n, namely $n \in \{1, 2, 3\}$. In addition, we know that $\sin(\alpha - \pi/2) = -\cos(\alpha)$, $\sin(\alpha - \pi) = -\sin(\alpha)$, $\sin(\alpha - \frac{3\pi}{2}) = \cos(\alpha)$. Therefore, it's clear that when n is even we obtain a sine function, while when n is odd a cos function. This shows that by applying this linear transformation to x, we obtain an even n for the sine and an odd n for the cosine, something that gives us back our solution contained in equation (3.79).

3.2 The free particle

When looking at the free particle, in theory it is the simplest case of all. Here the potential energy vanishes $V(x) = 0$; so far this is a sub-case of the previously discussed infinite square well example (3.17), where we take the limit to infinity for the two boundaries of the region with zero potential.
As the potential energy is zero, this reduces the time-independent Schrodinger equation to (3.18). However, the difference here is that there are no restriction of possible values of k and therefore no restriction on the total energy of the system E, as there are no boundary conditions for the general solution (3.22). This means that the free particle can take on *any* positive energy.
Multiplying by the standard time dependence $e^{-\frac{iEt}{\hbar}}$ we get

$$\Psi(x,t) = Ae^{ik\left(x - \frac{\hbar k}{2m}t\right)} + Be^{-ik\left(x + \frac{\hbar k}{2m}t\right)} \tag{3.86}$$

The shape of the waves do not change as the wave propagates, as the velocity of all the points on the wave is the same. Therefore, for a constant v, any combination of $x \pm vt$ represents the wave given above, that does not change shape. Travelling in the $\mp x$ direction at speed v, a minimum, maximum or any fixed point on the wave correlates to a fixed value of the argument giving

$$x \pm vt = constant \quad \text{or} \quad x = \mp vt + constant \tag{3.87}$$

This then means the first term $Ae^{ik\left(x-\frac{\hbar k}{2m}t\right)}$ in equation (3.86) denotes the wave moving to the *right* while the second component $Be^{-ik\left(x+\frac{\hbar k}{2m}t\right)}$ represents the wave moving to the *left*. As shown above, since the terms only differ by the sign in front of k, this can be reduced to

$$\Psi_k(x,t) = Ae^{i\left(kx-\frac{\hbar k^2}{2m}t\right)} \tag{3.88}$$

Allowing k to be negative to cover all cases that are travelling to the left then we can set

$$k \equiv \pm\frac{\sqrt{2mE}}{\hbar} \quad \text{with} \quad \begin{cases} k > 0 \text{ wave travels to the right} \\ k < 0 \text{ wave travels to the left} \end{cases} \tag{3.89}$$

The stationary states of the free particle are propagating waves with wavelength of $\lambda = \frac{2\pi}{|k|}$. The de Broglie formula states these waves carry momentum of

$$p = \hbar k \tag{3.90}$$

with speed

$$v_{quantum} = \frac{\hbar \mid k \mid}{2m} = \sqrt{\frac{E}{2m}} \tag{3.91}$$

Recall that the kinetic energy of a free particle is given by $E = \frac{1}{2}mv^2$ (since $V = 0$ this is pure kinetic), therefore

$$v_{classical} = \sqrt{\frac{2E}{m}} = 2v_{quantum} \tag{3.92}$$

However, this invokes a paradox at which the quantum mechanical wave travels at half the speed of the particle it is supposed to represent. In turn, the particle is travelling at the wrong velocity. On the other hand, the wave function Ψ_k does not have a physical meaning and so it is *not normalisable.* So one finds that

$$\int_{-\infty}^{+\infty} \Psi_k^* \Psi_k dx = \mid A \mid^2 \int_{-\infty}^{+\infty} dx \tag{3.93}$$

diverges. Hence, these separable solutions do not represent physically realised states - a free particle cannot and does not exist in a stationary state. Free particles do not exist with a definite energy.
The general solution to the time-independent Schrodinger equation is a linear combination of separable solutions , so it is a integral over the *continuous* variable k rather than the sum over the discrete index n.

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \hat{\phi}(k) e^{i\left(kx-\frac{\hbar k^2}{sm}t\right)} dk \tag{3.94}$$

The logic behind the derivation of this formula is that we are taking the sum over infinitesimal small values of k of a complex power series $\sum_{k=-\infty}^{+\infty} z^k$ where we define $z = e^{\frac{it}{L}}, \quad t \in [-\pi L, \pi L], \; L \to \infty$. Notice that we take the sum for all values of k, which takes both positive and negative values. In the appendix A we will present an intuitive derivation of this extension of Fourier series coefficient called Fourier transform.

Let $\hat{f}$, F be functions in $L^1(\mathbb{R})$. Then we define

$$\hat{f}(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} F(k) e^{ikx} dk \quad \text{and} \quad F(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \hat{f}(x) e^{-ikx} dk \tag{3.95}$$

where $F(k)$ is the Fourier transform of $f(x)$, while $f(x)$ is the inverse Fourier transform of $F(k)$. The factor $\sqrt{\frac{1}{2\pi}}$ in front of these integrals is the result of a substitution $x = 2\pi u$ as typically in Physics one expresses a generic function with respect to angular frequency and not the oscillating frequency. To restore symmetry between the two formulas of F and f one includes the factor $\sqrt{\frac{1}{2\pi}}$.

We do not have to worry about the normalisation coefficient as this is contained in $\hat{\phi}$. Notice that Ψ carries a range of k and therefore a range of energies and speeds. This is called a wave packet[4].

If we look closely at (3.94) and compare with (3.95), we see that $\Psi(x,0) = \psi(x)$ is the inverse Fourier transform of $\hat{\phi}(k)$

$$\Psi(x,0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \hat{\phi}(k) e^{ikx} dk \tag{3.96}$$

The Fourier transform of $\Psi(x,0)$ is then given by $\hat{\phi}$.

$$\hat{\phi}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \Psi(x,0) e^{-ikx} dx. \tag{3.97}$$

As a side note, notice that both $\hat{\phi}(x)$ and $\Psi(x,0)$ need to be well defined wave functions, so elements of $L^2(\mathbb{R})$, but also integrable functions over the real numbers, condition implied by taking $\hat{\phi}(x)$, $\Psi(x,0)$ as elements of $L^1(\mathbb{R})$. However, $L^2(\mathbb{R}) \subset L^1(\mathbb{R})$[5] so we do not need to impose any extra condition on the wave function other than being an element of $L^2(\mathbb{R})$.

The equation of wave packet is given by (3.94) where a wave packet is a superposition of sinusoidal waves, with the amplitude affected by the value of ϕ. The wave packet consists of ripples that are contained in an 'envelope', shown by figure 3.4. The group velocity is the speed of the envelope, which depends on the nature of the waves. This value differs from the individual velocity of the ripples, the phase velocity.
Depending on the nature of the waves, the group velocity can be equal, greater or less than the individual velocity of the ripples that make up the envelope: for example, for waves on a string the group velocity equals the phase velocity, while for water, the group velocity equals half of the phase velocity.

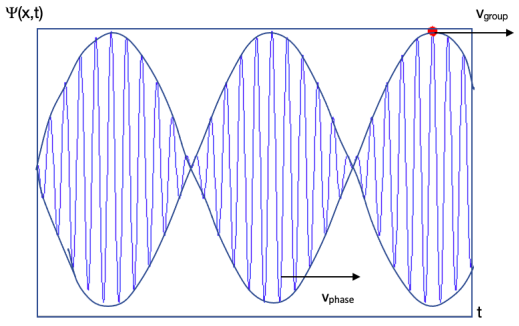


Figure 3.4: A wave packet with the "envelope" travelling at the group velocity shown by the green outline, and the "ripples" travelling at the phase velocity indicated in blue.

[4]Sinusoidal waves are not normalisable as they extend out to ∞ but superposition of these waves lead to interference and so allows them to be normalisable and also allows localisation.

[5]This can be proven using the Hölder-inequality for general norm p, q

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{\infty}^{\infty} \hat{\phi}(k) e^{i}(kx - \omega t) dk \tag{3.98}$$

where $\omega(k) = \frac{\hbar k^2}{2m}$. This now applies to *any* kind of wave packet, regardless of its dispersion relation. Where the dispersion relation is given by the formula for ω and a function of k. By expanding the function $\omega(k)$ about that point using a Taylor expansion, we get

$$\omega(k) \approx \omega(k_0) + \left(\frac{d\omega}{dk}\right)_{k=k_0} (k = k_0) + ... \tag{3.99}$$

And by only keeping the leading terms,

$$\omega(k) \simeq \omega_0 + \omega_0'(k - k_0) \tag{3.100}$$

where ω_0' is the derivative of ω with respect to k at point k_0. By changing variables, $s \equiv k - k_0$,

$$\begin{aligned}\Psi(x,t) &\approx \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \hat{\phi}(k_0 + s) e^{i[(k_0+s)x - (\omega_0 + \omega_0' s)t] ds} \\ &= \frac{1}{2\pi} e^{i(k_0 x - \omega_0 t)} \int_{-\infty}^{+\infty} \hat{\phi}(k_0 + s) e^{is(x - \omega_0' t) ds}\end{aligned}$$

The "ripples" are given by the term in front of the sinusoidal wave, which are travelling at $\frac{\omega_0}{k_0}$ speed. These are modulated by the "envelope", which is a function of $x - \omega_0' t$, propagating at the speed ω_0' giving the phase velocity

$$v_{phase} = \frac{\omega}{k} = \frac{\hbar k}{2m} \tag{3.101}$$

And the group velocity

$$v_{group} = \frac{d\omega}{dk} = \frac{\hbar k}{m} = 2v_{phase} \tag{3.102}$$

with both the individual and group velocities being evaluated at $k = k_0$. We can see if the phase velocity moves with the group velocity by

$$\begin{aligned}\Psi(x,t) &= \psi(x) e^{\frac{iEt}{A}} = e^{i(kx - \omega t)} \\ &= e^{ik(x - v_{phase} t)} \\ &= \Psi(x - v_{phase} t, 0)\end{aligned}$$

By rearranging we get

$$\begin{aligned}\Psi(x,t) &= \hat{\phi}(s + k_0) e^{i((s+k_0)x - (\omega_0 + \omega_0' t s)t)} \\ &= \left(e^{-i(\omega_0 - k_0 \omega_0')t}\right) \hat{\phi}(s + k_0) e^{i(s+k_0)(x - w_0' t)} \\ &= e^{-i(w_0 - k_0 v_g)t} \hat{\phi}(k) e^{ik(x - v_g t)} \\ &= e^{-i(\omega_0 - k_0 v_g)t} \frac{1}{\sqrt{2\pi}} \int_{\infty}^{\infty} \hat{\phi}(k) e^{ik(x - v_g t)} dk \\ &= e^{-i(w_0 - k_0 v_g)t} \psi(x - v_g t, 0)\end{aligned}$$

Proving that

$$|\psi(x,t)|^2 = |\psi(x - v_g t, 0)|^2 \tag{3.103}$$

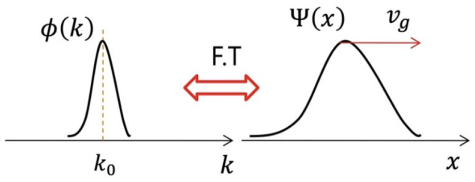


Figure 3.5: Graph describing a well defined group velocity of a wave packet

That is, the wave packet moves with group velocity which is same as the classical particle velocity: $v_{classical} = v_{group} = 2v_{phase}$. We can also see if $\Psi(x,t) = \Psi(x - v_{phase}t, 0)$ then we can say that the wave packet moves with v_{group}.
A "well-defined" group velocity can be seen in the figure below which is localized on one point, that is at k_0.

Example 3.2.1. In this example we are going to find the wave function of a free particle in the initially localised range of $-a < x < a$, which is released at time $t = 0$ where

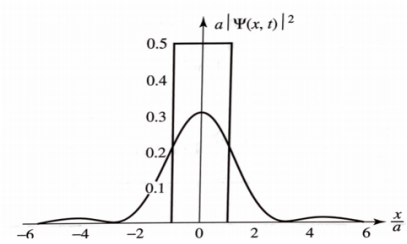


Figure 3.6: Graph of $|\ \Psi(x,t)\ |^2$ (equation (3.107)) with the rectangle describing $t = 0$ and the curve representing $t = \frac{ma^2}{\hbar}$.

$$\Psi(x,0) = \begin{cases} A, \textit{if} - a < x < a, \\ 0, \textit{otherwise.} \end{cases} . \tag{3.104}$$

Here A and a are *positive real* constants. First we need to normalise $\Psi(x,0)$ by integrating the wave function between the boundaries of the function

$$1 = \int_{-\infty}^{+\infty} |\ \Psi(x,0)\ |^2\, dx = |\ A\ |^2 \int_{-a}^{a} dx = 2a\ |\ A\ |^2 \tag{3.105}$$

Rearranging this gives the solution

$$A = \frac{1}{\sqrt{2a}} \tag{3.106}$$

We now calculate $\hat{\phi}(k)$ using the equation (3.97) within the given boundary conditions $a < x < a$.

$$\begin{aligned} \hat{\phi}(k) &= \frac{1}{\sqrt{2\pi}} \frac{1}{\sqrt{2a}} \int_{-a}^{a} e^{-ikx} dx = \frac{1}{2\sqrt{\pi a}} \frac{e^{-ikx}}{-ik} \Big|_{-a}^{a} \\ &= \frac{1}{k\sqrt{\pi a}} \left(\frac{e^{ika} - e^{-ika}}{2i} \right) \\ &= \frac{1}{\sqrt{\pi a}} \frac{\sin(ka)}{k}. \end{aligned}$$

Substituting this into equation (3.94) we get

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi a}} \int_{-a}^{a} \frac{\sin(ka)}{k} e^{i} \left(kx - \frac{\hbar k^2}{2m} t \right) dk. \tag{3.107}$$

This integral can be evaluated numerically, as shown by figure 3.6 .

3.3 Properties of the wave function

The wave functions which we derived in the previous section have some significant properties which we want to state formally: these can in fact be generalised to any wave functions and will emerge also in the following sections. To illustrate these properties we will use the wave function derived for the infinite square well.

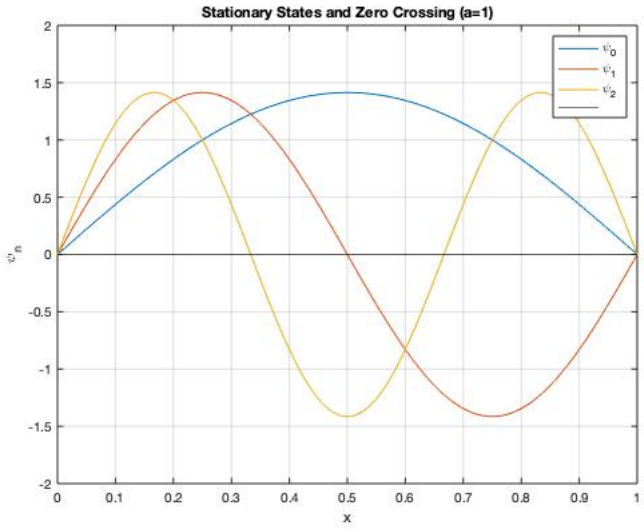


Figure 3.7: Stationary states and zero crossing

Proposition 3.3.1. *The functions ψ-s are alternately even and odd, with respect to the center of the well (whenever the potential is itself a symmetric function)*

Proposition 3.3.2. *With an increase in energy levels, successive states acquires one more node (zero-crossing), as shown in figure 3.7*

Proposition 3.3.3. *The functions ψ-s are mutually orthogonal, in the sense that:*

$$< \psi_m, \psi_n >_{L^2(\mathbb{R})} = \int_{\mathbb{R}} \psi_m(x)\psi_n(x)dx = 0, \tag{3.108}$$

Proof. For $m \neq n$:

$$\begin{aligned} \int_{\mathbb{R}} \psi_m(x)\psi_n(x)dx &= \frac{2}{a} \int_0^a \sin\left(\frac{m\pi}{a}x\right) \sin\left(\frac{n\pi}{a}x\right) dx \\ &= \frac{1}{a} \int_0^a \left[\cos\left(\frac{m-n}{a}\pi x\right) - \cos\left(\frac{m+n}{a}\pi x\right) \right] dx \end{aligned}$$

$$= \frac{1}{(m-n)\pi}\sin\left(\frac{m-n}{a}\pi x\right) - \frac{1}{(m+n)\pi}\sin\left(\frac{m-n}{a}\pi x\right)\Bigg|_0^a$$
$$= \frac{1}{\pi}\frac{\sin[(m-n)\pi]}{(m-n)} - \frac{\sin[(m+n)\pi]}{(m+n)} = 0$$

For $m = n$ we can use the result we found previously in the normalization section. In this case, $< \psi_m, \psi_n >_{L^2(\mathbb{R})} = 1$. We can combine orthogonality and normalization into a single equation:

$$\int \psi_n(x)\psi_n(x)dx = \delta_{m,n} \tag{3.109}$$

where $\delta_{m,n}$ -named the **Kronecker delta**- is defined by

$$\delta_{m,n} = \begin{cases} 0, & \text{if } m \neq n \\ 1, & \text{if } m = n \end{cases} \tag{3.110}$$

■

Notice that this confirms that the ψ-s form an orthonormal set, at least in the case considered (infinite square well). This can be generalised to all $\psi(x)$-s.

Proposition 3.3.4. *These functions ψ-s are complete. In other words, any other function $f(x)$ can be represented as a linear combination of them:*

$$f(x) = \sum_{n=1}^{\infty} c_n\psi_n(x) = \sqrt{\frac{2}{a}}\sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a}x\right) \tag{3.111}$$

In appendix C we provide some additional background theorems that justify the statements above. Proposition 3.3.2 will become useful in Chapter 4 when we will try to use the shooting method to identify the nodes (and eigenvalues) where the candidate wave function inverts itself.

3.4 Quantum harmonic oscillator

The quantum harmonic oscillator is one of the most significant problems in quantum mechanics. Its classical counterpart is governed by the Hooke's law

$$F = -kx = m\frac{d^2x}{dt^2} \tag{3.112}$$

Experimentally, one can determine that there is a linear relationship between the force F and the negative displacement $-x$, with the proportionality constant being k. The solution to equation (3.112) is given by

$$x(t) = A\cos(wt) + B\sin(wt) \tag{3.113}$$

where we define the frequency

$$\omega = \sqrt{\frac{k}{m}} \tag{3.114}$$

Assuming $x_0 = 0$, from the relation

$$F = -\frac{dV}{dx} = -kx \tag{3.115}$$

we can derive that the potential is given by

$$V(x) = \int_{x_0}^{x} ksds = \frac{1}{2}kx^2 \tag{3.116}$$

It's clear now that the quantum harmonic oscillator problem consists of

$$\hat{H}\psi(x) = -\frac{\hbar}{2m}\frac{d^2\psi(x)}{dx^2} + \hat{V}(x)\psi(x) = E\psi \tag{3.117}$$

where

$$\hat{V}(x) = \frac{1}{2}m\omega^2\hat{x}^2 \tag{3.118}$$

In this section we will look at the one-dimensional case where $x \in \mathbb{R}$, but all results can be easily generalised to more dimensions. There are two approaches used to solve this problem, one called algebraic method, another called analytic method and we'll show them both.

If we were to find the minimum of the potential $V(x)$ around some value x_0, assuming that $V(x)$ is analytic in a neighbourhood of x, we would use a Taylor expansion to estimate V:

$$V(x) = V(x)\big|_{x=x_0} + V^{(1)}(x)\big|_{x=x_0}(x - x_0) + \frac{1}{2}V^{(2)}(x)\big|_{x=x_0}(x - x_0)^2 + \mathcal{O}(x^3) \tag{3.119}$$

At this point we know that around the minimum x_0 the potential is convex[6] and the gradient is zero; if we center our coordinate system around $V(x_0)$ we would get

$$V(x) = \frac{1}{2}V^{(2)}(x)\big|_{x=x_0}(x - x_0)^2 + \mathcal{O}(x^3) \tag{3.120}$$

Without loss of generality, we can set $x_0 = 0$ and from equation (3.115) we obtain that $k = V^{(2)}(x)\big|_{x=0}$. This proves that *any* finite potential looks like an harmonic oscillator potential in an open ball $B_\epsilon(r_0)$ of radius $\epsilon > 0$ around its minimum $r_0 \in \mathbb{R}^3$. In other words, we can use the quantum harmonic oscillator as an approximation of many systems commonly used in nuclear physics or elementary particle physics.

Algebraic method

Using equations (3.117) and (3.118) together with the definition of $\hat{p}$, we can write the Hamiltonian operator $\hat{H}$ as

$$\hat{H} = \frac{1}{2}m\omega^2\left(\hat{x}^2 + \frac{\hat{p}^2}{m^2\omega^2}\right) \tag{3.121}$$

The expression in the parenthesis above resembles the module $|c|^2 = \left(\mathrm{Re}^2(c) + \mathrm{Im}^2(c)\right) = (\mathrm{Re}(c) + i\,\mathrm{Im}(c))\,(\mathrm{Re}(c) - i\,\mathrm{Im}(c))$ of a complex number c given real parameters a and b. Therefore we define an operator

$$\hat{C} := \hat{x} + \frac{i\hat{p}}{m\omega} \tag{3.122}$$

It follows that the product between $\hat{C}$ and its self-adjoint $\hat{C}^\dagger$ gives us

$$\begin{aligned}\hat{C}^\dagger\hat{C} = &\left(\hat{x} - \frac{i\hat{p}}{m\omega}\right)\left(\hat{x} + \frac{i\hat{p}}{m\omega}\right)\\ =&\hat{x}^2 + \frac{\hat{p}^2}{m^2w^2} + \frac{i}{m\omega}\left(\hat{x}\hat{p} - \hat{p}\hat{x}\right)\\ =&\ \hat{x}^2 + \frac{\hat{p}^2}{m^2w^2} - \frac{\hbar}{m\omega}\mathbb{1}\end{aligned} \tag{3.123}$$

[6] Namely, it implies that $V^{(2)}(x) \geq 0$.

where $\mathbb{1}$ indicates the identity operator defined in this case by

$$\begin{aligned}\mathbb{1}f :=& -\frac{i}{\hbar}[\hat{x},\hat{p}]f = -\frac{i}{\hbar}\left(x(-i\hbar)\frac{d}{dx}(f) - (-i\hbar)\frac{d}{dx}(xf)\right)\\ =& -\left(x\frac{df}{dx} - x\frac{df}{dx} - f\right)\\ =& f\end{aligned} \tag{3.124}$$

for a generic function f.
We can then rearrange (3.123) as

$$\hat{x}^2 + \frac{\hat{p}^2}{m^2w^2} = \hat{C}^\dagger\hat{C} + \frac{\hbar}{m\omega}\mathbb{1} \tag{3.125}$$

It follows from (3.121) that

$$\hat{H} = \frac{1}{2}m\omega^2\left(\hat{x}^2 + \frac{\hat{p}^2}{m^2\omega^2}\right) = \frac{1}{2}m\omega^2\hat{C}^\dagger\hat{C} + \frac{1}{2}\hbar\omega\mathbb{1} \tag{3.126}$$

If we compute the commutator of $\hat{C}$ and $\hat{C}^\dagger$ for a generic function f, we get using bilinearity that

$$\begin{aligned}[\hat{C},\hat{C}^\dagger]f =& \left[\hat{x} + \frac{i\hat{p}}{m\omega}, \hat{x} - \frac{i\hat{p}}{m\omega}\right]f\\ =& \left[\hat{x}, \hat{x} - \frac{i\hat{p}}{m\omega}\right]f + \left[\frac{i\hat{p}}{m\omega}, \hat{x} - \frac{i\hat{p}}{m\omega}\right]f\\ =& [\hat{x},\hat{x}]\,f - \left[\hat{x}, \frac{i\hat{p}}{m\omega}\right]f + \left[\frac{i\hat{p}}{m\omega}, \hat{x}\right]f - \left[\frac{i\hat{p}}{m\omega}, \frac{i\hat{p}}{m\omega}\right]f\\ =& \frac{i}{m\omega}\left(-[\hat{x},\hat{p}]\,f + [\hat{p},\hat{x}]\,f\right)\\ =& \frac{2\hbar}{m\omega}\mathbb{1}f\end{aligned} \tag{3.127}$$

This implies that

$$\left[\sqrt{\frac{m\omega}{2\hbar}}\hat{C}, \sqrt{\frac{m\omega}{2\hbar}}\hat{C}^\dagger\right] = \mathbb{1} \tag{3.128}$$

In order to obtain a "unit-free" operator, we introduce some new operators a and $a^\dagger$ defined by

$$\begin{cases}\hat{a} := \sqrt{\frac{m\omega}{2\hbar}}C = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} + \frac{i\hat{p}}{m\omega}\right)\\ \hat{a}^\dagger := \sqrt{\frac{m\omega}{2\hbar}}C^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} - \frac{i\hat{p}}{m\omega}\right)\end{cases} \tag{3.129}$$

whose commutator satisfies

$$\left[\hat{a}, \hat{a}^\dagger\right] = \mathbb{1} \tag{3.130}$$

The fact that (3.130) holds and that $\hat{a} = \left(\hat{a}^\dagger\right)^\dagger$ implies that $\hat{a}$ and $\hat{a}^\dagger$ are dimensionless. This can also be deduced by the fact that $\sqrt{\frac{m\omega}{2\hbar}}$ has unit $\left[\sqrt{\frac{[kg][s]}{[J][s]}}\right] = \left[\frac{1}{[m]}\right]$, while $\hat{x}$ and $\frac{\hat{p}}{m\omega}$ have both unit $[m]$. In addition, any product of the operators $\hat{a}$ and $\hat{a}^\dagger$ will be dimensionless as well.

One of the advantages of a "dimensionless" operator is that its respective eigenvalues will be dimensionless as well. This is relevant since the true argument of any wave functions are often unit-free. As an example, we typically solve the differential equation $y^{(2)}(t) + \alpha^2 y(t) = 0$ with respect to the variable t and not the frequency $\omega = \alpha t$.
Using definition (3.129), if we substitute $\hat{a}$ and $\hat{a}^\dagger$ back into (3.126), we obtain

$$\hat{H} = \frac{1}{2}m\omega^2\hat{C}^\dagger\hat{C} + \frac{1}{2}\hbar\omega\mathbb{1} = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right) = \hbar\omega\left(\hat{N} + \frac{1}{2}\right) \tag{3.131}$$

where we define the number operator $\hat{N}$ as

$$\hat{N} := \hat{a}^\dagger\hat{a} \tag{3.132}$$

Notice that by construction $\hat{N}$ is a *self-adjoint* (sometimes also called "hermitian") operator since

$$\hat{N}^\dagger = \left(\hat{a}^\dagger\hat{a}\right)^\dagger = \left(\hat{a}^\dagger\hat{a}\right) = \hat{N} \tag{3.133}$$

The reader can look at appendix C, definition C.2.9 for a formal definition. It follows via Theorem C.2.16, that $\hat{N}$ must have real eigenvalues which we call N; in addition, due to equation (3.131) we have that $\hat{N}$ coincides with the Hamiltonian up to a scale factor $\hbar\omega$ and an additive constant $\frac{\hbar\omega}{2}$. This implies that

$$E\psi(x) = \hat{H}\psi(x) = \hbar\omega\left(\hat{N} + \frac{1}{2}\right)\psi(x) = \hbar\omega\left(N + \frac{1}{2}\right)\psi \tag{3.134}$$

From (3.130) we infer that given $\hat{N}f = \hat{a}^\dagger\hat{a}f = Nf$,

$$\hat{N}\left(\hat{a}^\dagger f\right) = \hat{a}^\dagger\hat{a}\left(\hat{a}^\dagger f\right) = \hat{a}^\dagger\left(\hat{a}^\dagger\hat{a} + \mathbb{1}\right)f = \hat{a}^\dagger(N+1)f = (N+1)(\hat{a}^\dagger f) \tag{3.135}$$

for some generic function f. We can see that $\hat{a}^\dagger$ acts on f by increasing its eigenvalue of one unit. Since the commutator of the ladders operator is the identity, $\hat{a}$ must have the opposite effect, i.e. decreases the eigenvalue by one unit. This allow us to conclude that the eigenspace of $\hat{N}$ must be discrete. In fact, since both $\hat{a}$ and $\hat{a}^\dagger$ have a countable set of eigenvalues, the same must hold for $\hat{N}$. Hence, we can assume that $N \in \mathbb{N}_0$ as there exists always a bijection between a countable set and $\mathbb{N}_0$.
We deduce that the discrete energy levels are given by

$$E_N = \hbar\omega\left(N + \frac{1}{2}\right), \quad N \in \mathbb{N}_0 \tag{3.136}$$

In order to check if N is well defined at 0, we compute the expectation of the Hamiltonian

$$\begin{aligned} < \hat{H} >_\psi &= \int_{\mathbb{R}} \psi^* \hat{H}\psi dx = \int_{\mathbb{R}} \psi^* \left(\hbar\omega\hat{a}^\dagger\hat{a} + \frac{\hbar\omega}{2}\right)\psi dx \\ &= \int_{\mathbb{R}} \psi^* \left(\hbar\omega\hat{a}^\dagger\hat{a}\right)\psi dx + \int_{\mathbb{R}} \psi^* \left(\frac{\hbar\omega}{2}\right)\psi dx \\ &= \hbar\omega\int_{\mathbb{R}} \left(\hat{a}\psi\right)^* \left(\hat{a}\psi\right) dx + \frac{1}{2}\hbar\omega\int_{\mathbb{R}} \psi^*\psi dx \\ &= \hbar\omega < \hat{a}\psi, \hat{a}\psi >_{L^2(\mathbb{R})} + \frac{1}{2}\hbar\omega \geq \frac{1}{2}\hbar\omega \end{aligned} \tag{3.137}$$

Since the square of any generic norm is always bigger than zero, we have found a lower bound for any energy eigenstates E_N where the smallest N coincides with zero. It follows that for the ground state wavefunction ψ we require that

$$\hat{a}\psi_0 = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} + \frac{i\hat{p}}{m\omega}\right)\psi_0 = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} + \frac{\hbar}{m\omega}\frac{d}{dx}\right)\psi_0 \stackrel{!}{=} 0 \tag{3.138}$$

By rearranging we obtain

$$\frac{d\psi_0}{dx} = -\frac{m\omega}{\hbar} x\psi_0 \tag{3.139}$$

Using separation of variables we get

$$\psi_0(x) = Ae^{-\frac{m\omega}{2\hbar}x^2} \tag{3.140}$$

In order to determine A, we normalise ψ_0. Set $u := \sqrt{\frac{m\omega}{\hbar}}x$, then $du = \sqrt{\frac{m\omega}{\hbar}}dx$

$$\begin{aligned}\left(\int_{\mathbb{R}} |\psi_0(x)|^2 dx\right)^2 &= \left(\frac{\hbar}{m\omega}\right)\left(\int_{\mathbb{R}} A^2 e^{-u^2} du\right)^2 \\ &= \frac{\hbar A^4}{m\omega} 2 \iint_{\mathbb{R}>0} e^{-x^2} e^{-y^2} dxdy \\ &= \frac{\hbar A^4}{m\omega} 2 \iint e^{-r^2} r dr d\phi \\ &= \frac{-\hbar A^4}{m\omega} e^{-r^2}\Big|_0^\infty \pi \\ &= \frac{\hbar A^4}{m\omega}\pi\end{aligned} \tag{3.141}$$

Note that throughout the computation above we used that e^{u^2} is an even function, and we substituted polar coordinates r and ϕ, where $r \in (0, \infty)$, $\phi \in [0, \frac{\pi}{2}]$. It follows that the wave equation that describes the ground state is given by

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar}x^2} \tag{3.142}$$

In equation (3.138) we have seen that the operator $\hat{a}$ annihilates ψ_0. This also implies that $\hat{N}\psi_0 = 0$. Suppose that also $\hat{a}^\dagger$ cancels ψ_0, then we would get that the commutator $[\hat{a}, \hat{a}^\dagger]$ is 0 which is a contradiction with (3.130). Hence, we define

$$\psi_1 = \hat{a}^\dagger \psi_0 \tag{3.143}$$

Our claim is that ψ_1 is in fact an energy eigenstate of the Hamiltonian:

$$\hat{N}\psi_1 = \hat{N}\hat{a}^\dagger\psi_0 = \hat{N}\left(a^\dagger\psi_0\right) - a^\dagger\left(\hat{N}\psi_0\right) = [\hat{N}, \hat{a}^\dagger]\psi_0 \tag{3.144}$$

Note that

$$[\hat{N}, \hat{a}^\dagger] = [\hat{a}^\dagger\hat{a}, \hat{a}^\dagger] = \hat{a}^\dagger[\hat{a}, \hat{a}^\dagger] = \hat{a}^\dagger \tag{3.145}$$

It follows from (3.144) that

$$\hat{N}\psi_1 = [\hat{N}, \hat{a}^\dagger]\psi_0 = a^\dagger\psi_0 = \psi_1 \tag{3.146}$$

Thus, we have shown that ψ_1 is an eigenstate of $\hat{N}$ with eigenvalue equal to one. This corresponds to the energy eigenvalue $\frac{3}{2}\hbar\omega$ with respect to the Hamiltonian. The operator $\hat{a}^\dagger$ has increased the eigenvalue of the number operator $\hat{N}$ by exactly one unit. This is a general property of $\hat{a}^\dagger$ which is also named "raising" or "ladder" operator and it confirms our previous discussion in which we indicated that the eigenvalues of $\hat{N}$ could be identified as non-negative integers.

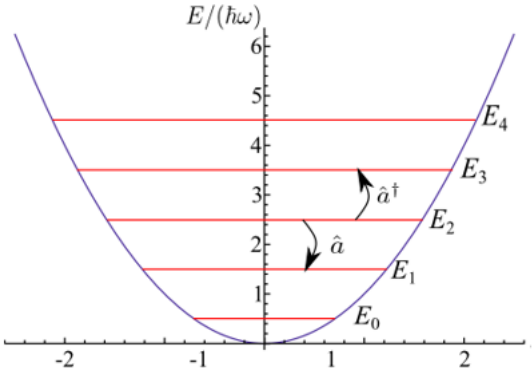


Figure 3.8: Raising or ladder operators in the quantum oscillator

Let's check by remembering that $\hat{a}\psi_0 = 0$ if ψ_1 has unitary norm:

$$\begin{aligned} < \psi_1, \psi_1 >_{L^2(\mathbb{R})} &= < \psi_0, \hat{N}\psi_0 >_{L^2(\mathbb{R})} \\ &= < \psi_0, \hat{a}\hat{a}^\dagger\psi_0 >_{L^2(\mathbb{R})} \\ &= < \psi_0, \hat{a}\hat{a}^\dagger\psi_0 - a^\dagger(\hat{a}\psi_0) >_{L^2(\mathbb{R})} \\ &= < \psi_0, [\hat{a}, \hat{a}^\dagger]\psi_0 >_{L^2(\mathbb{R})} \\ &= < \psi_0, \psi_0 >_{L^2(\mathbb{R})} = 1 \end{aligned} \tag{3.147}$$

We can now build the k-th state which has eigenvalue $N = k$, energy eigenvalue $E_N = \frac{2k+1}{2}\hbar\omega$ and eigenfunction $\psi_k := \left(\hat{a}^\dagger\right)^k \psi_0$ for $k \in \mathbb{N}$. Let ψ'_k be the non-normalised version of ψ_k, then

$$\begin{aligned} \hat{N}\psi'_k = \hat{N}\overbrace{\hat{a}^\dagger \dots \hat{a}^\dagger}^{k \text{ times}}\psi_0 &= \hat{N}\overbrace{\hat{a}^\dagger \dots \hat{a}^\dagger}^{k \text{ times}}\psi_0 - \overbrace{\hat{a}^\dagger \dots \hat{a}^\dagger}^{k \text{ times}}\hat{N}\psi_0 \\ = [\hat{N}, \underbrace{\hat{a}^\dagger \dots \hat{a}^\dagger}_{k \text{ times}}]\psi_0 &= k\underbrace{\hat{a}^\dagger \dots \hat{a}^\dagger}_{k-1 \text{ times}}\psi_0 = k\psi'_k \end{aligned} \tag{3.148}$$

Note that we used that $\left[\hat{N}, \left(\hat{a}^\dagger\right)^k\right] = k\left(\hat{a}^\dagger\right)^{k-1}$ (this relation that can be easily proved by induction) and that $\hat{N}\psi_0 = 0$ to derive the eigenvalue equation above. Since we are looking for wave functions with norm one, we compute the scalar product of the ψ'_k which are not normalised:

$$\begin{aligned} < \psi'_k, \psi'_k >_{L^2(\mathbb{R})} &= < \left(\hat{a}^\dagger\right)^k \psi_0, \left(\hat{a}^\dagger\right)^k \psi_0 >_{L^2(\mathbb{R})} \\ &= < \psi_0, (\hat{a})^k \left(\hat{a}^\dagger\right)^k \psi_0 >_{L^2(\mathbb{R})} \\ &= < \psi_0, (\hat{a})^{k-1} \left[\hat{a}, \left(\hat{a}^\dagger\right)^k\right] \psi_0 >_{L^2(\mathbb{R})} \\ &= < \psi_0, k\,(\hat{a})^{k-1} \left(\hat{a}^\dagger\right)^{k-1} \psi_0 >_{L^2(\mathbb{R})} \\ &= k < \psi_0, (\hat{a})^{k-2} \left[\hat{a}, \left(\hat{a}^\dagger\right)^{k-1}\right] \psi_0 >_{L^2(\mathbb{R})} \\ &= (k)\,(k-1) < \psi_0, (\hat{a})^{k-2} \left(\hat{a}^\dagger\right)^{k-2} \psi_0 >_{L^2(\mathbb{R})} \\ &= \cdots = k! < \psi_0, (\hat{a}) \left(\hat{a}^\dagger\right) \psi_0 >_{L^2(\mathbb{R})} \\ &= k! < \psi_0, \psi_0 >_{L^2(\mathbb{R})} = k! \end{aligned} \tag{3.149}$$

Therefore, the wave function ψ_N and the energy (evenly-spaced) eigenvalues are given by

$$\psi_N(x) = \sqrt{\frac{1}{N!}} \left(\hat{a}^\dagger\right)^N \psi_0, \quad E_N = \hbar\omega\left(N + \frac{1}{2}\right), \quad N \in \mathbb{N}_0 \tag{3.150}$$

while

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar}x^2} \tag{3.151}$$

Example 3.4.1. Using the generating formula contained in (3.150) we can derive explicitly ψ_1, ψ_2 and ψ_3.

$$\begin{aligned}
\psi_1(x) = A\hat{a}^\dagger\psi_0 = A\sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} - \frac{i\hat{p}}{m\omega}\right)\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar}x^2} \\
=A\left(\left(\frac{m\omega}{\hbar}\right)^3\left(\frac{1}{4\pi}\right)\right)^{\frac{1}{4}}\left(\hat{x} - \frac{\hbar}{m\omega}\frac{d}{dx}\right)e^{-\frac{m\omega}{2\hbar}x^2} \\
= A\left(\left(\frac{m\omega}{\hbar}\right)^3\left(\frac{1}{4\pi}\right)\right)^{\frac{1}{4}}\left(xe^{-\frac{m\omega}{2\hbar}x^2} + xe^{-\frac{m\omega}{2\hbar}x^2}\right) \\
= A\left(\left(\frac{m\omega}{\hbar}\right)\left(\frac{4}{\pi}\right)\right)^{\frac{1}{4}}\left(\left(\sqrt{\frac{m\omega}{\hbar}}x\right)e^{-\frac{1}{2}\left(\sqrt{\frac{m\omega}{\hbar}}x\right)^2}\right)
\end{aligned} \tag{3.152}$$

Thanks to (3.147) we already know that $A = 1$. Through explicit computation we get that for some real α

$$\int x^2 e^{-\alpha x^2} dx = -\frac{e^{-\alpha x^2}}{2\alpha}x + \int \frac{e^{-\alpha x^2}}{2\alpha} dx \tag{3.153}$$

Due to the dominance of the exponential function, the same integral computed over $\mathbb{R}$ gives us

$$\int_{\mathbb{R}} x^2 e^{-\alpha x^2} dx = \int_{\mathbb{R}} \frac{e^{-\alpha x^2}}{2\alpha} dx = \int_{\mathbb{R}} \frac{e^{-u^2}}{2\alpha^{\frac{3}{2}}} du = \frac{\sqrt{\pi}}{2\alpha^{\frac{3}{2}}} \tag{3.154}$$

If we choose $\alpha = \frac{m\omega}{2\hbar}$ we see that

$$\begin{aligned}
1 = \int_{\mathbb{R}} |\psi_1(x)|^2 dx = \int_{\mathbb{R}} \left(A\left(\left(\frac{m\omega}{\hbar}\right)^3\left(\frac{4}{\pi}\right)\right)^{\frac{1}{4}}\left(xe^{-\frac{m\omega}{2\hbar}x^2}\right)\right)^2 dx \\
= \left(A^2\left(\left(\frac{m\omega}{\hbar}\right)^3\left(\frac{4}{\pi}\right)\right)^{\frac{1}{2}}\right)\frac{\sqrt{\pi}}{2\alpha^{\frac{3}{2}}} = A^2
\end{aligned} \tag{3.155}$$

Similarly,

$$\begin{aligned}
\psi_2(x) = B\hat{a}^\dagger\hat{a}^\dagger\psi_0 = B\left(\left(\frac{m\omega}{\hbar}\right)^5\frac{1}{16\pi}\right)^{\frac{1}{4}}\left(\hat{x} - \frac{\hbar}{m\omega}\frac{d}{dx}\right)^2 e^{-\frac{m\omega}{2\hbar}x^2} \\
= 2B\left(\left(\frac{m\omega}{\hbar}\right)^5\frac{1}{16\pi}\right)^{\frac{1}{4}}\left(\hat{x} - \frac{\hbar}{m\omega}\frac{d}{dx}\right)xe^{-\frac{m\omega}{2\hbar}x^2} \\
= 2B\left(\left(\frac{m\omega}{\hbar}\right)^5\frac{1}{4^2\pi}\right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar}x^2}\left(x^2 + x^2 - \frac{\hbar}{m\omega}\right) \\
= \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}\left(2\left(x\sqrt{\frac{m\omega}{\hbar}}\right)^2 - 1\right)e^{-\frac{1}{2}\left(\sqrt{\frac{m\omega}{\hbar}}x\right)^2}
\end{aligned} \tag{3.156}$$

In order to find the constant B we define

$$I_n = \int_{\mathbb{R}} x^n e^{-x^2} dx = \frac{e^{-x^2}}{-2} x^{n-1}\Big|_{-\infty}^{+\infty} + \frac{1}{2}\int_{\mathbb{R}} (n-1)x^{n-2}e^{-x^2}dx = 0 + \frac{n-1}{2} I_{n-2} \tag{3.157}$$

where of course

$$I_0 = \int_{\mathbb{R}} x^0 e^{-x^2} dx = \sqrt{\pi}, \quad I_1 = \int_{\mathbb{R}} x^1 e^{-x^2} dx = 0 \tag{3.158}$$

Therefore we deduce that for all n that are *even integers:*

$$I_n = \frac{n-1}{2} I_{n-2} = \frac{(n-3)\,(n-1)}{2^2} I_{n-4} = \cdots = \frac{(n-1)\,(n-3)\ldots 3\;\;1}{2^{\frac{n}{2}}} I_0, \tag{3.159}$$

while for all n that are *odd integers:*

$$I_n = 0 \tag{3.160}$$

Now we can compute

$$\begin{aligned} \int_{\mathbb{R}} (2s^2-1)^2 e^{-s^2} ds =& \int_{\mathbb{R}} (4s^4 - 4s^2 + 1) e^{-s^2} ds \\ =& 4I_4 - 4I_2 + I_0 \\ =& \sqrt{\pi}\left(4\frac{3}{4} - 4\frac{1}{2} + 1\right) \\ =& 2\sqrt{\pi} \end{aligned} \tag{3.161}$$

We set $u := \sqrt{\frac{m\omega}{\hbar}}x$ and $c = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}$, $c' = \sqrt{\frac{m\omega}{\hbar}} = c^2\sqrt{\pi}$, so we obtain

$$1 = <\psi_2, \psi_2>_{L^2\mathbb{R}} = \; B^2 \frac{c^2}{c^2\sqrt{\pi}} 2\sqrt{\pi} = \; 2B^2 \tag{3.162}$$

which implies that $B = \frac{1}{\sqrt{2}}$.

By comparing (3.152) with (3.156), we deduce that we can express the wave equations more concisely if we use the substitution $u := \sqrt{\frac{m\omega}{\hbar}}x$ for the dimensionless variable u. The first three eigenfunctions and correspondent energy eigenvalues become

$$\psi_0(u) = \left(\left(\frac{m\omega}{\hbar\pi}\right)\right)^{\frac{1}{4}} e^{-\frac{u^2}{2}}, \quad E_0 = \frac{\hbar\omega}{2} \tag{3.163}$$

$$\psi_1(u) = \sqrt{2}\left(\left(\frac{m\omega}{\hbar\pi}\right)\right)^{\frac{1}{4}} (u)\, e^{-\frac{u^2}{2}}, \quad E_1 = \frac{3\hbar\omega}{2} \tag{3.164}$$

$$\psi_2(u) = \frac{1}{\sqrt{2}}\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \frac{\left(4u^2-2\right)}{2} e^{-\frac{u^2}{2}}, \quad E_2 = \frac{5\hbar\omega}{2} \tag{3.165}$$

We observe that 1, u, $2(2u^2-1)$ are the first three terms of a polynomial H_n named *Hermite polynomial* which we have analysed extensively in Appendix C. In addition, the normalisation factor of ψ_0 is recurrent. This suggests that a general eigenfunction ψ_n will have the form

$$\psi_n(u) = A_n \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \widetilde{H}_n(u) e^{-\frac{u^2}{2}}, \quad E_n = \frac{(2n+1)\hbar\omega}{2} \tag{3.166}$$

Here $\widetilde{H}_n$ represents the irreducible Hermite polynomial. Formula (3.159) gives us a framework to find the normalisation constant A_n. For example, since the third *Hermite polynomial* is given by

$$H_3 = 4(2u^3 - 3u) \tag{3.167}$$

we can compute using its irreducible factor

$$\begin{aligned}\int_{\mathbb{R}}(2u^3-3u)^2e^{-u^2}du &= \int_{\mathbb{R}}(4u^6+9u^2-12u^4)e^{-u^2}du\\ &= (4I_6-9I_2-12I_4)\\ &= \left(4\frac{15}{8}+9\frac{1}{2}-12\frac{3}{4}\right)\sqrt{\pi}\\ &= 3\sqrt{\pi}\end{aligned} \tag{3.168}$$

Our guess is that the wave function ψ_3 will be of the form

$$\psi_3(u) = A_3\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}\left(2u^3-3u\right)e^{-\frac{u^2}{2}} \tag{3.169}$$

since we are using the irreducible form of the Hermite polynomials. Therefore, it must hold that

$$(A_3)^{-2}\sqrt{\pi} = 3\sqrt{\pi} \tag{3.170}$$

Hence,

$$A_3 = \frac{1}{\sqrt{3}} \tag{3.171}$$

while

$$\psi_3(u) = \frac{1}{\sqrt{3}}\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}\left(2u^3-3u\right)e^{-\frac{u^2}{2}}, \quad E_3 = \frac{7\hbar\omega}{2} \tag{3.172}$$

To fully justify equation (3.170) we know that, since

$$\psi_n(u) = A_n\mu\widetilde{H}_n e^{-\frac{u^2}{2}} \quad \text{with} \quad u=\sqrt{\frac{m\omega}{\hbar}}x,\ \mu=\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \tag{3.173}$$

and $\frac{du}{dx} = \sqrt{\frac{m\omega}{\hbar}} = \mu^2\sqrt{\pi}$ it must hold that

$$\begin{aligned}&\int_{\mathbb{R}}A_n^2\mu^2\widetilde{H}_n(u)^2e^{-u^2}du = \int_{\mathbb{R}}A_n^2\mu^2\widetilde{H}_n(u)^2e^{-u^2}\frac{du}{dx}dx = \left(\int_{\mathbb{R}}A_n^2\mu^2\widetilde{H}_n^2e^{-u^2}dx\right)\frac{du}{dx}\\ &= ||\psi_n||^2_{L^2}\frac{du}{dx} = \mu^2\sqrt{\pi}\end{aligned} \tag{3.174}$$

Therefore, we get that

$$\mu^2\sqrt{\pi} \overset{!}{=} A_n^2\mu^2\underbrace{\int_{\mathbb{R}}\widetilde{H}_n^2(u)e^{-u^2}du}_{J_n} = A_n^2\mu^2J_n = A_n^2\mu^2\alpha\sqrt{\pi} \tag{3.175}$$

where thanks to equation (3.159)

$$\exists\alpha\in\mathbb{R}:\ \alpha := \sum_{j\in J\subset\mathbb{N}}I_j\frac{1}{I_0} = \frac{J_n}{I_0} \tag{3.176}$$

Hence, $A_n^{-2}\sqrt{\pi}\overset{!}{=}J_n$ which justifies equation (3.170).

Analytic method

We will now proceed with another derivation of the wave function that solves the time-independent Schrödinger equation for the quantum harmonic oscillator. We will develop our reasoning independently from the results which we obtained previously in order to offer the reader a true comparison of the two methods. Recall that we need to solve

$$\hat{H}\psi(x) = -\frac{\hbar}{2m}\frac{d^2\psi(x)}{dx^2} + \hat{V}(x)\psi(x) = E\psi \tag{3.177}$$

where

$$\hat{V}(x) = \frac{1}{2}m\omega^2\hat{x}^2 \tag{3.178}$$

To this purpose, let's define a variable $u := \frac{x}{a}$ which is "unit free" as typically this is the case for the argument of the wave function ψ, as motivated in the previous section. Hence, a must have unit *length*. Since $\hbar\omega$ has unit *energy*, we define a through the identity

$$m\omega^2 a^2 \stackrel{!}{=} \hbar\omega \tag{3.179}$$

In fact, $[kg\ \frac{rad^2}{s^2}\ m^2]$ on the left hand side is proportional to $[Joule]$ on the right hand side. By rearranging we obtain

$$a^2 = \frac{\hbar}{m\omega} \tag{3.180}$$

In addition,

$$x = au, \quad \frac{du}{dx} = \frac{1}{a}, \quad \frac{d^2u}{dx^2} = \frac{1}{a^2} \tag{3.181}$$

By plugging into the time-independent Schrödinger equation subject to the potential boundary condition, we obtain

$$-\frac{\hbar^2}{2ma^2}\psi^{(2)}(u) + \frac{1}{2}m\omega^2 a^2 u^2\psi(u) = E\psi(u) \tag{3.182}$$

Note that by construction

$$\hbar\omega = m\omega^2 a^2 = \frac{\hbar^2}{ma^2} \tag{3.183}$$

By plugging again into the time-independent Schrödinger equation we get

$$-\frac{\hbar\omega}{2}\psi^{(2)}(u) + \frac{1}{2}\hbar\omega u^2\psi(u) = E\psi(u) \tag{3.184}$$

Now we define

$$\epsilon := \frac{2E}{\hbar\omega} \ \leftrightarrow\ \hbar\omega = \frac{2E}{\epsilon} \tag{3.185}$$

and, by plugging in again in the Schrödinger equation we obtain

$$-\frac{2E}{2\epsilon}\psi^{(2)}(u) + \frac{2E}{\epsilon}u^2\psi(u) = E\psi(u) \tag{3.186}$$

Since we are not interest in the trivial solution $E = 0\ \forall u$, we divide by E and multiply by ϵ on both sides and get

$$-\psi^{(2)}(u) + u^2\psi(u) = \epsilon\psi(u) \tag{3.187}$$

Finally, we get a rearrangement that looks easier to work with than the original time-independent Schrödinger equation

$$\psi(u)(u^2 - \epsilon) = \psi^{(2)}(u) \tag{3.188}$$

where

$$u = \frac{x}{a} = x\sqrt{\frac{\hbar}{m\omega}}, \quad \epsilon = \frac{2E}{\hbar\omega} \tag{3.189}$$

Note that this is exactly the same substitution which we used before with the algebraic method, as it guarantees that the variable u is dimension free. In order to simplify further, we notice that e^{-x^2} is a solution of the differential equation $Ay(x) + Byx^2 = y^{(2)},\ A, B \in \mathbb{R}$, which is of the same type of (3.188).

$$\frac{d^2}{dx}e^{-x^2} = 4e^{-x^2}x^2 - 2e^{-x^2} \tag{3.190}$$

Hence, we use the *Ansatz*

$$\psi(u) = h(u)e^{-\frac{u^2}{2}} \tag{3.191}$$

which has derivatives

$$\psi^{(1)}(u) = h^{(1)}(u)e^{-\frac{u^2}{2}} - uh(u)e^{-\frac{u^2}{2}}, \tag{3.192}$$

$$\begin{aligned}\psi^{(2)}(u) =& h^{(2)}(u)e^{-\frac{u^2}{2}} - uh^{(1)}(u)e^{-\frac{u^2}{2}} - u\left(h^{(1)}(u)e^{-\frac{u^2}{2}} - uh(u)e^{-\frac{u^2}{2}}\right) \\ &- h(u)e^{-\frac{u^2}{2}} \\ =& e^{-\frac{u^2}{2}}\left(h^{(2)}(u) + h^{(1)}(u)(-2u) + h(u)(u^2 - 1)\right)\end{aligned} \tag{3.193}$$

By rearranging, the factor $e^{-\frac{u^2}{2}}$ simplifies as expected, and hence we get

$$\begin{aligned}&h^{(2)}(u) + h^{(1)}(u)(-2u) + h(u)\left(u^2 - 1 - u^2 + \epsilon\right) \\ &= h^{(2)}(u) + h^{(1)}(u)(-2u) + h(u)\left(\epsilon - 1\right) = 0\end{aligned} \tag{3.194}$$

This equation looks familiar as it closely resembles the *Hermite differential equation* which we discussed in the appendix C, theorem C.3.6. Hence, we set

$$\epsilon - 1 = 2n \ \leftrightarrow\ \epsilon = 2n + 1 \ \leftrightarrow\ E_n = \frac{2n+1}{2}\hbar\omega,\ n \in \mathbb{N}_0 \tag{3.195}$$

The time-independent Schrödinger equation becomes

$$h^{(2)}(u) + h^{(1)}(u)(-2u) + h(u)\left(2n\right) \tag{3.196}$$

which is now identical to the *Hermite differential equation*. Therefore, we know that a solution to (3.196) is given by

$$h(u) = AH_n(u), \quad A \in \mathbb{R} \tag{3.197}$$

This implies

$$\psi(u) = AH_n(u)e^{-\frac{u^2}{2}}, \quad A \in \mathbb{R} \tag{3.198}$$

As a side note, it is clear by comparison that $\epsilon - 1$ must be a non-negative integer in order for equation (3.194) to coincide with the *Hermite equation*. This implies that the energy will only take discrete values according to expression (3.195).

At this point we need to find the normalisation constant A. Remember that the original wave function was dependent on x, so we should integrate with respect to x in order to keep into account the determinant of the integral derived from the substitution $x = ua = u\sqrt{\frac{\hbar}{m\omega}}$, which is given by $\left|\frac{du}{dx}\right| = a = \sqrt{\frac{\hbar}{m\omega}}$. Hence,

$$\begin{aligned} 1 =& < \psi(x), \psi(x) >_{L^2(\mathbb{R})} = \int_{\mathbb{R}} |\psi(x)|^2 \, dx = a \int_{\mathbb{R}} |\psi(u)|^2 \, du \\ &= aA^2 \int_{\mathbb{R}} H_n^2(u) e^{-u^2} du = aA^2 2^n n! \sqrt{\pi} \end{aligned} \tag{3.199}$$

Note that in the last step we used the result proved in Appendix C. Solving for A, we get

$$A = \sqrt{\frac{1}{a 2^n n! \sqrt{\pi}}} = \left(\frac{m\omega}{\hbar\pi}\right)^{\frac{1}{4}} \left(\frac{1}{2^n n!}\right)^{\frac{1}{2}} \tag{3.200}$$

Hence, we have proven that the wave function that solves the quantum oscillator time-independent Schrödinger equation is given by

$$\psi_n(x) = \left(\frac{m\omega}{\hbar\pi}\right)^{\frac{1}{4}} \left(\frac{1}{2^n n!}\right)^{\frac{1}{2}} H_n\left(x\sqrt{\frac{m\omega}{\hbar}}\right) e^{-\frac{m\omega}{2\hbar}x^2} \tag{3.201}$$

with discrete energy levels given by

$$E_n = \frac{2n+1}{2}\hbar\omega, \; n \in \mathbb{N}_0 \tag{3.202}$$

Recall that the solution to the time-dependent Schrödinger equation was of the type $\Psi(x,t) = \psi(x)e^{-it\frac{E}{\hbar}}$. Hence,

$$\Psi_n(x,t) = \left(\frac{m\omega}{\hbar\pi}\right)^{\frac{1}{4}} \left(\frac{1}{2^n n!}\right)^{\frac{1}{2}} H_n\left(x\sqrt{\frac{m\omega}{\hbar}}\right) e^{-\omega\left(\frac{m}{2\hbar}x^2 + it\frac{2n+1}{2}\right)} \quad n \in \mathbb{N}_0 \tag{3.203}$$

Using the formula we just derived, we can write down the first four $\psi_n(x)$ to compare them with the results we derived previously:

$$\begin{aligned} \psi_0(x) =& \left(\frac{m\omega}{\hbar\pi}\right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar}x^2} \\ =& \left(\frac{m\omega}{\hbar\pi}\right)^{\frac{1}{4}} e^{-\frac{u^2}{2}} \\ \psi_1(x) =& \left(\frac{m\omega}{\hbar\pi}\right)^{\frac{1}{4}} \left(\frac{1}{2}\right)^{\frac{1}{2}} 2x\sqrt{\frac{m\omega}{\hbar}} e^{-\frac{m\omega}{2\hbar}x^2} \\ =& \left(\frac{m\omega}{\hbar\pi}\right)^{\frac{1}{4}} (2)^{\frac{1}{2}} u e^{-\frac{u^2}{2}} \\ \psi_2(x) =& \left(\frac{m\omega}{\hbar\pi}\right)^{\frac{1}{4}} \left(\frac{1}{2^3}\right)^{\frac{1}{2}} \left(4\left(x\sqrt{\frac{m\omega}{\hbar}}\right)^2 - 2\right) e^{-\frac{m\omega}{2\hbar}x^2} \\ =& \sqrt{\frac{1}{2}} \left(\frac{m\omega}{\hbar\pi}\right)^{\frac{1}{4}} \frac{4u^2 - 2}{2} e^{-\frac{u^2}{2}} \\ \psi_3(x) =& \left(\frac{m\omega}{\hbar\pi}\right)^{\frac{1}{4}} \left(\frac{1}{(16)(3)}\right)^{\frac{1}{2}} 4\left(2\left(x\sqrt{\frac{m\omega}{\hbar}}\right)^3 - 3x\sqrt{\frac{m\omega}{\hbar}}\right) e^{-\frac{m\omega}{2\hbar}x^2} \\ =& \sqrt{\frac{1}{3}} \left(\frac{m\omega}{\hbar\pi}\right)^{\frac{1}{4}} \left(2u^3 - 3u\right) e^{-\frac{u^2}{2}} \end{aligned} \tag{3.204}$$

Comparison of quantum and classical harmonic oscillator

In general terms, a simple harmonic oscillator is a system which has an harmonic motion around the origin. Here we will consider oscillations in one-dimension. The example we are going to use is a mass moving back and forth along the x-direction about the equilibrium position $x = 0$.

Classical harmonic oscillator

The idea that would be followed in classical mechanics is that the particle moves in response to a linear restoring force $F = -kx$, where x is the displacement from the origin. There are two turning point between which the motion occurs $x = \pm A$, where A is the amplitude of the motion. The position of the object is periodic in time with angular frequency $\omega = \sqrt{\frac{k}{m}}$, therefore the position can be written as $x(t) = A\ cos(\omega t + \varphi)$. This yields energy

$$E = \frac{1}{2}mu^2 + \frac{1}{2}kx^2 \tag{3.205}$$

Turning points are stationary so the velocity is $u = 0$; this in turn means that that the kinetic energy at the turning points is 0 and the energy is equal to the potential. The graph of potential energy versus displacement (figure 3.9) produces a parabola mimicking a shape similar to the movement of the particle. On the same graph we plot the total energy as an horizontal line with interception points at $\pm A$.

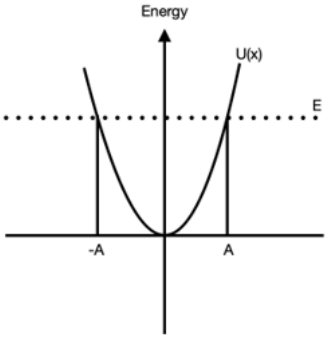


Figure 3.9: Graph of energy versus displacement from the origin

Visually, the vertical distance between the two graphs is the kinetic energy, which is essentially a rearrangement of the original energy equation. The potential energy well of a classical harmonic oscillator is depicted in the graph and is where the motion is confined between the two turning points.
Moreover, the area below the parabola and above the x-axis becomes negligible because the motion is confined to the area where kinetic energy is positive, this also means that the oscillator can not classically be found beyond its turning points.

Quantum harmonic oscillator

A limitation of the classical method applied to the classical harmonic oscillator is that it is not general, meaning that it cannot be used for small entities such as electrons. As we have already derived most of the results, we will summarise them below.
In the quantum harmonic oscillator, the potential energy is given by

$$V(x) = \frac{1}{2}m\omega^2 x^2, \quad \omega = \sqrt{\frac{k}{m}} \tag{3.206}$$

Combining this with the Time-independent Schrödinger equation gives

$$-\frac{h}{2m}\frac{\partial^2\psi}{\partial x^2} + \frac{1}{2}m\omega^2 x^2\psi = E\psi \tag{3.207}$$

In order to find the required energy eigenvalue and its eigenfunction, the requirement which arises is that the wave function must be normalisable. The allowed discrete energy levels are given by

$$E_n = \frac{2n+1}{2}\hbar\omega \quad n \in \mathbb{N}_0 \tag{3.208}$$

The wave functions that correspond to these energy eigenvalues are

$$\psi_n(x) = N_n e^{-\frac{m\omega}{2\hbar}x^2} H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right) \tag{3.209}$$

This further shows that, unlike the classical approach, the quantum approach allows only *certain discrete* values for the energy.

Comparison

As already mentioned, the quantum approach is very general and there are some other differences between the two frameworks. A major difference is that the lowest energies are different. In the classical approach it is zero, while in the quantum approach it's $\frac{\hbar\omega}{2}$. In fact, if the particle were at the bottom of the well motionless, its momentum and position would be be equal, something that would not be allowed according to the uncertainty principle. Furthermore, according to the classical interpretation the energy can not be found outside the parabola region, since the kinetic energy would have to be negative. However, this is possible in the quantum approach since the minimum level of energy is $\frac{\hbar\omega}{2}$.

Example 3.4.2. In this example we will look at the probability of finding the particle outside the classical allowed region in the ground state of the harmonic oscillator.
According to the classical approach, the allowed region for a particle with energy E is given by

$$A := \left\{ x \ : \ |x|^2 < a^2 = \frac{2E}{m\omega^2} \right\} \tag{3.210}$$

where a indicates the amplitude. Since $E = \frac{ka^2}{2} = \frac{m\omega^2 a^2}{2}$, we get that $\frac{2E}{m\omega^2} = a^2$. Recall that the probability distribution which describes the particles position in the ground state at time t is given by $|\Psi_0(x,t)|^2$. The probability that the particle lies in the classical allowed region is therefore

$$P(A) = \int_{-a}^{a} |\Psi_0(x,t)|^2 dx \tag{3.211}$$

In order to calculate the probability of finding the particle outside the classically allowed region we need to compute the complement of $P(A)$. Hence,

$$\begin{aligned} P(A^c) &= 1 - \int_{-a}^{a} |\Psi_0(x,t)|^2 dx \\ &= 1 - \int_{-a}^{a} \Psi_0(x,t)\Psi_0^*(x,t) dx \\ &= 1 - \int_{-a}^{a} \psi_0(x) e^{\frac{-iE_0 t}{\hbar}} \psi_0(x) e^{\frac{-iE_0 t}{\hbar}} dx \\ &= 1 - \int_{-a}^{a} [\psi_0(x)]^2 dx \\ &= 1 - \int_{-a}^{a} \left[\left(\frac{m\omega}{\pi\hbar} \right)^{\frac{1}{4}} \exp\left(-\frac{m\omega}{2\hbar} x^2 \right) \right]^2 dx \\ &= 1 - \sqrt{\frac{m\omega}{\pi\hbar}} \int_{-a}^{a} e^{-\frac{m\omega}{\hbar} x^2} dx \end{aligned} \tag{3.212}$$

Making the substitution

$$\epsilon = \sqrt{\frac{m\omega}{\hbar}} x, \quad d\epsilon = \sqrt{\frac{m\omega}{\hbar}} dx \tag{3.213}$$

we obtain

$$P(A^c) = 1 - \int_{-a}^{a} |\Psi_0(x,t)|^2 dx = 1 - \frac{1}{\sqrt{\pi}} \int_{-\sqrt{\frac{m\omega}{\hbar}}a}^{\sqrt{\frac{m\omega}{\hbar}}a} e^{\epsilon^2} d\epsilon \tag{3.214}$$

since the determinant obtained from the substitution cancels with the normalisation constant of ψ_0. If we use the symmetry of e^{ϵ^2} we get that

$$P(A^c) = 1 - \frac{2}{\sqrt{\pi}} \int_{0}^{\sqrt{\frac{m\omega}{\hbar}}a} e^{\epsilon^2} d\epsilon \tag{3.215}$$

To approximate this integral that cannot be computed symbolically, we introduce a function called the *error function*, which is defined as

$$erf(z) = \frac{2}{\sqrt{\pi}} \int_{0}^{z} e^{-x^2} dx \tag{3.216}$$

Hence,

$$P(A^c) = 1 - \int_{-a}^{a} |\Psi_0(x,t)|^2 dx = 1 - erf\left(\sqrt{\frac{m\omega}{\hbar}} a \right) \tag{3.217}$$

Since the energy of the ground state is known we can derive a:

$$\frac{\hbar\omega}{2} \stackrel{!}{=} \frac{1}{2} m\omega^2 a^2 \tag{3.218}$$

Solving for a

$$a = \sqrt{\frac{\hbar}{m\omega}} \tag{3.219}$$

This yields that the probability that the particle lies outside the classically allowed region in the ground state is

$$P(A^c) = 1 - erf(1) \approx 0.157 \tag{3.220}$$

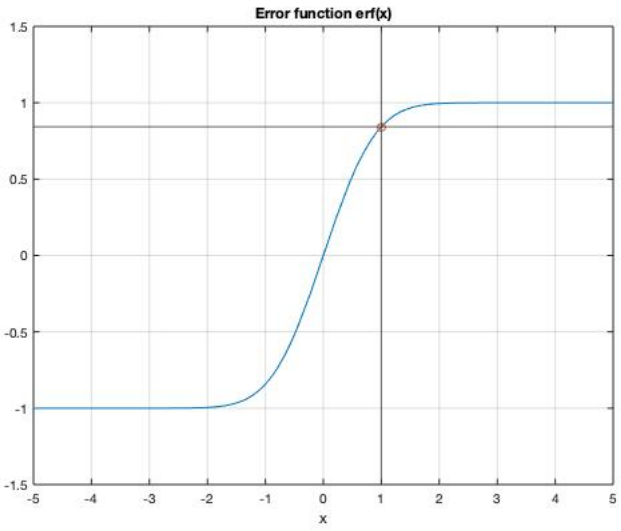


Figure 3.10: Error function: $erf(1)$

CHAPTER 4

Numerical methods

In this chapter we sketch how numerical methods can be used to closely approximate the solution of the Schrödinger equation. We will present the diagonalisation method and the shooting method via Range-Kutta four (RK4). In physics, computational techniques are widely used to check, apply and complement the theoretical approach. Therefore, we want to give a sense of how things might be solved in practice and compare exact and numerical results. Of course these processes could potentially be applied to any sort of problems involving this type of differential equations and initial value problems. In the final section of this chapter we look at quantum computing to draw some similarities with quantum mechanics. The sources of this chapter are [Boynd; Gri94; Lor11; MIT17a; MIT18; Sch16a].

4.1 Diagonalisation method

An intuitive way to define a derivative $\frac{d\psi(x)}{dx}$ is trough the delta notation:

$$\frac{d\psi(x)}{dx} = \lim_{\Delta x \to 0} \frac{\Delta\psi(x)}{\Delta x} \tag{4.1}$$

Let $x \in [0, a]$. Then, we can divide this interval in N equidistant segments $[x_j, x_{j+1}]$ where $0 \leq j \leq N$. At the values $x_0, x_1, \ldots, x_N$ the function ψ takes values $\psi_0, \psi_1, \ldots, \psi_N$. Using equation (4.1), we can approximate the derivative at $\bar{x} \in (x_j, x_{j+1})$

$$\frac{d\psi(\bar{x})}{dx} \approx \frac{\psi_{j+1} - \psi_j}{x_{j+1} - x_j} \quad \forall j \in \{0, 1, \ldots, N\} \tag{4.2}$$

As N tends to infinity, equation (4.2) will converge to equation (4.1) at $\bar{x}$. The second derivative at $\bar{x}$ can be approximated by

$$\begin{aligned} \frac{d^2\psi(\bar{x})}{dx^2} &\approx \frac{d\psi}{dx}\left(\frac{\psi_{j+1} - \psi_j}{x_{j+1} - x_j}\right) = \frac{d\psi}{dx}\left(\frac{\psi_{j+1}}{x_{j+1} - x_j}\right) - \frac{d\psi}{dx}\left(\frac{\psi_j}{x_{j+1} - x_j}\right) \\ &\approx \frac{(\psi_{j+1} - \psi_j) - (\psi_j - \psi_{j-1})}{(x_{j+1} - x_j)^2} = \frac{(\psi_{j+1} - 2\psi_j + \psi_{j-1})}{(x_{j+1} - x_j)^2} \quad \forall j \in \{0, 1, \ldots, N\} \end{aligned} \tag{4.3}$$

Let's define $V_j = V(x_j)$, then we can rewrite the time independent Schrödinger equation (3.8) as

$$-\left(\frac{\psi_{j+1} - 2\psi_j + \psi_{j-1}}{(x_{j+1} - x_j)^2}\right)\frac{\hbar^2}{2m} + V_j\psi_j = E\psi_j \tag{4.4}$$

Equivalently, equation (4.4) is given by

$$
\begin{aligned}
&-\left(\psi_{j+1}-2\psi_j+\psi_{j-1}\right)\frac{\hbar^2}{2m(\Delta x)^2}+V_j\psi_j= \\
&=-\frac{\hbar^2}{2m(\Delta x)^2}\left(\psi_{j+1}+\psi_{j-1}\right)+\psi_j\left(V_j+\frac{\hbar^2}{m(\Delta x)^2}\right)=E\psi_j
\end{aligned}
\tag{4.5}
$$

Define $\mu := \frac{\hbar^2}{2m(\Delta x)^2}$ and rewrite equation (4.5) as

$$
-\mu\left(\psi_{j+1}+\psi_{j-1}\right)+\psi_j\left(V_j+2\mu\right)=\mu\left(-\psi_{j+1}-\psi_{j-1}+\psi_j\left(v_j+2\right)\right)=E\psi_j \tag{4.6}
$$

where $v_j = \frac{V_j}{\mu}$. Since μ depends on $(\Delta x)^2$, we can define $\lambda := \frac{\hbar^2}{2m}$ such that $\mu = \frac{\lambda}{(\Delta x)^2}$. In addition, since we are taking equidistant intervals along the x direction,

$$
\Delta x = \frac{a}{(N+1)} \tag{4.7}
$$

which implies that

$$
\mu = \frac{\lambda}{(\Delta x)^2} = \frac{\lambda(N+1)^2}{a^2} \tag{4.8}
$$

Finally, we can rewrite equation (4.6) for $0 \leq j \leq N$ in matrix form:

$$
\frac{\lambda(N+1)^2}{a^2}\begin{pmatrix}
2+v_0 & -1 & 0\dots & & 0 \\
-1 & 2+v_1 & \ddots & \ddots & \vdots \\
0 & \ddots & \ddots & & 0 \\
\vdots & \ddots & \ddots & & -1 \\
0 & \dots & 0 & -1 & 2+v_N
\end{pmatrix}\begin{pmatrix}
\psi_0 \\ \psi_1 \\ \psi_2 \\ \vdots \\ \psi_{N-1} \\ \psi_N
\end{pmatrix} = E\begin{pmatrix}
\psi_0 \\ \psi_1 \\ \psi_2 \\ \vdots \\ \psi_{N-1} \\ \psi_N
\end{pmatrix} \tag{4.9}
$$

where the boundary condition derived by the potential V will determine

$$
v_j = \frac{V_j a^2}{(N+1)^2\lambda} \tag{4.10}
$$

Potentially, this setup could be used to solve general problems involving the Schrödinger equation. Of course, when $v_j = 0$ as in the infinite square well, this strategy results quite effective. As seen in chapter 3, the infinite square well problem within the walls where $x \in [0, a]$ can be simplified to

$$
\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} = E\psi(x) \tag{4.11}
$$

since the potential given by

$$
V(x) = \begin{cases} 0, & \text{if } 0 \leq x \leq a \\ \infty, & \text{if } x > a,\ x < 0 \end{cases} \tag{4.12}
$$

takes value 0 $\forall\ x \in [0, a]$. As discussed in chapter 3, this implies that the wave function takes value 0 at the boundaries, i.e.

$$
\psi(0) = \psi(a) = 0 \tag{4.13}
$$

which means that both start- and end- points are fixed at 0. In other words,

$$
\psi_0 = \psi_{N+1} = 0 \tag{4.14}
$$

Using the fact that the potential equals 0 within the infinite walls, we can rewrite equation (4.9) in matrix form by setting $v_j = 0\ \forall j$ in equation (4.9):

$$\frac{\lambda(N+1)^2}{a^2}\begin{pmatrix} 2 & -1 & 0\dots & & 0 \\ -1 & 2 & \ddots & \ddots & \vdots \\ 0 & \ddots & \ddots & & 0 \\ \vdots & \ddots & \ddots & & -1 \\ 0 & \dots & 0 & -1 & 2 \end{pmatrix}\begin{pmatrix} \psi_0 \\ \psi_1 \\ \psi_2 \\ \vdots \\ \psi_{N-1} \\ \psi_N \end{pmatrix} = E\begin{pmatrix} \psi_0 \\ \psi_1 \\ \psi_2 \\ \vdots \\ \psi_{N-1} \\ \psi_N \end{pmatrix}, \quad \lambda = \frac{\hbar^2}{2m} \tag{4.15}$$

At this point the eigenvalues can be computed using a mathematical software such as Matlab. These correspond to the eigenvalues of the matrix given in equation (4.15). As shown in figure 4.2, if we repeat this process for different values of N, we observe that if N increases the error diminishes. To estimate the error, we used the exact eigenvalues $\frac{n^2\pi^2\hbar^2}{2ma^2}$, $n \in 1, \dots, N$ which we derived in Chapter 3. When N goes to infinity, the n^{th} eigenvector of infinite

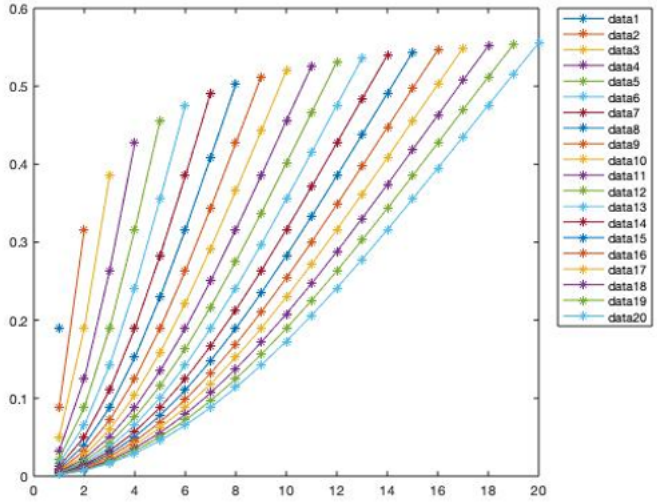


Figure 4.1: Eigenvalue error (y-axis) decreases as N (x-axis) increases

length $w_\infty = (\psi_1, \psi_2, \dots,)$ will coincide with the n^{th} eigenstate given by

$$\psi_n^{exact}(x) = \sqrt{\frac{2}{a}}\sin(\frac{n\pi x}{a}) \tag{4.16}$$

Therefore, the set of points given by $(x_j, \psi_j)_{0\leq j\leq N}$ where ψ_j is the j^{th} entry of the n^{th} eigenvalue will interpolate the n^{th} eigenstate. This is shown in figure 4.2 where the asterisks represent a the set of points $(x_j, \psi_j)_{0\leq j\leq N}$, while the continuous lines referred to the exact eigenstate. Since this result is independent from the parameters $\hbar$, a, m, we assumed wlog that $a = m = \hbar = 1$. In figure 4.5, we observe the first five eigenstates and eigenvectors for different values of N. As N increases, the length of the interval Δx goes to *zero* and this makes the discretisation of an eigenstate more accurate. Due to the more frequent number of oscillations in higher eigenstates, a bigger value of N is needed to obtain the same level of accuracy as in the lower eigenstates.
Instead of increasing the number of N "at infinity", one could derive an eigenvector with N entries and then use polynomial interpolation to approximate the eigenstate as this would likely be more computational efficient. This can be easily implemented in Matlab by using "polyfit" and "polyval". As an alternative, in Appendix D you can find an implementation of the Vandermonde polynomial interpolation in Matlab.

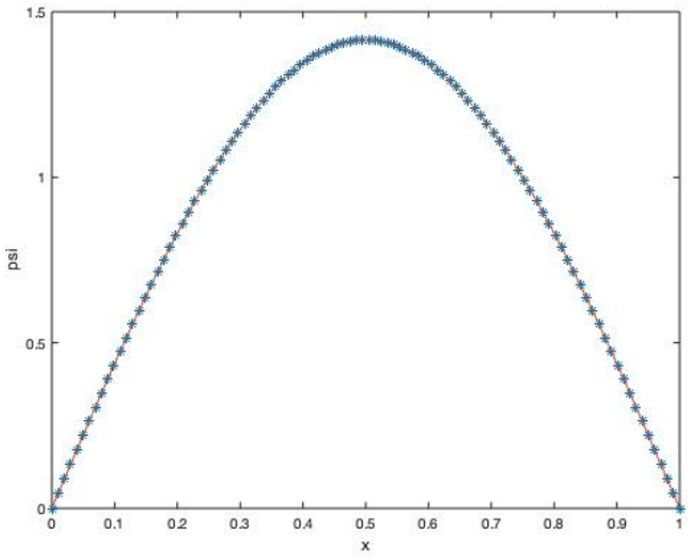
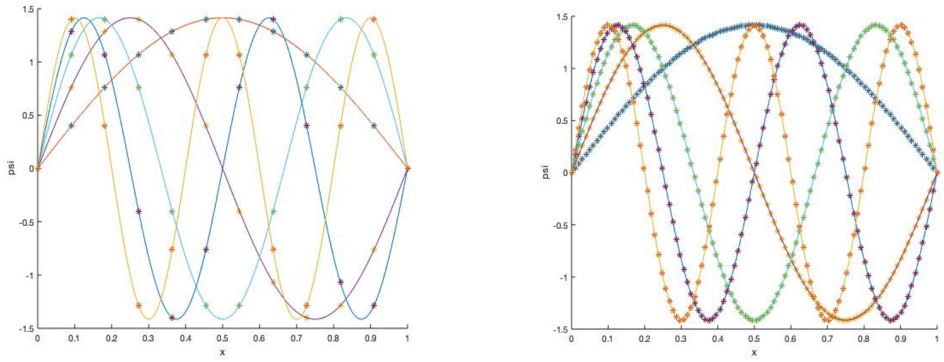


Figure 4.2: First- (or zero-) eigenstate of the infinite square well for $N = 100$, $a = 1$, $m = 1$, $\hbar = 1$



(a) $N = 10$ (b) $N = 100$

Figure 4.3: First five eigenstates ($a = \hbar = m = 1$) for different values of N

Let's go back to a point which we didn't fully dealt with, the normalisation constant. In Matlab, the eigenvectors are automatically normed by default, so the problem of normalisation can be avoided. However, when solving the eigenvalue problem described in equation 4.9 "by hand", one has to consider it. Let's do an example for $N = 3$. Using equation (4.15), we can write the eigenvalue problem as

$$\frac{\lambda(3+1)^2}{2a^2}\begin{pmatrix} 2 & -1 & 0 \\ -1 & 2 & -1 \\ 0 & -1 & 2 \end{pmatrix}\begin{pmatrix}\psi_1 \\ \psi_2 \\ \psi_3\end{pmatrix} = E\begin{pmatrix}\psi_1 \\ \psi_2 \\ \psi_3\end{pmatrix}, \quad \lambda = \frac{\hbar^2}{2m} \tag{4.17}$$

Note that to be totally consistent with the previous setting we should start the vector at ψ_0 and end it at ψ_4: in this case however, $\psi_0 = \psi_4 = 0$, therefore the real unknown entries of the eigenvectors are the central ones since the first and the last entry equal zero. For simplicity we will omit those entries. The eigenvalues are given by[1]

[1]Note that to identify the eigenvalues λ_i of a matrix M we can use a program such as Matlab or we can

$$E_1 = \frac{16\hbar^2}{a^2 m} \tag{4.18}$$

$$E_2 = \frac{8\hbar^2(2-\sqrt{2})}{a^2 m} \tag{4.19}$$

$$E_3 = \frac{8\hbar^2(2+\sqrt{2})}{a^2 m} \tag{4.20}$$

The correspondent normalised eigenvectors are then

$$v_1 = \frac{1}{\sqrt{2}}\begin{pmatrix}-1\\0\\1\end{pmatrix} v_2 = \frac{1}{2}\begin{pmatrix}1\\\sqrt{2}\\1\end{pmatrix} v_3 = \frac{1}{2}\begin{pmatrix}1\\-\sqrt{2}\\1\end{pmatrix} \tag{4.21}$$

It can be easily verified that they build an orthonormal base of the correspondent eigenspace of eigenvectors. This is a consequence of the fact that the matrix we built is symmetric so it has real eigenvalues and orthogonal eigenvectors according to the Spectral Theorem.
We need to verify that these eigenvectors are the eigenstates of a wave function with unitary norm. Hence, we impose

$$1 \stackrel{!}{=} \int_0^a |\psi(x)|^2 dx \tag{4.22}$$

Using the Sympson's rule for integration, we can approximate the integral above. Let $\Delta x = \frac{a}{N+1}$. Then for a function f we have that

$$\begin{aligned}\int_0^a f(x)dx \approx \\ &\approx \frac{\Delta x}{3}(f(x_0) + 4f(x_1) + 2f(x_2) + 4f(x_3) + \cdots + \\ &+ 4f(x_{N-2}) + 2f(x_{N-1}) + 4f(x_N) + f(x_{N+1})) \\ &\approx \frac{a}{3(N+1)}((f(x_0) + 4f(x_1) + 2f(x_2) + 4f(x_3) + \cdots + \\ &+ 4f(x_{N-2}) + 2f(x_{N-1}) + 4f(x_N) + f(x_N + 1))\end{aligned} \tag{4.23}$$

If we take $f = |\psi|^2$, $N = 3$, a normalisation constant A, then using the first eigenvector v_0 we obtain

$$\begin{aligned}1 \stackrel{!}{=} \int_0^a |A\psi(x)|^2 dx &\approx \frac{A^2 a}{3(3+1)}\left(\psi_0^2 + 4\psi_1^2 + 2\psi_2^2 + 4\psi_3^2 + \psi_4^2\right) \\ &= \frac{A^2 a}{12}\left(4\psi_1^2 + 2\psi_2^2 + 4\psi_3^2\right)\end{aligned} \tag{4.24}$$

Using the eigenvector v_1, we deduce that $\psi_2 = 0,\ \psi_2 = -\psi_1$. Hence,

$$1 \stackrel{!}{=} \int_0^a |A\psi(x)|^2 dx \approx \frac{A^2 a}{12}\left(4\psi_1^2 + 2\psi_2^2 + 4\psi_3^2\right) = \frac{A^2 a}{12}\left(4\frac{\psi_3^2}{2} + 4\frac{\psi_3^2}{2}\right) = \frac{A^2 a}{3} \tag{4.25}$$

Hence, the normalisation constant A is given by

$$A = \sqrt{\frac{3}{a}} \tag{4.26}$$

while the eigenvector w_1 of the normed eigenfunctions is given by $w_1 = Av_1$, so

derive them analytically using $\det(\lambda_i I - M)$.

$$w_1 = \sqrt{\frac{3}{2a}} \begin{pmatrix} -1 \\ 0 \\ 1 \end{pmatrix} \tag{4.27}$$

If we repeat the same procedure for the second eigenvalue E_2, we get that

$$\frac{A^2 a}{12}\left(4\psi_1^2 + 2\psi_2^2 + 4\psi_3^2\right) = \frac{A^2 a}{12}\left(8\frac{\psi_1^2}{4} + 2\left(2\frac{\psi_1^2}{4}\right)\right) = \frac{A^2 a}{4} \tag{4.28}$$

where we used that $\psi_1 = \psi_3$ while $\psi_2 = \psi_1\sqrt{2}$. This implies that $A = \frac{2}{\sqrt{a}}$. Hence, the second eigenvector of the normalised eigenstate is

$$w_2 = \sqrt{\frac{1}{a}} \begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix} \tag{4.29}$$

Since $v_2 = -v_3$ we deduce that the normalisation constant will be again $A = -\frac{2}{\sqrt{a}}$. Hence, the third eigenvector of the normalised eigenstate is

$$w_3 = \sqrt{\frac{1}{a}} \begin{pmatrix} 1 \\ -\sqrt{2} \\ 1 \end{pmatrix} \tag{4.30}$$

4.2 Shooting method via Runge-Kutta four

In this section we will try to solve numerically the quantum harmonic oscillator problem, or more in general the time-dependent Schrödinger equation characterised by an even potential. Let's start by recalling that the quantum harmonic oscillator problem can be reduced to

$$\hat{H}\psi(x) = -\frac{\hbar}{2m}\frac{d^2\psi(x)}{dx^2} + \hat{V}(x)\psi(x) = E\psi \tag{4.31}$$

where

$$\hat{V}(x) = \frac{1}{2}m\omega^2\hat{x}^2 \tag{4.32}$$

As we motivated in Chapter 3, it is very important to solve the problem with respect to a unit-free variable

$$u := \frac{x}{a} \tag{4.33}$$

where we identify the length factor a such that the energy equation

$$m\omega^2 a^2 = \hbar\omega \tag{4.34}$$

holds. Since we want to apply a numerical method, it makes even more sense to adopt the same convention in order to plot the results with respect to this unit free variable and simplify the computations. As we derived previously, we can simplify the quantum harmonic oscillator problem to obtain the following equation:

$$\psi(u)(u^2 - \epsilon) = \psi^{(2)}(u), \quad \epsilon = \frac{2E}{\hbar\omega} \tag{4.35}$$

Integration methods such as the Euler method typically solve first-order ODEs. Therefore, before proceeding we need to reduce this differential equation. A differential equation of the form

$$y^{(2)} = by^{(1)} + cy \tag{4.36}$$

can be rewritten as a system of equations

$$\begin{pmatrix} y^{(1)} \\ y^{(2)} \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ c & b \end{pmatrix} \begin{pmatrix} y \\ y^{(1)} \end{pmatrix} \leftrightarrow v^{(1)} = Av, \quad v = \begin{pmatrix} y \\ y^{(1)} \end{pmatrix}, \quad A = \begin{pmatrix} 0 & 1 \\ c & b \end{pmatrix} \tag{4.37}$$

In our case we set $b = 0$, $c = (u^2 - \epsilon)$. We also name $\Theta = \psi^{(1)}$ to obtain two first order ODEs. Hence, we get

$$\begin{pmatrix} \Theta \\ \Theta^{(1)} \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ c & 0 \end{pmatrix} \begin{pmatrix} \psi(u) \\ \psi^{(1)}(u) \end{pmatrix} = \begin{pmatrix} \psi^{(1)}(u) \\ \psi(u)(u^2 - \epsilon) \end{pmatrix} \tag{4.38}$$

As discussed in Appendix A, we could use a numerical method such as the Euler method to solve this type of ordinary differential equations. Note that in this case we need to apply the method twice for each of the two rows of equation (4.38). This does not affect the computational time since $\mathcal{O}(N^k) + \mathcal{O}(N^k) = \mathcal{O}(N^k)$ where $k \in \mathbb{N}$ and $\mathcal{O}(N^k)$ is the error of the same order of N^k.
Let's consider an interval $I \subset \mathbb{R}$ that starts at $t_0 \in \mathbb{R}$ and that is divided in N equidistant segments of length h [2]. Both rows in equation (4.38) can be generalised through the following problem

$$y'(t) = f(t, y(t)), \quad y(t_0) = y_0 \tag{4.39}$$

for some function f, a differentiable function y and a given initial condition where $y_0 \in \mathbb{R}$. In one case we can identify $f \equiv \Theta$ while $y(t) \equiv \psi(u)$; in the other case we can identify $f \equiv \psi(u)(u^2 - \epsilon)$, while $y(t) \equiv \Theta^{(1)}(u)$. Note that we use t instead of u since this approach can be generalised to any chosen independent variable (e.g. $t = x$ if we were to consider the infinite square well as defined in Section 4.1). For simplicity, in order to illustrate the logic behind the method, we will refer to the general functions $y(t)$ and $f(t, y(t))$, since both equations are of the same type. We can define

$$t_n := t_{n-1} + h = t_0 + nh, \quad n \in 1, 2, \ldots, N \tag{4.40}$$

$$y_n := y(t_n), \quad y(t_0) = y_0 \in \mathbb{R} \tag{4.41}$$

To solve problem (4.39) on I with the Euler method we would use the iteration defined by

$$y_{n+1} = y_n + hf(t_n, y_n) \longleftrightarrow \frac{y_{n+1} - y_n}{h} = f(t_n, y_n), \quad y(t_0) = y_0, \tag{4.42}$$

In Appendix D we provided an implementation in Matlab of the Euler method. Instead of using this method, we will adopt another one called Runge-Kutta four steps (RK4) method which solves the same initial value problem and is part of a family of methods called of course Runge-Kutta. The fourth-order method is typically a good choice since it guarantees a good balance between cost of computation and accuracy. Note that RK4 is the highest explicit RK method whose accuracy equals the number of steps, namely 4. The order of the method refers to the change in the error of the numerical solution as the step size is decreased. In other words in a fourth order method, if $err(h) := |y - y_n(h)|$ is the error assuming a step size h, then $err(h) = \mathcal{O}(h^4)$ as $h \to 0$.
RK4 will give an exact answer if the solution is a polynomial of fourth degree, while the Euler method will give an exact answer if the solution is a line. Hence, RK4 seems a better choice than Euler for the quantum harmonic oscillator as we know that the solution is proportional to the Hermite polynomials. In addition, the Euler method is a first order method while RK4 is a fourth order method. As a general consideration, the error tends to be lower with RK4 than Euler but this is not true in all cases (e.g. a line). RKn method can be derived using the n-th Taylor expansion of $y(t_{n+1})$ together with the lower order RK recursions.

[2] In the diagonalisation method we took for instance $I = [0, a]$

The recursion of the first order RK method coincides with the one of the explicit Euler method given by

$$y_{n+1} = y_n + hf(t_n, y_n),\ n = 0, 1, 2, \ldots, N \tag{4.43}$$

It can be motivated using the rectangular integral approximation since

$$y_{n+1} - y_n = \int_{t_n}^{t_{n+1}} f(t_s, y_s)ds \approx (t_{n+1} - t_n)f(t_n, y_n) = hf(t_n, y_n) \tag{4.44}$$

The second order RK method can be derived starting from the 2^{nd} order Taylor polynomial:

$$y(t_{n+1}) = y(t_n) + h\frac{dy}{dt}\Big|_{t_n} + \frac{h^2}{2}\frac{d^2y}{dt^2}\Big|_{t_n} + \mathcal{O}(h^3) \tag{4.45}$$

Since we know that $f(t, y(t)) = y'$ we get that

$$\frac{d^2y}{dt^2} = \frac{d^2f(t, y(t))}{dt^2} = \frac{\partial f}{\partial t} + \frac{\partial f}{\partial y}\frac{dy}{dt} = \frac{\partial f}{\partial t} + f\frac{\partial f}{\partial y} \tag{4.46}$$

Hence, $y(t_{n+1}) = y_{n+1}$ simplifies to

$$y_{n+1} = y_n + hf(t_n, y_n) + \frac{h^2}{2}\left[\frac{\partial f}{\partial t} + f\frac{\partial f}{\partial y}\right](t_n, y_n) + \mathcal{O}(h^3) \tag{4.47}$$

Now, from the first order RK method define

$$k_1 = hf(t_n, y_n) \tag{4.48}$$

We define k_2 as

$$k_2 = hf(t_n + ah, y_n + bk_1) = h\left(f(t_n, y_n) + ah\frac{\partial f}{\partial t}(t_n, y_n)\right) + \mathcal{O}(h^3) \tag{4.49}$$

By substituting back in equation (4.50), we get

$$y_{n+1} = y_n + (c + d)hf(t_n, y_n) + dh^2\left[a\frac{\partial f}{\partial t} + bf\frac{\partial f}{\partial y}\right](t_n, y_n) + \mathcal{O}(h^3) \tag{4.50}$$

By comparison

$$c + d = 1 \tag{4.51}$$

$$ad = \frac{1}{2} \tag{4.52}$$

$$bd = \frac{1}{2} \tag{4.53}$$

If we choose $a = b = 1$ and $c = d = \frac{1}{2}$ we obtain the classical second order RK method

$$k_1 = hf(t_n, y_n) \tag{4.54}$$

$$k_2 = hf(t_n + h, y_n + k_1) \tag{4.55}$$

$$y_{n+1} = y_n + \frac{k_1 + k_2}{2} \tag{4.56}$$

Using a similar approach we can derive RK4 which is given by

$$k_1 = hf(t_n, y_n) \tag{4.57}$$

$$k_2 = hf\left(t_n + \frac{h}{2}, y_n + \frac{k_1}{2}\right) \tag{4.58}$$

$$k_3 = hf\left(t_n + \frac{h}{2}, y_n + \frac{k_1}{2}\right) \tag{4.59}$$

$$k_4 = hf(t_n + h, y_n + k_3) \tag{4.60}$$

$$y_{n+1} = y_n + \frac{k_1}{6} + \frac{k_2}{3} + \frac{k_3}{3} + \frac{k_4}{6} + \mathcal{O}(h^5) \tag{4.61}$$

Such a method can be easily implemented in several programming languages. In the appendix we added a version of the RK4 method in Python.
Recall that we need to solve

$$\begin{pmatrix} \Theta \\ \Theta^{(1)} \end{pmatrix} = \begin{pmatrix} \psi^{(1)} \\ \psi(u^2 - \epsilon) \end{pmatrix}, \quad \epsilon = \frac{2E}{\hbar\omega} \tag{4.62}$$

Before applying RK4, we still need to fix the two initial conditions, namely

$$\psi(u = 0) = a_1 \tag{4.63}$$

$$\Theta(u = 0) = \psi'(u = 0) = a_2 \tag{4.64}$$

We pick a_1 arbitrarily, say $a_1 = 1$. Assume that $a_2 \neq 0$, then $\Theta = \psi'$ would be discontinuous at $u = 0$ for an even wave function ψ which is symmetric around the origin. Such a discontinuity is not possible when we have an even potential and it should be considered only for a delta function. Therefore, given the even potential we have to fix $a_2 = 0$.

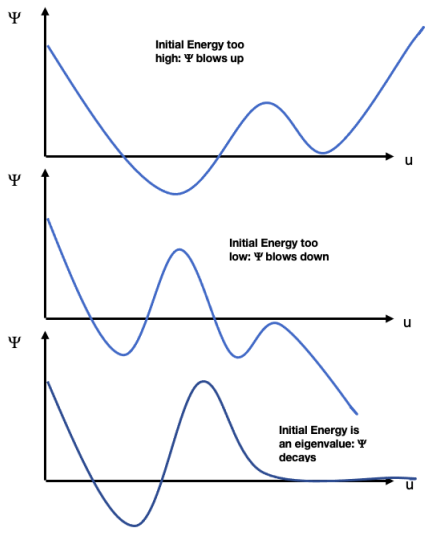
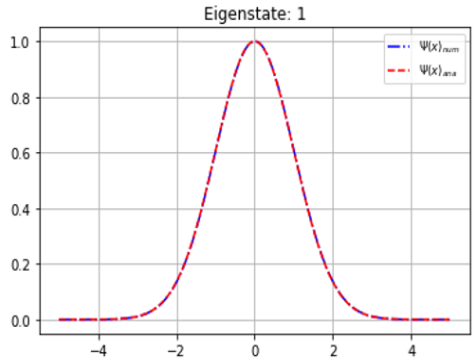


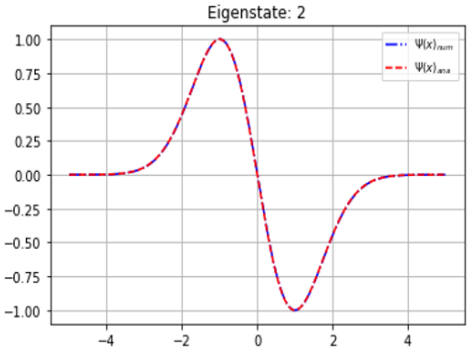
Figure 4.4: Shooting method: shooting for the wave function with norm one

The next step is to pick an initial level of energy E_0 and "shoot" for wave functions that decay as u goes to infinity. These are in fact the wave functions that have $L^2(\mathbb{R})$ norm one. If the wave function blows up then the initial level of energy is too high. If the wave function blows to minus infinity then the initial level of energy is too low. When the wave function decays it means that we picked the right level of energy and identified an eigenvalue for that level of energy. The eigenstate ψ for that eigenvalue is obtained by applying twice RK4 to the system described in equation (4.38).

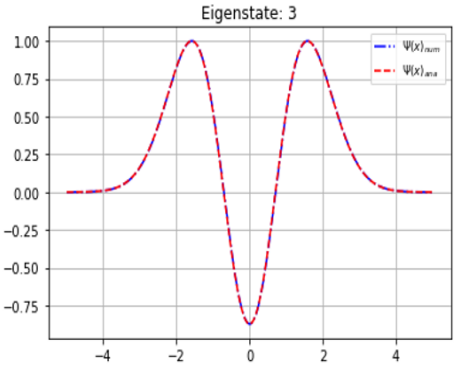
Using Python, we identified the first four eigenstates of the quantum harmonic oscillator. We picked several levels of energy to identify the eigenvalues through the numerical resolution of the system described previously using RK4. Notice that once the level of energy is optimised, the numerical resolution is very accurate as shown below (graphical comparison with the analytical solution).



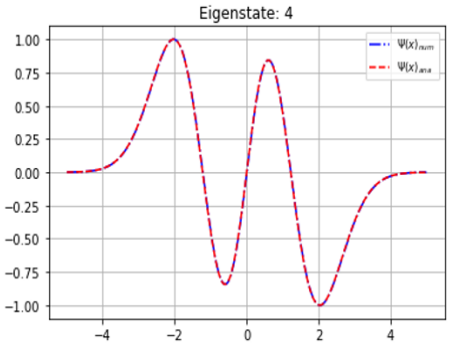
(a) First eigenstate



(b) Second eigenstate



(c) Third eigenstate



(d) Fourth eigenstate

Figure 4.5: Quantum harmonic oscillator: shooting method via RK4

The code developed (Appendix D) allowed us to find numerically the different eigenvalues for the quantum oscillator problem. We started with some arbitrary level of energies, one for each of the two initial value problems -equation (4.62)- and applied the RK4 iteration to identify the correspondent eigenstate with norm one. We plotted explicitly the first four eigenstates together with the exact analytical solution. As mentioned, from a visual comparison the numerical solutions appear to be very accurate, something that confirms at least qualitatively the validity of our previous considerations about the error.

4.3 Overview on quantum computers

As we have seen, numerical methods can be used to solve problems that are very important in Physics. If numerical methods are at the intersection between Maths and Computing, in this section we will move towards the Computing field even further, with a very limited overview on quantum computing. As a side note, this section is partially based on two presentations [Kon19; War19] given at the Quantum Computing in Finance Conference, London in 2019. In order to understand quantum computing, one needs a general understanding of the quantum framework, so Quantum Physics becomes very important. One could argue it

will be necessary to introduce the fundamentals of quantum mechanics much earlier in the learning process when quantum computers will become widely available.
In classical computing, the architecture is organised in binary *bits*, hence there are only two states (represented logically by 0s and 1s) which can be used to store information. This implies that calculations are deterministic, meaning that there is 100% certainty about an output when a certain input is given.
In quantum computing, information can be stored in a superposition of the two states described above as 0s and 1s. More formally, the quantum binary state -the *qubit*- can be expressed as

$$|\psi\rangle = \alpha|0\rangle + \beta|1\rangle$$

where α, β are scalars such that $|\alpha|^2 + |\beta|^2 = 1$. Note that the Bra-ket notation is an equivalent way to express eigenstates. As an example one could take

$$|0\rangle = \begin{pmatrix}1\\0\end{pmatrix},\ |1\rangle = \begin{pmatrix}0\\1\end{pmatrix} \tag{4.65}$$

while an example of $|\psi\rangle$ is given by

$$|\psi\rangle = \begin{pmatrix}\cos\frac{\phi}{2}\\ e^{i\phi}\sin\frac{\phi}{2}\end{pmatrix}$$

This implies that calculations are "probabilistic" or in other words will be based on random variables, meaning that there exists multiple outputs given a certain input.
In classical computing, there are only two logic gates operating on a single bit, namely the *identity* and the *not* gate. In quantum computing there are infinitely many logic gates that act on a single qubit. Below some examples.
The quantum NOT gate or Pauli X (P_x)that flips the qubit

$$P_x|0\rangle = \begin{pmatrix}0&1\\1&0\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = \begin{pmatrix}0\\1\end{pmatrix} = |1\rangle$$

$$P_x|1\rangle = \begin{pmatrix}0&1\\1&0\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix} = \begin{pmatrix}1\\0\end{pmatrix} = |0\rangle$$

The Hadamard gate H that creates superposition

$$H|0\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1&1\\1&-1\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\0\end{pmatrix} + \frac{1}{\sqrt{2}}\begin{pmatrix}0\\1\end{pmatrix} = \frac{1}{\sqrt{2}}\left(|0\rangle + |1\rangle\right)$$

$$H|1\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1&1\\1&-1\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\0\end{pmatrix} - \frac{1}{\sqrt{2}}\begin{pmatrix}0\\1\end{pmatrix} = \frac{1}{\sqrt{2}}\left(|0\rangle - |1\rangle\right)$$

Other common examples are the Pauli Y P_y and Pauli Z P_z given by

$$P_y = \begin{pmatrix}0&-i\\i&0\end{pmatrix},\ P_z = \begin{pmatrix}1&0\\0&-1\end{pmatrix}$$

Note that logical gates can be thought as operators and in fact Pauli matrices (P_x,P_y,P_z) are used to describe the spin of a particle.
Quantum computers, due to their different architecture, are much faster than any classical computers. As an example, Google announced that it has developed a quantum computer which is 100 M times faster than any classical computer. There is the potential to revolutionise fields such as Medicine, Physics, Genetics or Finance. To solve problems very common in logistic such as the Travelling Salesman Problem one could apply the quantum approach under the framework of the quantum harmonic oscillator. This process of finding the global minimum is referred to as quantum annealing and figure 4.6 gives an intuitive idea. This technology is still being developed and in figure 4.7 we observe some applications. As an

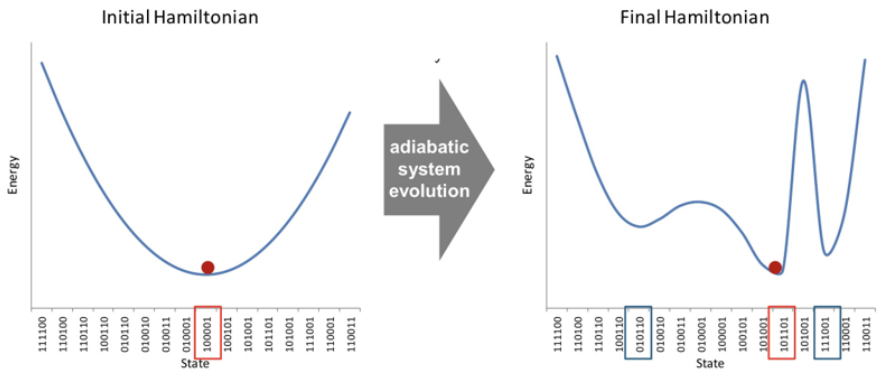


Figure 4.6: Quantum annealing [Kon19]

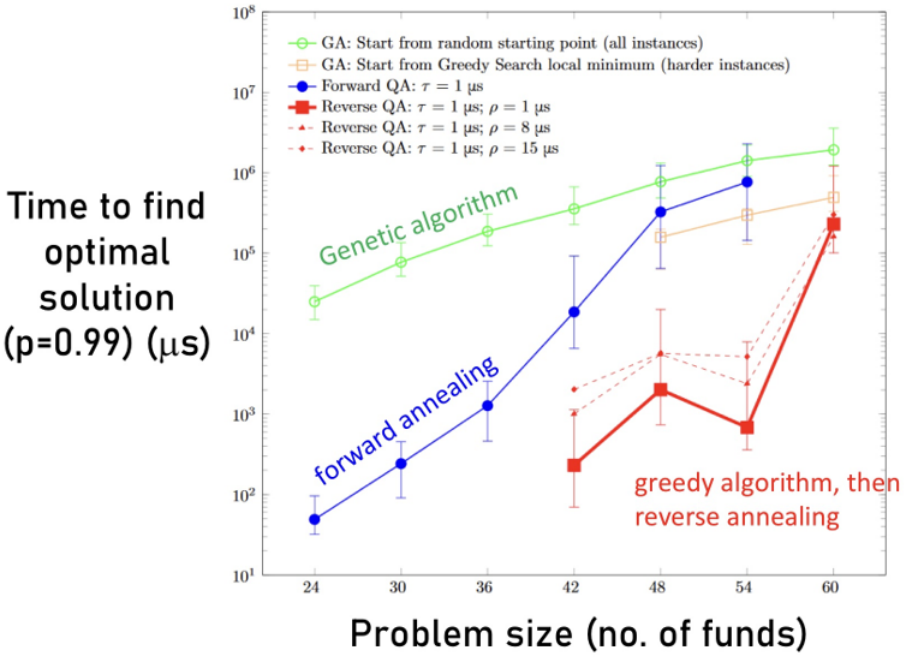


Figure 4.7: Quantum applications in computing [War19]

example, reverse annealing is an approach developed to tackle portfolio optimisation problems based on an enormous amount of data (e.g. daily trades spanning for 10 years).
Different companies are focusing on different aspects of quantum computing: in the hardware space, we find big players such as Google, IBM and Fujitsu but also innovative startups such as Rigetti and PsiQuantum. If we look at the software space there are companies that are working on specific aspects such as error correction or platform development. Even more companies are developing quantum applications in fields such as Machine Learning, Problem Optimisation and Quantum Chemistry.

CHAPTER 5

Conclusions

In this dissertation we discussed the role of differential equations in quantum mechanics, which is the basis for the quantum description of nature. Life is about change and chaos so the best instrument to measure it should be derivatives (and differential equations) since by definition these measure infinitesimal change. As we showed throughout these pages, operators help us generalize this concept and specify the "type of change" we are measuring. Of course, the entire idea of quantum mechanics is something that remains at times controversial as for the concept of discretisation of energy which we would expect to be a continuous construct. At the same time, Schrödinger's cat still makes us cast doubts on the difference between death and life; random variables bring even more uncertainty to the table and this again plays against the human nature which is desperately looking for an exact (simple) description of reality.

When this model was first proposed, several controversies emerged among some of the most famous physicists of that time, including Albert Einstein [EPR35]. As mentioned in the **Introduction**, "ontological questions" on quantum mechanics are discussed until today (again by Nobel-prize physicists as t'Hooft [t H20]), and despite the overwhelming experimental success of the quantum mechanical language in theoretical models of nature the origin of some funding concepts - as the uncertainty relations - is still a subject of debate. In our essay, we have not dealt with these fundamental questions, and adopted the point of view that quantum mechanics is one of the strongest widely accepted models for the description of nature.

Within our narrow analysis, we provided a minimal mathematical framework which is the base for the probabilistic interpretation. We also found explicit expressions for eigenvalues and eigenstates of two main cases defined by their specific potential, namely the infinite square well and the quantum harmonic oscillator. We used numerical techniques to alternatively deal with these problems and end up with the same results. At times, we derived separately analytical results that were required to solve certain problems (Hermite polynomials, Fourier theory).

As we discussed in Chapter 4, the quantum approach is also behind one of the most revolutionary technologies of our times, quantum computers. Instead of the certainty of the states (bits) of 1s (TRUE) and 0s (FALSE), quantum computers use a general state called *qubit* which can be both a 0 or a 1 or a superposition of the two. Other than philosophical considerations that one could make about moving from a framework with just two states to another with multiple infinite states, there is the potential that quantum mechanics will become much more important in the future. A developer who will write code for quantum computers will need to at least understand the basic framework of quantum mechanics and there are indeed divulgative sources that try to address this challenge.

To conclude, the quantum mechanics framework is very powerful and what we developed in these chapters can be considered not only an application of differential equations in nature but also a starting point to better understand one of the latest disruptive technologies, quantum computers.

Appendices

APPENDIX A

Introductory Fourier analysis

In this section we want to introduce the concept of Fourier transform and its inverse. This is part of a wide field in mathematics, Fourier analysis, which has many applications in many areas of science. Before defining the Fourier transform, first we need to introduce the concept of Fourier series.

Definition A.0.1. Let A be a set. Let f be a function $A \to A$. Then f is periodic with period L if $\exists L \in \mathbb{R}^{>0}$ such that $\forall x \in A: \ f(x) = f(x+L)$

Example A.0.2. The function $\sin(x)$ has period $L = 2\pi$ since $\forall c \in \mathbb{R}, \ \forall x \in [c, c+2\pi]: \ sin(x) = sin(x+2\pi)$

Definition A.0.3. Let f be a periodic function $\mathbb{R} \to \mathbb{C}$ of period $2L$. Then the Fourier series of f is given by

$$f(x) = \sum_{-\infty}^{\infty} c_n e^{\frac{in\pi}{L}x}, \ c_n \in \mathbb{C} \tag{A.1}$$

Remark A.0.4. Note that since $c_n \in \mathbb{C}$ there are some real coefficients $a_n, \ b_n$ such that $c_n = \frac{a_n}{2} - i\frac{b_n}{2}$. It follows that

$$\begin{aligned} f(x) &= \sum_{-\infty}^{\infty} c_n e^{\frac{in\pi}{L}x} = \sum_{-\infty}^{\infty} \left(\frac{a_n}{2} - i\frac{b_n}{2}\right) e^{\frac{in\pi}{L}x} \\ &= \frac{a_0}{2} + \sum_{n=1}^{\infty} \left(\frac{a_n}{2} - i\frac{b_n}{2}\right) e^{\frac{in\pi}{L}x} + \sum_{n=1}^{\infty} \left(\frac{a_n}{2} + i\frac{b_n}{2}\right) e^{-\frac{in\pi}{L}x} \\ &= \frac{a_0}{2} + \sum_{n=1}^{\infty} \frac{a_n}{2} \left(e^{\frac{in\pi}{L}x} + e^{-\frac{in\pi}{L}x}\right) + \sum_{n=1}^{\infty} \frac{b_n}{2i} \left(e^{\frac{in\pi}{L}x} + e^{-\frac{in\pi}{L}x}\right) \\ &= \frac{a_0}{2} + \sum_{n=1}^{\infty} a_n \cos\left(\frac{in\pi}{L}x\right) + \sum_{n=1}^{\infty} b_n \sin\left(\frac{in\pi}{L}x\right) \end{aligned} \tag{A.2}$$

Hence, we can look at cos and sin as the two vectors that span the infinite dimensional vector spaces of periodic functions defined by all functions f (as expressed in the definition above).

Remark A.0.5. In order to derive the coefficient c_n let's recall that a Laurent Series of an analytical function $f(z)$ around a point $\text{◻} \ \epsilon \ \mathbb{C}$ is given by:

$$f(z) = \sum_{n=-\infty}^{\infty} c_n (z - \text{◻})^n \tag{A.3}$$

If we take ◻ to be zero, while we set $z = e^{\frac{i\pi}{L}x}$ we get back the Laurent Series of $f(x)$ as given in equation A.1. In other words, for different values of L we are considering all z that form a

complex circle of radius 1.
In complex analysis there is a theorem -often called Laurent Theorem- that states that the coefficient of a Laurent Series referring to an analytical function f is given by

$$c_n = \frac{1}{2\pi i}\int_{\upsilon}\frac{f(z)}{(z-\mathbb{o})^{n+1}}dz \tag{A.4}$$

where υ is a closed curve around $\mathbb{o}$. Again, if we take $\mathbb{o}$ to be zero while we set $z = e^{\frac{i\pi}{L}x}$ we get that

$$c_n = \frac{1}{2\pi i}\int_{\upsilon}\frac{f(z)}{(z-\mathbb{o})^{n+1}}dz = \frac{1}{2L}\int_{\upsilon}\frac{f(x)}{e^{\frac{in\pi}{L}x}}dx \tag{A.5}$$

Assuming that the period of f lies between $x \in [d, d+2L] \subset \mathbb{R}$ we get that

$$c_n = \frac{1}{2L}\int_{d}^{d+L} f(x)e^{-\frac{in\pi}{L}x}dx \tag{A.6}$$

Note that this formula can be used to derive a_n and b_n as defined above. Since $a_n = c_n + c_{-n}$ while $b_n = (c_n - c_{-n})i$ we get that

$$a_n = \frac{1}{2L}\int_{d}^{d+L} f(x)\left(e^{-\frac{in\pi}{L}x} + e^{\frac{in\pi}{L}x}\right)dx = \frac{1}{L}\int_{d}^{d+L} f(x)\cos\left(\frac{in\pi}{L}x\right)dx \tag{A.7}$$

Similarly,

$$b_n = \frac{1}{2L}\int_{d}^{d+L} f(x)\left(-e^{-\frac{in\pi}{L}x} + e^{\frac{in\pi}{L}x}\right)dx = \frac{1}{L}\int_{d}^{d+L} f(x)\sin\left(\frac{in\pi}{L}x\right)dx \tag{A.8}$$

Consider now again equation (A.1) given by

$$f(x) = \sum_{-\infty}^{\infty} c_n e^{\frac{in\pi}{L}x},\ c_n \in \mathbb{C} \tag{A.9}$$

Suppose we want to take a linear combination over a continuous range of values: instead of summing up over $-\infty, \ldots, -1, 0, 1, \ldots, n$ we want to to sum up over a continuous interval $(-\infty, \infty)$. This might be justified for instance because there are some assumptions that need to hold: as shown for the free particle, we might not allow for discrete values for the level of energy in order to normalise the wave function. To achieve this, we extend the limit of the period to infinity.
Define $X[n] = \frac{1}{2}\int_T f(w)e^{-in\pi\omega}dw$, where $\omega = \frac{x}{L}$, T is the interval that contains the period of f over w. Then

$$f(w) = \frac{1}{L}\sum_{-\infty}^{\infty} LX[n]e^{in\pi\omega} = \sum_{-\infty}^{\infty} X[n\omega]e^{in\pi\omega}\Delta\omega \tag{A.10}$$

If we take the limit of $L \to \infty$, or equivalently, of $\Delta\omega \to 0$, we get that

$$f(w) = \lim_{\Delta\omega\to 0}\sum_{-\infty}^{\infty} X[n\omega]e^{in\pi\omega x}\Delta\omega = \int_{-\infty}^{\infty} X[n\omega]e^{in\pi\omega}d\omega \tag{A.11}$$

We can rewrite this as

$$f(t) = \int_{-\infty}^{\infty} C_n e^{in\pi t} dt,\ C_n \in \mathbb{C} \tag{A.12}$$

The coefficient C_n will then be given by

$$C_n = \int_{-\infty}^{\infty} f(t) e^{-in\pi t} dt \tag{A.13}$$

Definition A.0.6. Let f be an integrable function. We define the Fourier transform of f as

$$F(\omega) = \int_{-\infty}^{\infty} \hat{f}(t) e^{-2\pi i\omega t} dt \tag{A.14}$$

Definition A.0.7. Let f be an integrable function. We define the inverse of the Fourier transform of f as

$$\hat{f}(t) = \int_{-\infty}^{\infty} F(\omega) e^{2\pi i\omega t} d\omega \tag{A.15}$$

Observation A.0.8. *We can consider the Fourier transform as an extension of the Fourier series in the sense that we take the period of the function to tend to infinity. The Fourier transform is denoted in terms of the frequency domain that tells us the values of the signal at different frequencies. A continuous signal in the time domain can be represented by a sum of sinusoids which is described by its frequency, amplitude and phase.*
Equation A.14 shows that the function of time, $\hat{f}(t)$ turns to a function of frequency, $F(\omega)$ and Equation A.15 does the exact opposite.

APPENDIX B

Background on numerical methods

B.1 Matrix diagonalisation

In this section we look at the matrix diagonalisation process [Cox19].

Definition B.1.1. Let $A \in M_{n,n}(\mathbb{R})$, $x \in V$ where V is a $\mathbb{K}$ $n-$dimensional vectorspace. The scalar $\lambda \in \mathbb{K}$ is called eigenvalue of A iff $Ax = \lambda x$. The vector x is called eigenvector of A.

Remark B.1.2. Note that the Spectral theorem implies that when A is symmetric or hermitian (when $\mathbb{K} = \mathbb{C}$), then the eigenvalue λ will be real while the eigenvectors will span an orthogonal base.

Remark B.1.3. Let $A, \mathbb{1} \in M_{n,n}(\mathbb{R})$. It can be shown that λ is an eigenvalue iff $\det(\lambda\mathbb{1} - A) = 0$. Similarly, x is an eigenvector iff $x \in \ker(A)$.

Definition B.1.4. Two matrices $A, B \in M_{n,n}(\mathbb{C})$ are similar iff there exists $P \in \mathbb{GL}_n(\mathbb{C})$ such that

$$B = P^{-1}AP \tag{B.1}$$

Remark B.1.5. Note that B can be seen as the transformation matrix of A with respect to the bases represented by the column vectors of P. In addition, the similarity of matrices is an equivalence relation that implies that A and B share the characteristic polynomials, the eigenvalues and the Trace.

Definition B.1.6. A matrix $A \in M_{n,n}(\mathbb{C})$ is diagonalisable if it is similar to a diagonal matrix D, i.e. $\exists\ P \in \mathbb{GL}_n(\mathbb{C})$ such that

$$A = P^{-1}DP \tag{B.2}$$

Remark B.1.7. One can show that the diagonal entries of D are the eigenvalues of A, while P^{-1} contains the eigenvectors of A.

Example B.1.8. Consider a 2×2 matrix

$$A = \begin{pmatrix} 3 & 0 \\ 8 & -1 \end{pmatrix}$$

We start off by finding the determinant

$$det(\lambda I - A) = -\begin{pmatrix} 3-\lambda & 0 \\ 8 & -1-\lambda \end{pmatrix} = 0 \longrightarrow -(3-\lambda)(-1-\lambda) + 0$$

From here we can see that the eigenvalues are $\lambda_1 = 3$ and $\lambda_2 = -1$. Now we find the eigenvectors of these eigenvalues.
For $\lambda_1 = 3 \longrightarrow \begin{pmatrix} 0 & 0 \\ 8 & 4 \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix} = 0$, we obtain $8x - 4y = 0$, hence $y = 2x$.

This gives us the basis

$$Eig_3 = \left\{ \lambda \begin{pmatrix} 1 \\ 2 \end{pmatrix} \middle| \lambda \in \mathbb{R} \right\}$$

For $\lambda_1 = -1 \longrightarrow \begin{pmatrix} 4 & 0 \\ 8 & 0 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = 0$, where $x = 0$ and y will be anything. This gives us the basis

$$Eig_{-1} = \left\{ \lambda \begin{pmatrix} 0 \\ 1 \end{pmatrix} \middle| \lambda \in \mathbb{R} \right\}$$

From the two eigenspaces ("eigenstates"), we obtain

$$P = \begin{pmatrix} 1 & 0 \\ 2 & 1 \end{pmatrix}, \; P^{-1} = \begin{pmatrix} 1 & 0 \\ -2 & 1 \end{pmatrix}, \; D = \begin{pmatrix} 3 & 0 \\ 0 & -1 \end{pmatrix}$$

Then we have

$$A = PDP^{-1} = \begin{pmatrix} 1 & 0 \\ 2 & 1 \end{pmatrix} \begin{pmatrix} 3 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ -2 & 1 \end{pmatrix}$$

.

B.2 Simpson rule

In this section we look at the Simpson rule more closely [Ker19].
The Simpson rule is a numerical method to obtain approximations for definite integrals. In simpler terms, we use parabolic arcs to obtain better results rather than using straight lines, which is what we use in the trapezium rule.
When we have 3 points, we are able to find the quadratic equation through them. The

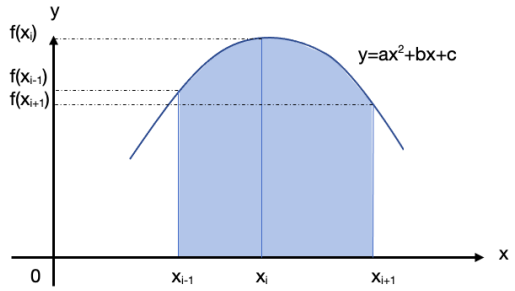


Figure B.1: The quadratic passing through the three points

Simpson rule reads

$$\int_a^b f(x)dx = \frac{\Delta x}{3}\Big[f(x_0)+4(fx_1)+2(fx_2)+4(fx_3)+\ldots 2f(x_{n-2})+4f(x_{n-1})+f(x_n)\Big] \quad \text{(B.3)}$$

Remark B.2.1. From Equation B.3, we see that the values in between are multiplied by the coefficients the 4 and 2 and they keep alternating. The first and last values however, are not multiplied by any coefficient.

Example B.2.2. Consider the integral

$$\int_0^3 \frac{1}{1+x^5}dx, \quad n = 6 \quad \text{(B.4)}$$

First we calculate Δx which is $\frac{b-a}{n} = \frac{3-0}{6} = 0.5$ Now we have our x coordinates $0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, 3$. Since we have 6 sub-intervals, we have 7 points. From this, we get

- $f(x_0) = f(0) = 1$
- $f(x_1) = f\left(\frac{1}{2}\right) = \frac{32}{33}$
- $f(x_2) = f(1) = \frac{1}{2}$
- $f(x_3) = f\left(\frac{3}{2}\right) = \frac{32}{275}$
- $f(x_4) = f(2) = \frac{1}{33}$
- $f(x_5) = f\left(\frac{5}{2}\right) = \frac{32}{3157}$
- $f(x_6) = f(3) = \frac{1}{244}$

Now, we just substitute these values into Equation B.3,

$$\frac{1}{6}\left[1+4\left(\frac{32}{33}\right)+2\left(\frac{1}{2}\right)+4\left(\frac{32}{275}\right)+2\left(\frac{1}{33}\right)+4\left(\frac{32}{3157}\right)+\left(\frac{1}{244}\right)\right] = 1.074915 \approx 1.07 \quad \text{(B.5)}$$

Note that the exact solution which can be computed using Matlab is $1.06588 \approx 1.07$. Of course, a greater value for n would have given us a more accurate answer.

APPENDIX C

Vector spaces and operatorial algebra

C.1 General vector space theory

The goal of this section is to formally introduce concepts which we used throughout these chapters. This include the space of square integrable functions L^2, the Hilbert space, linear operators, norm and orthonormality. This appendix is inspired by [Camnd; Chu20; For20; Glond; Gre03; Lan16; MIT06; MIT17b; MIT17c; MIT17d; Shend]. Notice that we only stating the most important definitions and theorems without providing any proofs since this is the not the focus of this paper.

Definition C.1.1. A linear vector space V over a field $\mathbb{F}$ is a set of elements, called vectors, which is closed under addition and multiplication by scalars. This means that $\forall u, v \in V \ \forall \lambda, \mu \in \mathbb{F} : \lambda u + \mu v \in V$. Elements in V satisfy:

- $\forall u, v \in V : u + v = v + u \in V$ (addition is commutative)
- $\forall u, v, w \in V, \ \forall a, b \in \mathbb{F} : \ u + (v + w) = (u + v) + w$ and $(ab)u = a(bu)$ (associativity).
- There is a vector $0 \in V$ such that $\forall u \in V : \ 0 + u = u$ (additive identity).
- $\forall v \in V \ \exists u \in V$ such that $v + u = 0$ (additive inverse).
- The element $1 \in \mathbb{F}$ satisfies $\forall v \in V : \ 1v = v$ (multiplicative identity).
- $\forall u, v \in V, \forall a, b \in \mathbb{F} : \ a(u+v) = au + av$ and $(a+b)v = av + bv$ (distributive property).

Example C.1.2. Let X be a non-empty set. Let V be a $\mathbb{F}$ vector space. The set of functions $f : X \to V$ form a $\mathbb{F}$ vector space V_X with respect to

$$(f + g) : X \to V, \ x \to f(x) + g(x)$$

$$\lambda(f) : X \to V, \ x \to \lambda f(x)$$

Definition C.1.3. A list of vectors $(v_1, v_2, ..., v_n)$, with $v_i \in V$ is said to be linearly independent if given the scalars $a_1, \dots a_n$ and the equation

$$a_1 v_1 + a_2 v_2 + ... + a_n v_n = 0$$

there exists only one solution given by $a_1 = a_2 = \cdots = a_n = 0$.

Definition C.1.4. The span of a list of vectors $(v_1, v_2, \dots v_n) \in V$, written as $span(v_1, v_2, \dots, v_n)$, is the set of all linear combinations of these vectors

$$a_1 v_1 + a_2 v_2 + \dots a_n v_n, \ a_i \in \mathbb{F}, \ 1 \leq i \leq n$$

.

Definition C.1.5. A vector space V is spanned by a list $(v_1, v_2, \dots v_n)$ if $V = span(v_1, v_2, \dots v_n)$.

Definition C.1.6. A basis of V is a list of vectors in V that both spans V and is linearly independent.

Definition C.1.7. A linear operator L on a vector space V is a function that takes V to V such that:

$$\forall u, v \in V,\ \forall \lambda, \mu \in \mathbb{F} :\ L(\lambda u + \mu v) = \lambda L(u) + \mu L(v)$$

Example C.1.8. Let V be the space of polynomials $\mathbb{P}[x]$, L the differentiation operator $L[p] = \frac{dp}{dx}$. Then L is a linear operator.

Definition C.1.9. A bilinear operator L on a vector space V is a function that takes $V \times V$ to V such that:

$$\forall u_1, u_2, v_1, v_2 \in V,\ \forall \lambda, \mu \in \mathbb{F} :$$
$$L(\lambda u_1 + \mu u_2, v) = \lambda L(u_1, v) + \mu L(u_2, v)$$

and

$$L(u, \lambda v_1 + \mu v_2) = \lambda L(u, v_1) + \mu L(u, v_2)$$

Definition C.1.10. Let V be a vector space. An inner product on V is a function

$$< , >: V \times V \to \mathbb{R}$$

which is

- symmetric, that is $< u, v >=< v, u >$.
- bilinear
- positive definite, that is $\forall v \in V : < v, v > \geq 0$ and $< v, v >= 0$ implies $v = 0$

Definition C.1.11. An norm on a $\mathbb{F}$ vector space V is a function, traditionally denoted,

$$\|\cdot\| :\ V \to \mathbb{R}^{\geq 0}$$

that satisfies $\forall x, y \in V$ and $\forall \alpha \in \mathbb{F}$:

- $\|x\| = 0 \to x = 0$
- $\|\alpha x\| = |\alpha| \|x\|$
- $\|x + y\| \leq \|x\| + \|y\|$

Lemma C.1.12. *Let V be vector space with a scalar product $< \cdot, \cdot >$. Consider a function*

$$\|\cdot\|_i :\ V \to \mathbb{R}^{\geq 0}$$

that it's defined by

$$\|v\|_i := \sqrt{< v, v >}\ \ \forall\ v \in V \tag{C.1}$$

Then $\|\cdot\|_i$ is a norm which is called induced norm on the vector space V with a scalar product $< \cdot, \cdot >$.

Example C.1.13. Let f be a measurable function. The $p-$norm of f is defined by

$$\|f\|_p := \left(\int |f|^p d\mu \right)^{\frac{1}{p}}$$

where p is a positive integer. This is the norm that equips L^p spaces that we will introduce shortly.

Definition C.1.14. A set O on a vector space V with scalar product $< , >$ is said to be orthogonal iff $\forall\ v_i, v_j \in O : < v_i, v_j >= 0$ for $i \neq j$. $O \subset V$ is orthonormal iff it is orthogonal and $\forall\ v_i, v_j \in O : < v_i, v_j >= 1$ for $i = j$.

Definition C.1.15. Let X be a non-empty set. A metric on X is a map

$$d : X \times X \to \mathbb{R}$$

that maps all pairs $(x, y) \in X \times X$ into a real number such that the following properties hold:

- $\forall\ x, y \in X :\ d(x, y) \geq 0$ and $d(x, y) = 0 \leftrightarrow\ x = y$
- $\forall\ x, y \in X :\ d(x, y) = d(y, x)$
- $\forall\ x, y, z \in X :\ d(x, z) \leq d(x, y) + d(y, z)$

Definition C.1.16. A Cauchy sequence is a sequence $a_1, a_2, \ldots$ such that the metric $d(a_m, a_n)$ satisfies

$$\lim_{min(m,n)\to\infty} d(a_m, a_n) = 0.$$

Definition C.1.17. A complete metric is a metric in which every Cauchy sequence is convergent.

Definition C.1.18. A space X equipped with a measure defined by its norm $\|\cdot\|$ is called a *Banach Space* if it is complete.

Definition C.1.19. An *Hilbert space* consists of a vector space $\mathcal{H}$ with a scalar product $< \cdot, \cdot >$ such that its norm defined by $\|f\| := \sqrt{< f, f >}$ makes $\mathcal{H}$ a complete metric space. When the metric defined by its norm isn't complete, then $\mathcal{H}$ is named an inner product space.

Example C.1.20. Examples of Hilbert spaces are:

- $\mathbb{R}^n$ where $< h, g >$ is the standard dot product $\forall h, g \in \mathbb{R}^n$
- $\mathbb{C}^n$ where $< h, g >:= h \cdot (g^*)^t\ \forall h, g \in \mathbb{C}^n$ where $\cdot$ represents the standard matrix multiplication

Definition C.1.21. Let X be a set. A relation $\sim$ between the elements of the set X is called equivalence relation if it satisfies:

- $\forall\ x \in X :\ x \sim x$
- $\forall\ x, y \in X :\ x \sim y$ implies $y \sim x$
- $\forall\ x, y, z \in X :\ x \sim y$ and $y \sim z$ implies $x \sim z$

Definition C.1.22. Let $\sim$ be an equivalence relation on X and $x \in X$ a certain element of X. The set of elements $y \in X$ which are equivalent to x builds the equivalence class of x, i.e.

$$[x] := \Big\{ y \in X : x \sim y \Big\}$$

Definition C.1.23. Let $(\Omega, \mathcal{A})$ and $(\Omega', \mathcal{A}')$ be spaces equipped with a measure. Let $\mathcal{A}, \mathcal{A}'$ be $\sigma-$algebras. A map $\phi : \Omega \to \Omega'$ is called measurable if $\phi^{-1}(\mathcal{A}') \subset \mathcal{A}$, where the preimage of $\mathcal{A}'$ is defined by

$$\phi^{-1}(\mathcal{A}') = \Big\{ w \in \Omega :\ \phi(w) \in \mathcal{A}' \Big\}$$

Definition C.1.24. Consider a property P. P holds almost everywhere if there is a set X in a sigma-algebra such that the measure $\mu(X) = 0$, and such that every elements $x \in X^c$ possesses the property P.

Example C.1.25. Let $h,\ g$ be measurable functions; then define $f \sim g \leftrightarrow h = g$ almost everywhere. Note that this is an equivalence relation on the set of measurable functions.

Definition C.1.26. Let $\mathcal{L}$ be the set of all measurable functions such that their $p-$norm is less then ∞. Let $\sim$ be the equivalence relation defined in the example C.1.25. Then the L^p space is given by the set of equivalence classes on $\mathcal{L}$ with respect to the equivalence relation $\sim$.

Example C.1.27. The set of square integrable functions that satisfy $\int_{\mathbb{R}} |f|^2 d\mu < \infty$ is an $L^2(\mathbb{R})$ space. $L^2(\mathbb{R})$ together with the scalar product (with respect to the measure μ)

$$< f, g >:= \int f g^* d\mu$$

forms an infinite-dimensional Hilbert space.

C.2 Operators and properties

In this section we look more closely at operators, eigenvalues and their general properties in quantum mechanics.

Definition C.2.1. An observable is any property of a system that can be measured such as position, momentum or energy.

Definition C.2.2. An operator $\mathcal{O} : f^{(n)}\mathcal{I} \to f(\mathcal{I})$ assigns to every function f in $f^{(n)}(\mathcal{I})$ a function $\mathcal{O}(f)$ in $f(I)$. It is therefore a mapping between two function spaces. In other words, it's a map that acts on functions.

Example C.2.3. An important class of operators are the linear operators which we introduced before.

Example C.2.4. An important class of linear operators are the self-adjoint operators. We will focus on self-adjoint operators that act on the Hilbert space $L^2(\mathbb{R})$. The Hamiltonian is an example of self-adjoint operator.

Definition C.2.5. Let $\mathcal{O} :\ L^2(\mathbb{R}) \to L^2(\mathbb{R})$ be a linear operator. The adjoint of $\mathcal{O}$, denoted by $\mathcal{O}^\dagger$ or $\mathcal{O}^*$, is an operator acting on the dual space with the property:

$$\forall f, g \in L^2(\mathbb{R}) : \int_{\mathbb{R}} f^* \mathcal{O}[g] d\mu = \int_{\mathbb{R}} (\mathcal{O}[f])^* g d\mu$$

Notation C.2.6. Using a shorter notation, this is expressed as

$$< f, \mathcal{O} g >=< \mathcal{O}^* f, g >$$

Remark C.2.7. Note that this is consistent with the scalar product notation on L^2 where

$$< f, g >:= \int_{\mathbb{R}} f^* g d\mu$$

Example C.2.8. The expectation operator defined in Chapter 2 is an example of operator.

Definition C.2.9. An operator $\mathcal{O}$ is called self-adjoint iff $\mathcal{O}^* = \mathcal{O}$.

Remark C.2.10. Note that by construction, the product $\mathcal{O}\mathcal{O}^*$ is a self-adjoint operator since $(\mathcal{O}\mathcal{O}^*)^* = (\mathcal{O}^{**}\mathcal{O}^*) = (\mathcal{O}\mathcal{O}^*)$. Physicists often call self-adjoint operators Hermitian operators.

Example C.2.11. The Hamiltonian, the Number operator defined in Chapter 3 are examples of self-adjoint operators.

Observation C.2.12. *In quantum mechanics, to every observable O there exists a correspondent adjoint operator $\mathcal{O}$. Knowledge of the state of $\Psi(x,t)$ at some time t determines a knowledge of the expectation value of every observable.*

Observation C.2.13. *A measurement happens when there is an interaction with a physical system in order to yield a numerical result. In general, the outcome of a measurement is a state of zero-uncertainty, meaning that the uncertainty of an obseervable O is 0. The mean to perform these measurements are operators that act on observables.*

Remark C.2.14. Note that any state with vanishing uncertainty in the observable O is an eigenstate of the corresponding self-adjoint operator $\mathcal{O}$. On the other hand, the value of a measurement of an observable O coincides with an eigenvalue of the corresponding operator $\mathcal{O}$.

Theorem C.2.15. *Let $\Psi \in L^2(\mathbb{R})$ be a wave function, $\mathcal{O}$ a self-adjoint operator acting on Ψ. Then Ψ can be expressed as a linear combination of the eigenvectors (eigenstates) of $\mathcal{O}$.*

Theorem C.2.16. *The eigenvalues of a self-adjoint operator (i.e. a self-adjoint endomorphismus) $\mathcal{O}$ are real.*

Corollary C.2.17. *Thanks to theorem C.2.16, the energy eigenvalues of the Hamiltonian must be real. Note that the two theorems above are often referred to as Spectral Theorems for compact operators and apply to any $\mathbb{R}-$Hilbert space.*

Theorem C.2.18. *If two eigenvectors (eigenstates) of a self-adjoint operator correspond to different eigenvalues, then the two eigenvectors are orthogonal.*

Let's now imagine that we were looking for an instrument that would allow us to measure two observables simultaneously. Such a measurement needs to leave both observables in a state of zero uncertainty. For instance, by applying this operator to momentum and position we should not get zero. The operator that satisfies this requirements is called *commutator*.

Definition C.2.19. Given two operators $\mathcal{A}$ and $\mathcal{B}$, their commutator is defined by

$$[\mathcal{A},\mathcal{B}] = \mathcal{A}\mathcal{B} - \mathcal{B}\mathcal{A}$$

Remark C.2.20. Note that two observables $\mathcal{A}$ and $\mathcal{B}$ are simultaneously measureable (share the same eigenstates) if and only if their commutators $[\mathcal{A},\mathcal{B}] = 0$. Thanks to Heisenberg uncertainty principle we conclude that $[\hat{x},\hat{p}] \neq 0$, as we cannot measure them simultaneously.

C.3 Hermite polynomial

Due to the strong connection that exists between the solutions of the quantum oscillator and the Hermite polynomial, we dedicate this section to prove some important identities that are extremely useful in the derivation of the wave function via analytical method.

Definition C.3.1. The Hermite polynomials $H_n(x)$, n ϵ $\mathbb{N}_0$, in $\mathbb{R}[x]$ are defined by

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} e^{-x^2}, n \in \mathbb{N}_0 \tag{C.2}$$

Example C.3.2. With this representation we get the first Hermite polynomials directly by differentiation

- $H_0(x) = (-1)^0 e^{x^2} e^{-x^2} = 1$
- $H_1(x) = (-1)^1 e^{x^2} e^{-x^2}(-2x) = 2x$

- $H_2(x) = (-1)^2 e^{x^2} e^{-x^2}(4x^2 - 2) = 4x - 2$
- $H_3(x) = (-1)^3 e^{x^2} e^{-x^2}(-8x^3 + 12x) = 8x^3 - 12x$
- $H_4(x) = (-1)^4 e^{x^2} e^{-x^2}(16x^4 - 48x^2 + 12) = 16x^4 - 48x^2 + 12$

These are represented in Figure C.1 below.
Often, an Hermite Polynomial is expressed through its generating function:

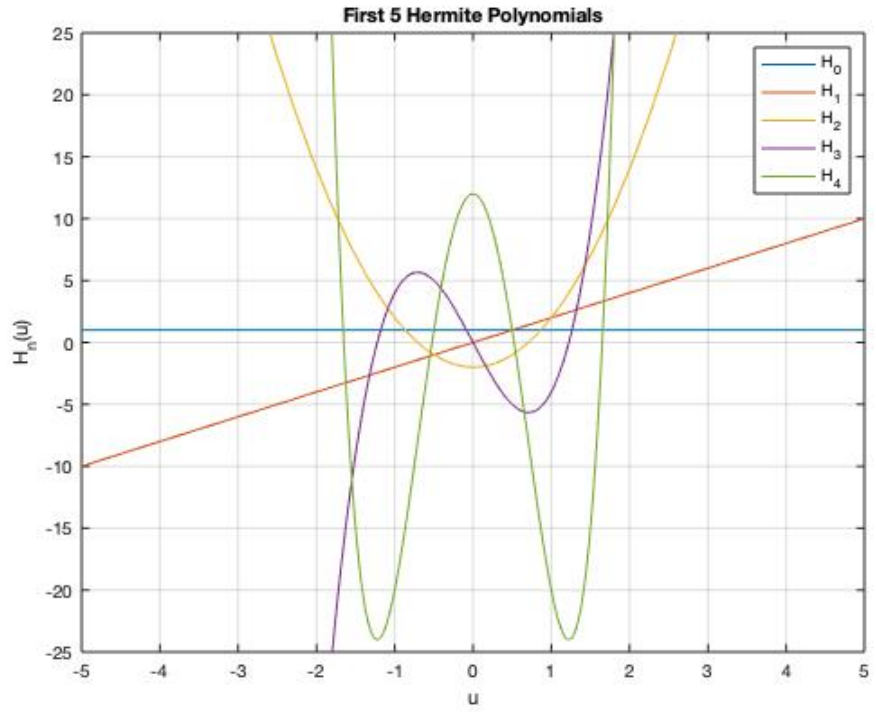


Figure C.1: The first five Hermite polynomials $H_n(u)$

Definition C.3.3. The generating function of an Hermite polynomial $H_n(x)$ is given by

$$w(x,t) := e^{2xt-t^2} \tag{C.3}$$

Lemma C.3.4.

$$w(x,t) := e^{2xt-t^2} = \sum_{n=0}^{\infty} \frac{H_n(x)}{n!} t^n \tag{C.4}$$

Proof. The function w is continuous differentiable with respect to $t \in \mathbb{R}$, so there exists a Taylor series around $t = 0$ for a fixed x:

$$w(x,t) := e^{2xt-t^2} = \sum_{n=0}^{\infty} \frac{w^{(n)}(x,0)}{n!} t^n \tag{C.5}$$

If we take the term inside the sum we get that

$$\begin{aligned} w^{(n)}(x,0) &= \left[\frac{\partial^n}{\partial t^n} w(x,t)\right]_{t=0} = \left[\frac{\partial^n}{\partial t^n} e^{2xt-t^2}\right]_{t=0} \\ &= \left[\frac{\partial^n}{\partial t^n} e^{2xt-t^2+x^2-x^2}\right]_{t=0} = e^{x^2}\left[\frac{\partial^n}{\partial t^n} e^{-(x-t)^2}\right]_{t=0} \end{aligned} \tag{C.6}$$

Through the change of variable $u = x - t$, $\frac{d^n}{dt^n} = \frac{d^n}{du^n}(-1)^n$ we get

$$\begin{aligned} e^{x^2}\left[\frac{\partial^n}{\partial t^n}e^{-(x-t)^2}\right]_{t=0} &= (-1)^n e^{x^2}\left[\frac{d^n}{du^n}e^{-u^2}\right]_{u=x} \\ &= (-1)^n e^{x^2}\left(\frac{d^n}{dx^n}e^{-x^2}\right) = H_n(x) \end{aligned} \tag{C.7}$$

which proves (C.4). ■

Hermite recursion formulas

Theorem C.3.5. *For all $x \in \mathbb{R}$, $n \in \mathbb{N}$ applies*

a . $H_{n+1}(x) - 2xH_n(x) + 2nH_{n-1}(x) = 0$,

b . $H_n^{(1)}(x) = 2nH_{n-1}(x)$,

c . $H_n^{(2)} - 2xH_n^{(1)}(x) + 2nH_n(x) = 0$.

Proof. We start by using the generating function $w(x,t)$

a)

$$\begin{aligned} \frac{\partial}{\partial t}w(x,t) = \frac{\partial}{\partial t}e^{2xt-t^2} &= (2x-2t)e^{2xt-t^2} = (2x-2t)w(x,t) \\ \leftrightarrow \frac{\partial}{\partial t}w(x,t) - (2x-2t)w(x,t) &= 0, \end{aligned} \tag{C.8}$$

which leads us to use the power series

$$\begin{aligned} &\frac{\partial}{\partial t}\sum_{n=0}^{\infty}\frac{H_n(x)}{n!}t^n - (2x-2t)\sum_{n=0}^{\infty}\frac{H_n(x)}{n!}t^n = 0 \\ &\leftrightarrow \frac{\partial}{\partial t}\frac{H_n(x)}{n!}t^n - (2x-2t)\sum_{n=0}^{\infty}\frac{H_n(x)}{n!}t^n - 2x\sum_{n=0}^{\infty}\frac{H_n(x)}{n!}t^n + 2t\sum_{n=0}^{\infty}\frac{H_n(x)}{n!}t^n = 0 \end{aligned} \tag{C.9}$$

These power series can now be differentiated within their convergence radius and hence

$$\sum_{n=1}^{\infty}\frac{H_n(x)}{(n-1)!}t^{n-1} - 2x\sum_{n=0}^{\infty}\frac{H_n(x)}{n!}t^n + 2\sum_{n=0}^{\infty}\frac{H_n(x)}{n!}t^{n+1} = 0 \tag{C.10}$$

Now, we shift the index of summation and so we get

$$\begin{aligned} &\sum_{n=0}^{\infty}\frac{H_{n+1}(x)}{n!}t^n - 2x\sum_{n=0}^{\infty}\frac{H_n(x)}{n!}t^n + 2\sum_{n=1}^{\infty}\frac{H_{n-1}(x)}{(n-1)!}t^n = 0 \\ &\leftrightarrow \underbrace{H_1(x) - 2xH_0(x)}_{=0} + \sum_{n=1}^{\infty}\frac{H_{n+1}(x)}{n!}t^n - 2x\sum_{n=1}^{\infty}\frac{H_n(x)}{n!}t^n + 2\sum_{n=1}^{\infty}\frac{H_{n-1}(x)}{(n-1)!}t^n = 0 \end{aligned} \tag{C.11}$$

which allows us to compare the coefficients of t_n

$$\frac{H_{n+1}(x)}{n!} - 2x\frac{H_n(x)}{n!} + 2\frac{H_{n-1}(x)}{(n-1)!} = 0 \tag{C.12}$$

which is equivalent to a).
b) Following the same steps as above we first differentiate the generating function w with respect to x

$$\begin{aligned} &\frac{\partial}{\partial x} w(x,t) = \frac{\partial}{\partial x} e^{2xt-t^2} = 2te^{2xt-t^2} = 2tw(x,t) \\ &\leftrightarrow \frac{\partial}{\partial x} w(x,t) = 2tw(x,t) = 0, \end{aligned} \tag{C.13}$$

and so the w can be rewritten using its series representation in (C.4)

$$\begin{aligned} &\frac{\partial}{\partial x} \sum_{n=0}^{\infty} \frac{H_n(x)}{n!} t^n - 2t \sum_{n=0}^{\infty} \frac{H_n(x)}{n!} t^n = 0 \\ &\leftrightarrow \sum_{n=0}^{\infty} \frac{H_n'(x)}{n!} t^n - 2 \sum_{n=0}^{\infty} \frac{H_n(x)}{n!} t^{n+1} = 0 \\ &\leftrightarrow \underbrace{H_0'(x)}_{=0} + \sum_{n=1}^{\infty} \frac{H_n'(x)}{n!} t^n - 2 \sum_{n=0}^{\infty} \frac{H_n(x)}{n!} t^{n+1} = 0 \end{aligned} \tag{C.14}$$

Now, shifting the index of summation, we obtain

$$\sum_{n=1}^{\infty} \frac{H_n'(x)}{n!} t^n - 2 \sum_{n=1}^{\infty} \frac{H_n - 1(x)}{(n-1)!} t^n = 0, \tag{C.15}$$

and again, from the comparison of coefficients t^n we get

$$\frac{H_n'(x)}{n!} - 2 \frac{H_{n-1}(x)}{(n-1)!} = 0, \tag{C.16}$$

giving us b).

c) From a) and b) and for $n \geq 2$

$$H_n''(x) = \left(H_n'(x)\right)' \overset{b}{=} 2nH_{n-1}'(x) \overset{b}{=} 4n(n-1)H_{n-2}(x), \tag{C.17}$$

and so we see

$$\begin{aligned} &H_n''(x) - 2xH_n'(x) + 2nH_n(x) \\ &= 4n(n-1)H_{n-2}(x) - 4nxH_{n-1}(x) + 2nH_n(x) \\ &= 2n \underbrace{\left(2(n-1)H_{n-2}(x) - 2xH_{n-1}(x) + H_n(x)\right)}_{=0} \\ &= 0 \end{aligned} \tag{C.18}$$

For $n = 1$ we obtain

$$\begin{aligned} &H_1''(x) - 2xH_1'(x) + 2H_1(x) \\ &= (2x)'' - 2x(2x)' + 4x \\ &= 0 - 4x + 4x \\ &= 0 \end{aligned} \tag{C.19}$$

■

Hermite differential equation

The previous recursion formulas allow us to define the *Hermite differential equation*. Let $n \in \mathbb{N}_0$. Then we have

$$y'' - 2xy' + 2ny = 0 \tag{C.20}$$

Theorem C.3.6. *The Hermite polynomials satisfy the Hermite differential equation*

$$y'' - 2xy' + 2ny = 0, \quad n \in \mathbb{N}_0 \tag{C.21}$$

Proof. Note that this follows directly from theorem C.3.5, part *c*. ■

Orthogonality and normality

Theorem C.3.7. *Hermite polynomials $H_n(x)$ are orthogonal with respect to the weight e^{-x^2}. Hence we get*

$$\int_{-\infty}^{\infty} e^{-x^2} H_n(x) H_m(x) dx = 0, \tag{C.22}$$

where $m \neq n$.

Remark C.3.8. Note that this makes the wave functions that we obtained in Section 3.4 orthogonal on $L^2(\mathbb{R})$ as we would expect, since $\psi_n,\ n \in \mathbb{N}_0$ was of the form $H_n(x)e^{-\frac{x^2}{2}}$.

On the other hand, the following theorem holds

Theorem C.3.9.

$$\int_{-\infty}^{\infty} e^{-x^2} H_n^2(x) dx = 2^n n! \sqrt{\pi}, \tag{C.23}$$

where $m = n$.

Corollary C.3.10. *From C.3.9 we conclude that a function $\psi_n = e^{-\frac{x^2}{2}} H_n \sqrt{\frac{1}{2^n n! \sqrt{\pi}}},\ n \in \mathbb{N}_0$ must have unitary norm on $L^2(\mathbb{R})$.*

We will prove only theorem C.3.9; theorem C.3.7 can be derived for instance using the *Hermite differential equation*.

Proof. An easy approach is to use induction over $n \in \mathbb{N}_0$. We first consider the cases where $n = 0$ and $n = 1$.

$$\int_{-\infty}^{\infty} e^{-x^2} H_0^2(x) dx = \int_{-\infty}^{\infty} e^{-x^2} dx = I_0 = \sqrt{\pi} = 2^0 0! \sqrt{\pi}, \tag{C.24}$$

$$\begin{aligned} \int_{-\infty}^{\infty} e^{-x^2} H_1^2(x) dx &= \int_{-\infty}^{\infty} 4e^{-x^2} x^2 dx \\ &= 4 \int_{-\infty}^{\infty} e^{-x^2} x^2 dx = 4I_2 = 4\left(\frac{1}{2} I_0\right) = 2\sqrt{\pi} = 2^1 1! \sqrt{\pi} \end{aligned} \tag{C.25}$$

In the section dedicated to the algebraic method applied to the quantum oscillator, we introduced the formula to compute I_n. We have shown that the integral of e^{-x^2} over $\mathbb{R}$, namely I_0, is equal to $\sqrt{\pi}$.
For $n \geq 2$: recall that from the recursion formula *a*. we proved that

$$H_{n+1}(x) - 2xH_n(x) + 2nH_{n-1}(x) = 0 \tag{C.26}$$

If we replace n by $n - 1$ and multiply by $H_n(x)$ on both sides of (C.26) we get

$$H_n^2(x) - 2xH_{n-1}(x)H_n(x) + 2(n-1)H_{n-2}(x)H_n(x) = 0, \tag{C.27}$$

Furthermore, if we multiply (C.26) by $H_{n-1}(x)$ on both sides so we get

$$H_{n+1}(x)H_{n-1}(x) - 2xH_n(x)H_{n-1}(x) + 2nH_{n-1}^2(x) = 0, \tag{C.28}$$

Equation (C.27) is then subtracted by the first equation and multiplied by e^{-x^2}. Thus, we get

$$\begin{aligned}
&H_n^2(x) - 2nH_{n-1}(x) + 2(n-1)H_{n-2}(x)H_n(x) - H_{n+1}(x)H_{n-1}(x) = 0 \\
&\leftrightarrow e^{-x^2}\big(H_n^2(x) - 2nH_{n-1}(x) \\
&+ 2(n-1)H_{n-2}(x)H_n(x) - H_{n+1}(x)H_{n-1}(x)\big) = 0 \\
&\leftrightarrow e^{-x^2}H_n^2(x) - 2ne^{-x^2}H_{n-1}^2(x) \\
&+ 2(n-1)e^{-x^2}H_{n-2}(x)H_n(x) - e^{-x^2}H_{n+1}(x)H_{n-1}(x)
\end{aligned} \tag{C.29}$$

Integrating over the interval $(-\infty, \infty)$, we get

$$\begin{aligned}
&\int_{-\infty}^{\infty} e^{-x^2}H_n^2(x)dx - 2n\int_{-\infty}^{\infty} e^{-x^2}H_{n-1}^2(x) \\
&+ 2(n-1)\int_{-\infty}^{\infty} \underbrace{e^{-x^2}H_{n-2}(x)H_n(x)}_{=0 \text{ due to orthogonality}} - \int_{-\infty}^{\infty} \underbrace{e^{-x^2}H_{n+1}(x)H_{n-1}(x)}_{=0 \text{ due to orthogonality}} = 0 \\
&\leftrightarrow \int_{-\infty}^{\infty} e^{-x^2}H_n^2(x)dx = 2n\int_{-\infty}^{\infty} e^{-x^2}H_{n-1}^2(x)dx
\end{aligned} \tag{C.30}$$

Define

$$B_n := \int_{-\infty}^{\infty} e^{-x^2}H_n^2(x)dx, \quad B_0 := \int_{-\infty}^{\infty} e^{-x^2}H_0^2(x)dx \tag{C.31}$$

Note that, since $H_0 = 1$, $B_0 = I_0 = \sqrt{\pi}$.
Then we have thanks to (C.30) that

$$B_n = 2nB_{n-1} = 2n\left(2\left(n-1\right)B_{n-2}\right) = \cdots = 2^n n!B_0 = 2^n n!I_0 = 2^n n!\sqrt{\pi} \tag{C.32}$$

Finally, we conclude that

$$\int_{-\infty}^{\infty} e^{-x^2}H_n(x)H_m(x)dx = 2^n n!\sqrt{\pi}\delta_{n,m}, \quad \forall n, m \in \mathbb{N}_0 \tag{C.33}$$

■

APPENDIX D

Code

In this appendix we share the code which was developed for this project. All rights are reserved. For the diagonalisation method Matlab was the best choice given that it is optimised for matrix operations. The implementation of the shooting method via RK4 was done in Python (via Spyder version 4.1). We also added additional pieces of code related to topics which we touched upon such as the Euler Method or the numerical solutions of ordinary differential equations.

D.1 Matlab

This section contains the following implementations:

- Diagonalisation method and analytical resolution of the 3×3 case
- Euler method
- Vandermonde polynomial interpolation
- Resolution of ODEs using Matlab

```
% Diagonaisation method in the infinite square well
% Author: Guido Bassi
% All rights reserved



clear variables
N = 20;
H = diag(2*ones(1,N))-1*diag(ones(1,N-1),-1)-1*diag(ones(1,N-1),1);


h = 1
```

```
h =
     1
```

```
m = 1
```

```
m =
     1
```

```
a = 1
```

```
a =
     1
```

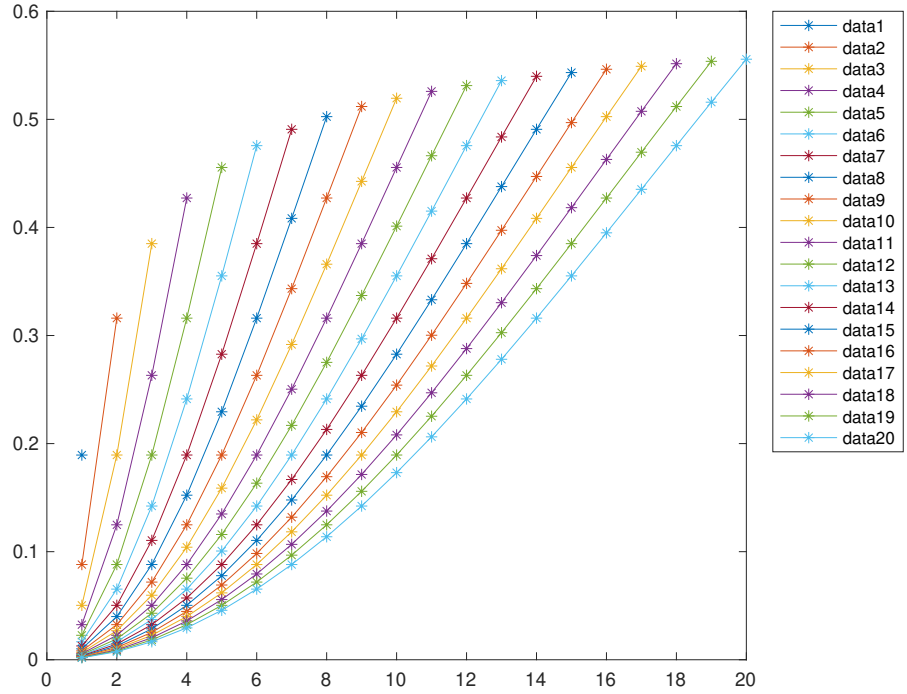
```
lambda = ((N + 1) ^ 2/2)*(h ^ 2/m*a ^ 2)
```

```
lambda =
     441/2
```

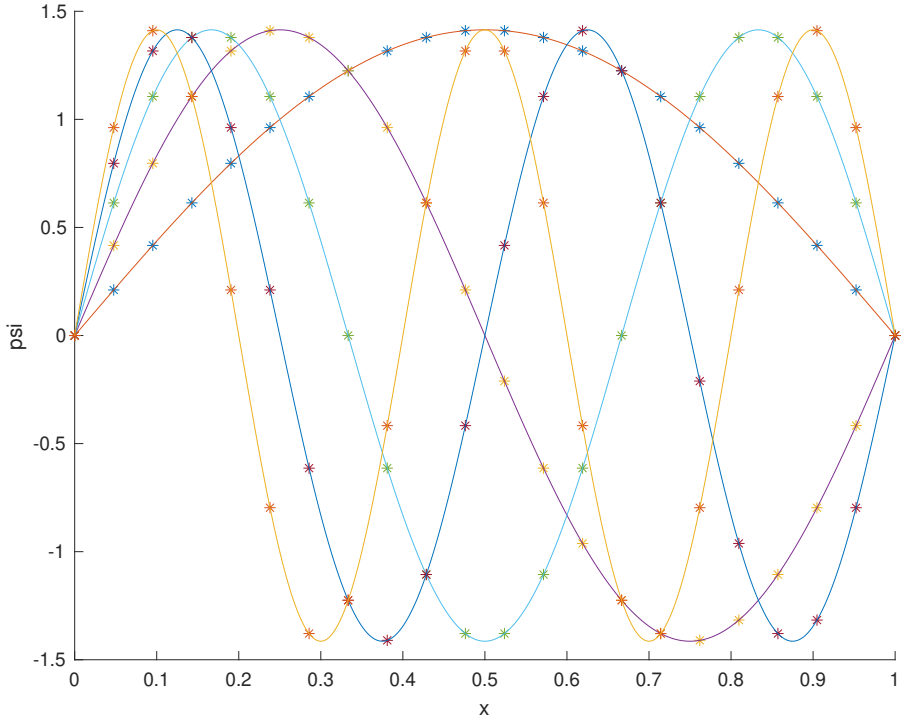
```
h = (a)/(N + 1)
```

```
h =
     1/21
```

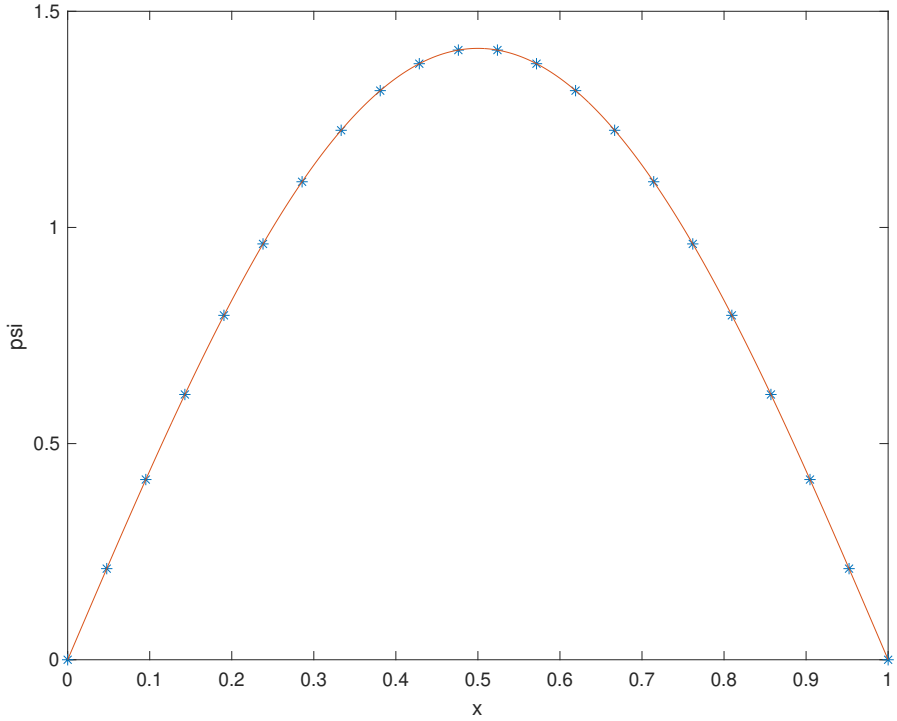
```
 % Plotting the eigenvalues error
tspan = 0:h:a;
Hc = lambda*H;
[C,D] = eig(Hc);

err = zeros(N,N);
for i = 2:N
    H_i = diag(2*ones(1,i))-1*diag(ones(1,i-1),-1)-1*diag(ones(1,i-1),1);
    lambda_i = ((i + 1) ^ 2/2)*(h ^ 2/(m*a ^ 2));
    Hc_i = lambda_i*H_i;
    [C_i,D_i] = eig(Hc_i);
    vex = 1:i;
    vex = (vex. ^ 2).*(pi ^ 2*h ^ 2/(2*m*a ^ 2));
    err(i,1:i) = (vex-diag(D_i).')./vex;
end

err(1,1) = .18941;

for i = 1:N
    plot(err(i,1:i),'-*')
    hold on
end
legend('Location','bestoutside')
hold off
```




```
% Plotting the eigenstates
sqrt(N+1).*C;


x = 0:.001:1;

clf
for i = 1:5
   y = sqrt(2)/a*sin((i*pi).*x./a) ;
   hold on
   if (C(1,i) < 0)
   plot(tspan,[0; -sqrt(N+1).*C(:,i); 0],'*')
   end
   if (C(1,i) > 0)
   plot(tspan,[0; sqrt(N+1).*C(:,i); 0],'*')
   end
   plot(x,y)
end

hold off
xlabel('x')
ylabel('psi')
```




```
y = sqrt(2)/a*sin(1*pi.*x./a) ;
plot(tspan,[0; sqrt(N + 1).*C(:,1); 0],'*')
hold on
plot(x,y)
hold off
xlabel('x')
ylabel('psi')
```




```
% Analytical derivation of the eigenstates for the 3x3 case
HH = [2 -1 0;-1 2 -1;0 -1 2]
```

HH =

$$\begin{matrix} 2 & -1 & 0 \\ -1 & 2 & -1 \\ 0 & -1 & 2 \end{matrix}$$

```
format rational
syms h_bar m a
HH = (16*h_bar^2/(2*m*a^2)).*HH
```

HH =

$$\begin{pmatrix} \frac{16\,\bar{h}^2}{a^2\,m} & \sigma_1 & 0 \\ \sigma_1 & \frac{16\,\bar{h}^2}{a^2\,m} & \sigma_1 \\ 0 & \sigma_1 & \frac{16\,\bar{h}^2}{a^2\,m} \end{pmatrix}$$

where

$$\sigma_1 = -\frac{8\,\bar{h}^2}{a^2\,m}$$

```
[M,N] = eig(HH)
```

M =

$$\begin{pmatrix} -1 & 1 & 1 \\ 0 & \frac{\sqrt{2}\,\bar{h}^2-2\,\bar{h}^2}{\bar{h}^2}+2 & 2-\frac{\sqrt{2}\,\bar{h}^2+2\,\bar{h}^2}{\bar{h}^2} \\ 1 & 1 & 1 \end{pmatrix}$$

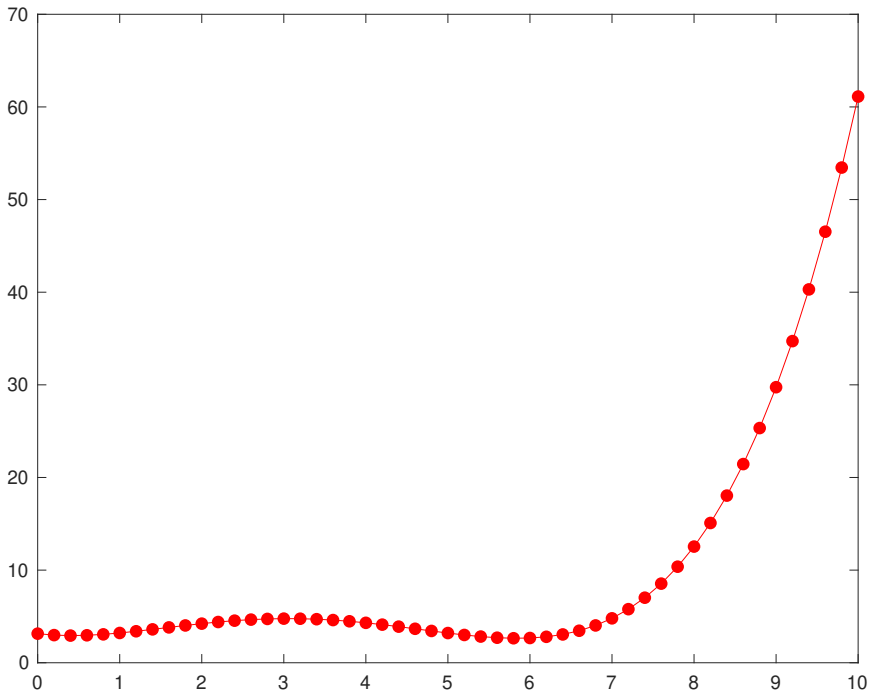
N =

$$\begin{pmatrix} \frac{16\,\bar{h}^2}{a^2\,m} & 0 & 0 \\ 0 & -\frac{8\left(\sqrt{2}\,\bar{h}^2-2\,\bar{h}^2\right)}{a^2\,m} & 0 \\ 0 & 0 & \frac{8\left(\sqrt{2}\,\bar{h}^2+2\,\bar{h}^2\right)}{a^2\,m} \end{pmatrix}$$

```
% Euler method and Vandermonde interpolation
% Author: Guido Bassi
% All rights reserved


% compute the value of y(b) given the initial condition
% y'(a) = y0 for the initial value problem
% y' = g(t,y(t)) where g can be defined below in the EulerM
% function (Euler Method)
EulerM(0,1,1,100)
```

```
ans =
    1.927480089920862
```

```
% Vandermonde interpolation
% Interpolation can be used to find the polynomial
% which best approximates a given function

clear
clc
format long;

A = [0 2 3 5 6];
Aout = [3.1402;4.2222;4.7634;3.2065;2.6712];
n = size(A,2);
V = fliplr(vander(A));
if det(V)~ = 0
    w = V\Aout;
end

syms x
syms Pol(x)

Pol = poly2sym(flip(w.')); % interpolated function

syms g
plot(0:0.2:10,subs(Pol,x,0:0.2:10),'r.-','MarkerSize',20);
hold on
hold off
```




```
disp((Pol));
```

$$\frac{163798420447257\,x^4}{4503599627370496} - \frac{2034255935684899\,x^3}{4503599627370496} + \frac{7059409929901771\,x^2}{4503599627370496} - \frac{4855736082234565\,x}{4503599627370496} + \frac{15701}{5000}$$

```
disp(w);
```

```
   3.140200000000000
  -1.078189999999993
   1.567503888888882
  -0.451695555555553
   0.036370555555555
```

```
function fun = EulerM(a,b,y0,N)  % N is an integer
 % Compute y(b) given y' = g(t,y(t)) with boundary y'(a) = y0

format long

h = ((b-a)/N);
 %  Define g
g = @(t,y)(t).^3 + t*y;
 % g = @(t,y)y;
 % g = @(t,y)t/y;

X = zeros(1,N + 1);
Y = zeros(1,N + 1);
X(1) = a;
Y(1) = y0;
 % tic
for i = 1:N
    X(i + 1) = X(i) + h;
    Y(1 + i) = Y(i) + h*g(X(i + 1), Y(i));
```

```
end
 % toc

fun = (Y(i));

end
```

```
% ODEs in Matlab
% Author: Guido Bassi
% All rights reserved
```

Solving ordinary differential equations in Matlab

```
% symbolic
syms x(t) y(t)

odex = diff(x) == 5.*x + 4.*y;
odey = diff(y) == 4.*x + 5.*y;

odes = [odex;odey]
```

$$\mathrm{odes}(\mathrm{t}) = \begin{pmatrix} \frac{\partial}{\partial t}\, x(t) = 5\,x(t) + 4\,y(t) \\ \frac{\partial}{\partial t}\, y(t) = 4\,x(t) + 5\,y(t) \end{pmatrix}$$

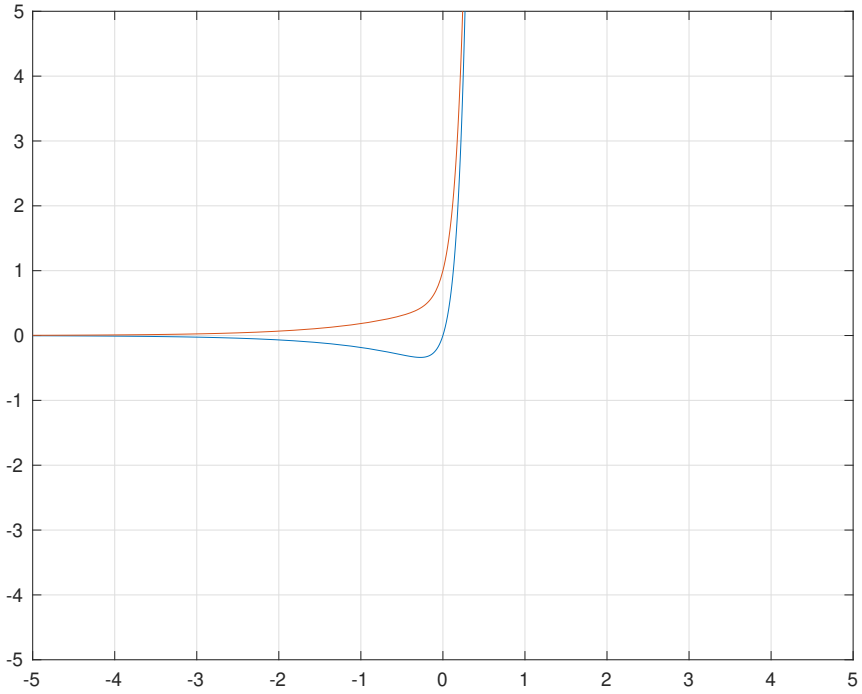
```
% [xSol,ySol] = dsolve(odes);

boundx = x(0) == 0;
boundy = y(0) == 1;
boundary = [boundx;boundy]
```

$$\mathrm{boundary} = \begin{pmatrix} x(0) = 0 \\ y(0) = 1 \end{pmatrix}$$

```
[xSol,ySol] = dsolve(odes,boundary)
```

$$\mathrm{xSol} = \frac{\mathrm{e}^{9\,t}}{2} - \frac{\mathrm{e}^{t}}{2}$$
$$\mathrm{ySol} = \frac{\mathrm{e}^{9\,t}}{2} + \frac{\mathrm{e}^{t}}{2}$$

```
fplot(xSol)
ylim([-5 5])
hold on
grid on
fplot(ySol);
hold off
```



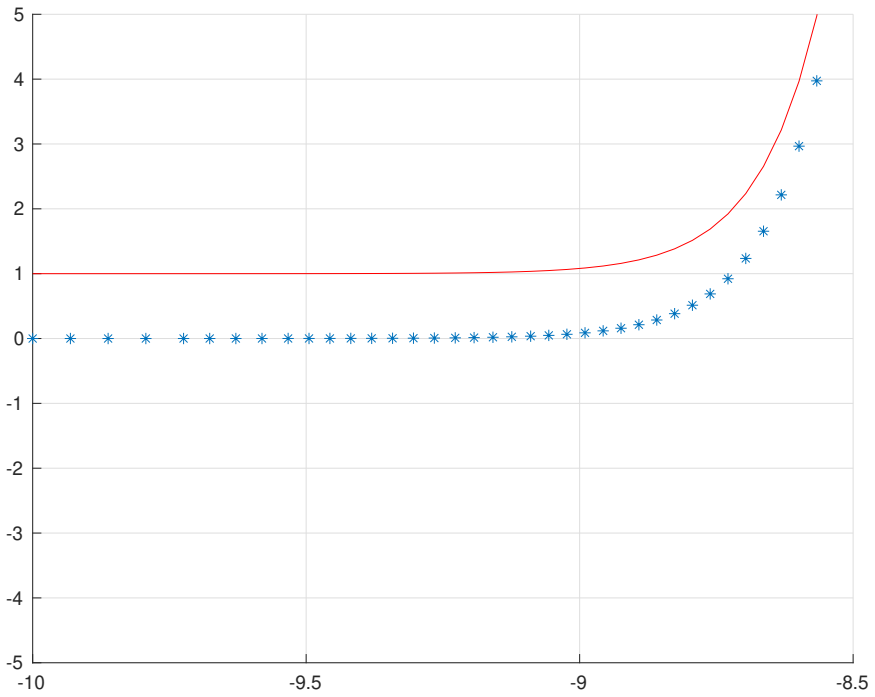

```
% Linear ODEs

tRange = [-10 10]
```

```
tRange  =  1x2
   -10     10
```

```
y0 = [0.00001;0.99999]
```

```
y0  =  2x1
   0.000010000000000
   0.999990000000000
```

```
[tSol,YSol] = ode45(@MyLDE,tRange,y0);

x = YSol(:,1);
y = YSol(:,2);
Fig1 = figure;
hold on
plot(tSol,x,'*');
ylim([-5 5]);
grid on
plot(tSol,y,'r');
```




```
function z = MyLDE(t,Y)


x = Y(1);
y = Y(1);

dxdt = 5.*x + 4.*y;
dydt = 4.*x + 5.*y;

z = [dxdt;dydt];

end
```

D.2 Python

This section contains the code created to solve the quantum harmonic oscillator. As mentioned, the method adopted is the the shooting method via RK4.

```
"""
Created on Tue Mar  9 02:10:41 2021

@author: guidobassi
"""



# -*- coding: utf-8 -*-
"""
Spyder Editor

All rigths reserved.
"""

import matplotlib.pyplot as plt
import numpy as np


def SchrEq(z, r, V, E):
    w,v = z
    dvdx = [v, (V-E)*w]
    return np.asarray(dvdx)


def Normalisation(wavefct):
    c_norm = max(wavefct)
    return wavefct*(1/(c_norm))

def ZerosFinder(val):
    return np.where(np.diff(np.signbit(val)))[0]


def RK4(g, psi0, u, V, E):
    m=len(u)
    w=np.array([psi0]*m)
    for i in range(m - 1):
        h = u[i+1] - u[i]
        k1 = h*g(w[i], u[i], V[i], E)
        k2 = h*g(w[i]+0.5*k1, u[i] + 0.5*h, V[i], E)
        k3 = h*g(w[i]+0.5*k2, u[i] + 0.5*h, V[i], E)
        k4 = h*g(w[i] +k3, u[i+1], V[i], E)
        w[i+1] = w[i]+ (k4 + 2.0*(k3 + k2) + k1) / 6.0
    return w

```

```
def EnergyFinder(Elow, Eup, Root, psi0, x, V):
    tolerance = 1e-12
    EU = Eup
    EL = Elow
    w = [1]
    while (abs(EU - EL) > tolerance or abs(w[-1]) > 1e-3):
        E0 = (EU + EL)/2.0
        w = RK4(SchrEq, psi0, x, V, E0)[:, 0]
        nodes= len(ZerosFinder(w))-1
        if nodes > Root + 1:
            EU = E0
            continue
        if nodes < Root - 1:
            EL = E0
            continue
        if (nodes % 2 == 0):
            if ((w[len(w)-1] <= 0.0)):
                EU = E0
            else:
                EL = E0
        elif nodes > 0:
            if ((w[len(w)-1] <= 0.0)):
                EL = E0
            else:
                EU = E0
        elif nodes < 0: EL = E0
    return EU , EL




def Shooting(E,nodes):
    w_0 = 0.0
    v_0 = 1.0
    w_init = np.asarray([w_0, v_0])
    h_mesh = 1.0/100.0
    x = np.arange(-5.0, 5.0+h_mesh, h_mesh)
    V = x**2 # potential
    EL,EU = EnergyFinder(E[0], E[1], nodes, w_init, x , V)
    wU=RK4(SchrEq, w_init, x, V, EL)[:, 0]
    wL= RK4(SchrEq, w_init, x, V, EL)[:, 0]
    return EL , EU , Normalisation(wL), Normalisation(wU), x

```

```python
def Analytical_Solution(x, nodes):
    if(nodes == 1):
        return np.exp(-(x)**2/2)
    elif(nodes == 2):
        return np.sqrt(2.0)*(x)*np.exp(-(x)**2/2)*(-1)
    elif (nodes == 3):
        return (1.0/np.sqrt(2.0))*(2.0*(x)**2-1.0)*np.exp(-(x)**2/2)
    elif (nodes == 4):
        return (1.0/np.sqrt(3.0))*(2.0*(x)**3-3.0*x)*np.exp(-(x)**2/2)*(-1)
    elif (nodes == 5):
        return (1.0/np.sqrt(24.0))*(4.0*(x)**4-12.0*x**2+3.)*np.exp(-(x)**2/2)
    else:
        print("No analytical solution")
        print("The output will be the trivial solution")
        return np.zeros(len(x))



E_0 =[0.1, 100.0]


nodes = np.arange(1, 6, 1)


print( "Here come the first 5 eigenstates")
print("\n")

print("Quantum Harmonic Oscillator: Shooting method via RK4")
figqho = plt.figure()
for j in nodes:
    EL, EU, psiLow, psiUp, x = Shooting(E_0, j)
    psi_ana = Analytical_Solution(x , j)
    print("The energy eigenvalue = %s " % (EU, ))
    plt.cla()
    plt.clf()
    plt.plot(x , psiUp , 'b-.', label=r'$\Psi(x)_{num}$')
    plt.plot(x, Normalisation(psi_ana), 'r--',label=r'$\Psi(x)_{ana}$')
    plt.title('Eigenstate: %s' % (j, ))
    plt.legend(loc='best', fontsize='small')
    plt.grid()
    plt.show()
```

```
Console 1/A

Quantum Harmonic Oscillator: Shooting method via RK4
The energy eigenvalue = 1.0000083335211944

Figures now render in the Plots pane by default. To make them also appear inline in the Console, uncheck "Mute
Inline Plotting" under the Plots pane options menu.

 The energy eigenvalue = 3.000008342037761
The energy eigenvalue = 5.000008507956068
The energy eigenvalue = 7.000010796102268
The energy eigenvalue = 9.000033664937813


In [2]:
```

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