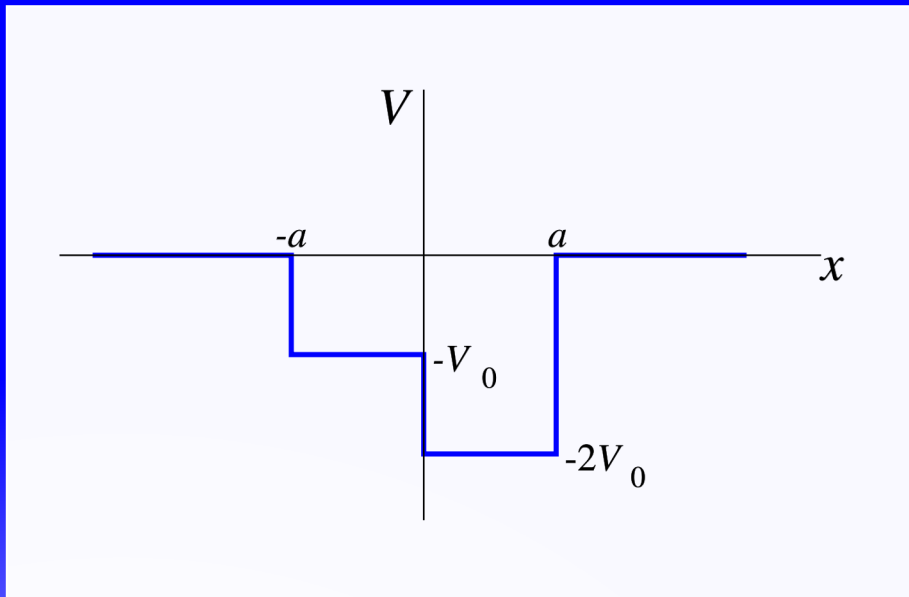


# Quantum Mechanics I



Niels Walet

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# Chapter 1

## Introduction

One normally makes a distinction between quantum mechanics and quantum physics. Quantum physics is concerned with those processes that involve discrete energies, and quanta (such as photons). Quantum Mechanics concerns the study of a specific part of quantum physics, those quantum phenomena described by Schrödinger's equation.

Quantum physics plays a rôle on small (atomic and subatomic) scales (say length scales of the order of  $10^{-9}\text{m}$ ) and below. You can see whether an expression has a quantum-physical origin as soon as it contains Planck's constant in one of its two guises

$$\begin{aligned}h &= 6.626 \cdot 10^{-34}\text{Js}, \\ \hbar &= h/2\pi = 1.055 \cdot 10^{-34}\text{Js}.\end{aligned}\tag{1.1}$$

Here we shall shortly review some of the standard examples for the break-down classical physics, which can be described by introducing quantum principles.

### 1.1 Black-body radiation

In the 19th century there was a lot of interest in thermodynamics. One of the areas of interest was the rather contrived idea of a black body: a material kept at a constant temperature  $T$ , and absorbing any radiation that falls on it. Thus all the light that it emits comes from its thermal energy, non of it is reflected from other sources. A very hot metal is pretty close to this behaviour, since its thermal emission is very

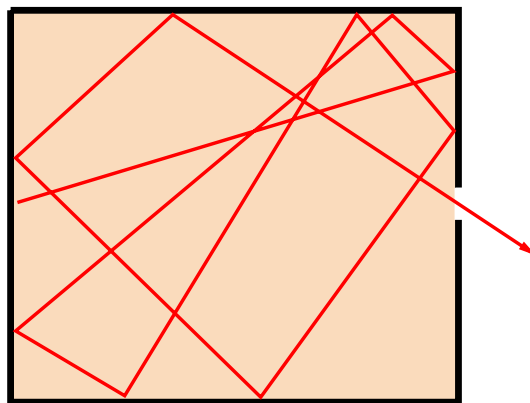


Figure 1.1: An oven with a small window

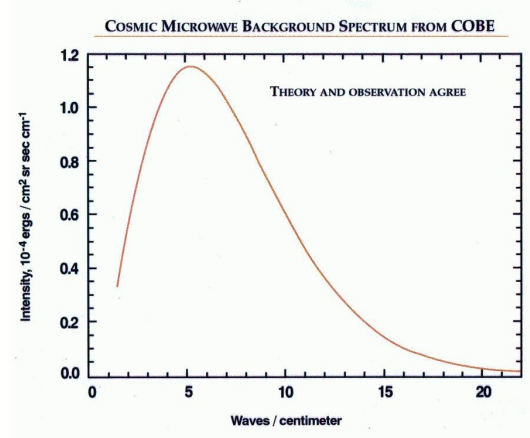


Figure 1.2: The black-body spectrum as measured by COBE. ()

much more intense than the environmental radiation. A slightly more realistic device is an oven with a small window, which we need to observe the emitted radiation, see Fig. 1.1. The laws of thermal emission have been well tested on such devices. A very different example is the so-called 3 K microwave radiation (Penzias and Wilson, Nobel price 1978). This is a remnant from the genesis of our universe, and conforms extremely well to the black-body picture, as has been shown by the recent COBE experiment, see Fig. 1.2.

The problem with the classical (Rayleigh-Jeans) law for black-body radiation is that it does suggest emission of infinite amounts of energy, which is clearly nonsensical. Actually it was for the description of this problem Planck invented Planck's constant! Planck's law for the energy density at frequency  $\nu$  for temperature  $T$  is given by

$$\rho(\nu, T) = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{h\nu/kT} - 1}. \quad (1.2)$$

The interpretation of this expression is that light consists of particles called photons, each with energy  $h\nu$ .

If we look at Planck's law for small frequencies  $h\nu \ll kT$ , we find an expression that contains no factors  $h$  (Taylor series expansion of exponent)

$$\rho(\nu, T) = \frac{8\pi\nu^2 kT}{c^3}. \quad (1.3)$$

This is the Rayleigh-Jeans law as derived from classical physics. If we integrate these laws over all frequencies we find

$$E = \int_0^\infty d\nu \rho(\nu, T) = \frac{8\pi^5 k^4}{15c^3 h^3} T^4 \quad (1.4)$$

for Planck's law, and infinity for the Rayleigh-Jeans law. The  $T^4$  result has been experimentally confirmed, and predates Planck's law.

## 1.2 Photo-electric effect

When we shine a lamp on a metal surface, electrons escape the surface. This is a simple experimental fact, that can easily be demonstrated. The intriguing point is that it takes a minimum frequency of light to remove electrons from a metal, and different metals require different minimal frequencies. Intensity plays no rôle in the threshold.

The explanation for this effect is due to Einstein (actually he got the Nobel price for this work, since his work on relativity was too controversial). Suppose once again that light is made up from photons.



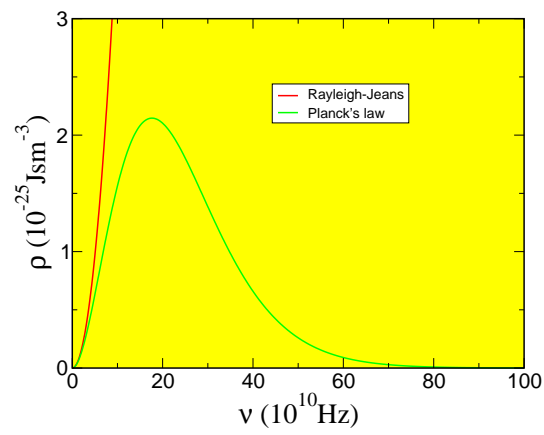


Figure 1.3: A comparison between the Rayleigh-Jeans and Planck's law

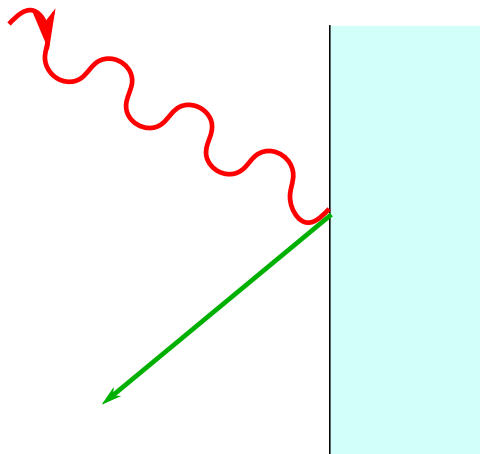


Figure 1.4: The photo-electric effect, where a single photon removes an electron from a metal.

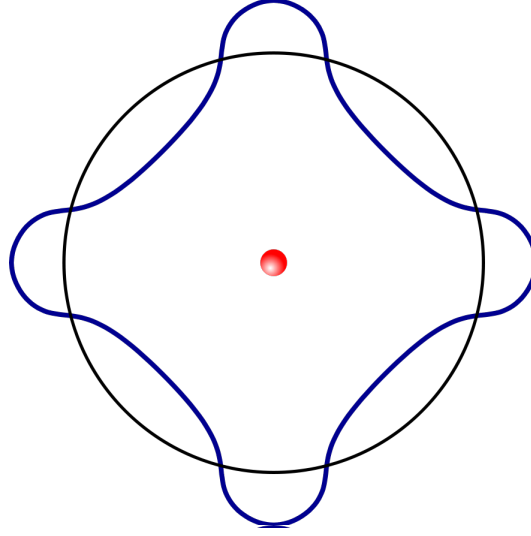


Figure 1.5: The Bohr model of the hydrogen atom, where a particle wave fits exactly onto a Kepler orbit.

Assume further that the electrons are bound to the metal by an energy  $E_B$ . Since they need to absorb light to gain enough energy to escape from the metal, and it is extremely unlikely that they absorb multiple photons, the individual photons must satisfy

$$h\nu > E_B. \quad (1.5)$$

Thus the minimal frequency is  $\nu_0 = E_B/h$ . This is based on the quantum nature of light.

### 1.3 Hydrogen atom

The classical picture of the hydrogen atom is planetary in nature: an electron moves in an Kepler orbit around the proton. The problem is that there is a force acting on the electron, and accelerated charges radiate (that is what a radio is based on). This allows the atom to lose energy in a continuous way, slowly spiraling down until the electron lies on the proton. Now experiment show that this is not the case: There are a discrete set of lines in the light emitted by hydrogen, and the electron will never lose all its energy. The first explanation for this fact came from Niels Bohr, in the so-called old quantum theory, where one assumes that motion is quantised, and only certain orbits can occur. In this model the energy of the Balmer series of Hydrogen is given by

$$E_n = -\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{2\pi^2 m e}{h^2} \frac{1}{n^2}. \quad (1.6)$$

Clearly this is of quantum origin again.

### 1.4 Wave particle duality

If waves (light) can be particles (photons), can particles (electrons, etc.) be waves? de Broglie gave a positive answer to this question, and argued that for a particle with energy  $E$  and momentum  $p$

$$E = h\nu \quad (1.7)$$

$$p = h/\lambda \quad (1.8)$$

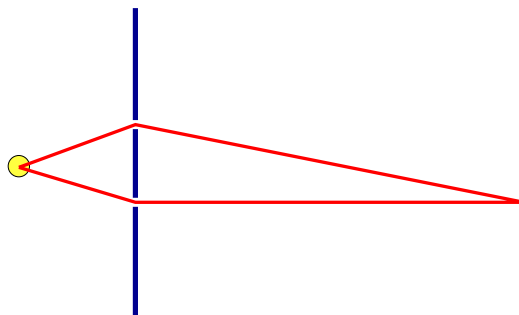


Figure 1.6: A double-slit experiment

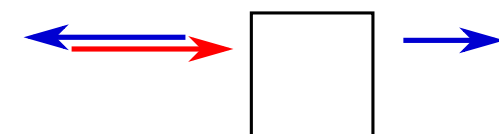


Figure 1.7: The tunneling phenomenon, where a particle can sometimes be found at the other side of a barrier.

where  $\nu$  and  $\lambda$  are the frequency and the wavelength, respectively. These are exactly the relations for a photon.

One way to show that this behaviour is the correct one is to do the standard double slit experiment. For light we know that we have constructive or destructive interference if the difference in the distance traveled between two waves reaching the same point is an integer (integer plus one half) times the wavelength of the light. With particles we would normally expect them to travel through one or the other of each of the slits. If we do the experiment with a lot of particles, we actually see the well known double-slit interference.

## 1.5 Uncertainty

A wave of sharp frequency has to last infinitely long, and is thus completely delocalised. What does this imply for matter waves? One of the implications is the uncertainty relation between position and momentum

$$\Delta x \Delta p \gtrsim \frac{1}{2} \hbar. \quad (1.9)$$

This implies that the combined accuracy of a simultaneous measurement of position and momentum has a minimum. This is not important in problems on standard scales, for the following practical reason. Suppose we measure the velocity of a particle of 1g to be  $1 \pm 10^{-6}$  m/s. In that case we can measure its position no more accurately than  $5 \cdot 10^{-26}$  m, a completely outrageous accuracy (remember, this is  $10^{-16}$  times the atomic scale!)

## 1.6 Tunneling

In classical mechanics a billiard ball bounces back when it hits the side of the billiard. In the quantum world it might actually "tunnel" through. Let me make this a little clearer. Classically a particle moving in the following potential would just be bouncing back and forth between the walls. This can be easily seen from conservation of energy: The kinetic energy can not go negative, and the total energy is conserved.

Where the potential is larger than the total energy, the particle cannot go. In quantum mechanics this is different, and particles can penetrate these classically forbidden regions, escaping from their cage.

This is a wave phenomenon, and is related to the behaviour of waves in impenetrable media: rather than oscillatory solutions, we have exponentially damped ones, that allow for some penetration. This also occurs in processes such as total reflection of light from a surface, where the tunneling wave is called “evanescent”.

## Chapter 2

# Concepts from classical mechanics

Before we discuss quantum mechanics we need to consider some concepts of classical mechanics, which are fundamental to our understanding of quantum mechanics.

### 2.1 Conservative fields

In all our discussions I will only consider forces which are conservative, i.e., where the total energy is a constant. This excludes problems with friction. For such systems we can split the total energy in a part related to the movement of the system, called the kinetic energy (Greek *κίνησις*=to move), and a second part called the *potential energy*, since it describes the potential of a system to produce kinetic energy.

An extremely important property of the potential energy is that we can derive the forces as a derivative of the potential energy, typically denoted by  $V(\mathbf{r})$ , as

$$\mathbf{F} = -\left(\frac{\partial}{\partial x} V(\mathbf{r}), \frac{\partial}{\partial y} V(\mathbf{r}), \frac{\partial}{\partial z} V(\mathbf{r})\right). \quad (2.1)$$

A typical example of a potential energy function is the one for a particle of mass  $m$  in the earth's gravitational field, which in the flat-earth limit is written as  $V(\mathbf{r}) = mgz$ . This leads to a gravitational force

$$\mathbf{F} = (0, 0, -mg) \quad (2.2)$$

Of course when total energy is conserved, that doesn't define the zero of energy. The kinetic energy is easily defined to be zero when the particle is not moving, but we can add any constant to the potential energy, and the forces will not change. One typically takes  $V(\mathbf{r}) = 0$  when the length of  $\mathbf{r}$  goes to  $\infty$ .

### 2.2 Energy function

Of course the kinetic energy is  $\frac{1}{2}mv^2$ , with  $\mathbf{v} = \dot{\mathbf{r}} = \frac{d}{dt}\mathbf{r}$ . The sum of kinetic and potential energy can be written in the form

$$E = \frac{1}{2}mv^2 + V(\mathbf{r}). \quad (2.3)$$

Actually, this form is not very convenient for quantum mechanics. We rather work with the so-called momentum variable  $\mathbf{p} = m\mathbf{v}$ . Then the energy functional takes the form

$$E = \frac{1}{2} \frac{\mathbf{p}^2}{m} + V(\mathbf{r}). \quad (2.4)$$

The energy expressed in terms of  $\mathbf{p}$  and  $\mathbf{r}$  is often called the (classical) Hamiltonian, and will be shown to have a clear quantum analog.

## 2.3 Simple example

We can define all these concepts (velocity, momentum, potential) in one dimension as well as in three dimensions. Let us look at the example for a barrier

$$V(x) = \begin{cases} 0 & |x| > a \\ V_0 & |x| < a \end{cases} \quad (2.5)$$

We can't find a solution for  $E$  less than 0 (no solution for  $v$ ). For energy less than  $V_0$  the particles can move left or right from the barrier, with constant velocity, but will make a hard bounce at the barrier (sign of  $v$  is not determined from energy). For energies higher than  $V_0$  particles can move from one side to the other, but will move slower if they are above the barrier.

## Chapter 3

# The Schrödinger equation

### 3.1 The state of a quantum system

Let us first look at how we specify the state for a classical system. Once again, we use the ubiquitous billiard ball. As any player knows, there are three important aspects to its motion: position, velocity and spin (angular momentum around its centre). Knowing these quantities we can in principle (no friction) predict its motion for all times. We have argued before that quantum mechanics involves an element of uncertainty. We cannot predict a state as in classical mechanics, we need to predict a probability. We want to be able to predict the outcome of a measurement of, say, position. Since position is a continuous variable, we cannot just deal with a discrete probability, we need a probability density. To understand this fact look at the probability that we measure  $x$  to be between  $X$  and  $X + \Delta X$ . If  $\Delta X$  is small enough, this probability is directly proportional to the length of the interval

$$P(X < x < X + \Delta X) = \mathcal{P}(X)\Delta X \quad (3.1)$$

Here  $\mathcal{P}(X)$  is called the probability density. The standard statement that the total probability is one translates to an integral statement,

$$\int_{-\infty}^{\infty} dx \mathcal{P}(x) = 1 \quad (3.2)$$

(Here I am lazy and use the lower case  $x$  where I have used  $X$  before; this is a standard practice in QM.) Since probabilities are always positive, we require  $\mathcal{P}(x) \geq 0$ .

Now let us try to look at some aspects of classical waves, and see whether they can help us to guess how to derive a probability density from a wave equation. The standard example of a classical wave is the motion of a string. Typically a string can move up and down, and the standard solution to the wave equation

$$\frac{\partial^2}{\partial x^2} A(x, t) = \frac{1}{c^2} \frac{\partial^2}{\partial t^2} A(x, t) \quad (3.3)$$

can be positive as well as negative. Actually the square of the wave function is a possible choice for the probability (this is proportional to the intensity for radiation). Now let us try to argue what wave equation describes the quantum analog of classical mechanics, i.e., quantum mechanics.

The starting point is a propagating wave. In standard wave problems this is given by a plane wave, i.e.,

$$\psi = A \Re \exp(i(kx - \omega t + \phi)). \quad (3.4)$$

This describes a wave propagating in the  $x$  direction with wavelength  $\lambda = 2\pi/k$ , and frequency  $\nu = \omega/(2\pi)$ . We interpret this plane wave as a propagating beam of particles. If we define the probability as the square of the wave function, it is not very sensible to take the real part of the exponential: the probability would be an oscillating function of  $x$  for given  $t$ . If we take the complex function  $A \exp(i(kx - \omega t + \phi))$ , however, the probability, defined as the absolute value squared, is a constant ( $|A|^2$ ) independent

of  $x$  and  $t$ , which is very sensible for a beam of particles. Thus we conclude that the wave function  $\psi(x, t)$  is complex, and the probability density is  $|\psi(x, t)|^2$ .

Using de Broglie's relation

$$p = \hbar/\lambda, \quad (3.5)$$

we find

$$p = \hbar k. \quad (3.6)$$

The other of de Broglie's relations can be used to give

$$E = h\nu = \hbar\omega. \quad (3.7)$$

One of the important goals of quantum mechanics is to generalise classical mechanics. We shall attempt to generalise the relation between momenta and energy,

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} \quad (3.8)$$

to the quantum realm. Notice that

$$\begin{aligned} p\psi(x, t) &= \hbar k\psi(x, t) = \frac{\hbar}{i} \frac{\partial}{\partial x} \psi(x, t) \\ E\psi(x, t) &= \hbar\omega\psi(x, t) = \frac{\hbar i \partial}{\partial t} \psi(x, t) \end{aligned} \quad (3.9)$$

Using this we can guess a wave equation of the form

$$\frac{1}{2m} \left( \frac{\hbar}{i} \frac{\partial}{\partial x} \right)^2 \psi(x, t) = \frac{\hbar i \partial}{\partial t} \psi(x, t). \quad (3.10)$$

Actually using the definition of energy when the problem includes a potential,

$$E = \frac{1}{2}mv^2 + V(x) = \frac{p^2}{2m} + V(x) \quad (3.11)$$

(when expressed in momenta, this quantity is usually called a "Hamiltonian") we find the time-dependent Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x, t) + V(x)\psi(x, t) = \frac{\hbar i \partial}{\partial t} \psi(x, t). \quad (3.12)$$

We shall only spend limited time on this equation. Initially we are interested in the time-independent Schrödinger equation, where the probability  $|\psi(x, t)|^2$  is independent of time. In order to reach this simplification, we find that  $\psi(x, t)$  must have the form

$$\psi(x, t) = \phi(x)e^{-iEt/\hbar}. \quad (3.13)$$

If we substitute this in the time-dependent equation, we get (using the product rule for differentiation)

$$-e^{-iEt/\hbar} \frac{\hbar^2}{2m} \frac{d^2}{dx^2} \phi(x) + e^{-iEt/\hbar} V(x)\phi(x) = Ee^{-iEt/\hbar} \phi(x). \quad (3.14)$$

Taking away the common factor  $e^{-iEt/\hbar}$  we have an equation for  $\phi$  that no longer contains time, the *time-independent Schrödinger equation*

$$\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \phi(x) + V(x)\phi(x) = E\phi(x). \quad (3.15)$$

The corresponding solution to the time-dependent equation is the standing wave (3.13).



## 3.2 Operators

Notice that in deriving the wave equation we replaced the number  $p$  or  $k$  by a differential acting on the wave function. The energy (or rather the Hamiltonian) was replaced by an “operator”, which when multiplied with the wave function gives a combination of derivatives of the wave function and function multiplying the wave function, symbolically written as

$$\hat{H}\psi(x, t) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x, t) + V(x)\psi(x, t). \quad (3.16)$$

This appearance of operators (often denoted by hats) where we were used to see numbers is one of the key features of quantum mechanics.

## 3.3 Analysis of the wave equation

One of the important aspects of the Schrödinger equation(s) is its linearity. For the time independent Schrödinger equation, which is usually called an eigenvalue problem, the only consequence we shall need here, is that if  $\phi(x)$  is a eigen function (a solution for  $E_i$ ) of the Schrödinger equation, so is  $A\phi_i(x)$ . This is useful in defining a probability, since we would like

$$\int_{-\infty}^{\infty} |A|^2 |\phi_i(x)|^2 dx = 1 \quad (3.17)$$

Given  $\phi_i(x)$  we can thus use this freedom to “normalise” the wave function! (If the integral over  $|\phi(x)|^2$  is finite, i.e., if  $\phi(x)$  is “normalisable”.)

### Example 3.1:

As an example suppose that we have a Hamiltonian that has the function  $\psi_i(x) = e^{-x^2/2}$  as eigen function. This function is not normalised since

$$\int_{-\infty}^{\infty} |\phi_i(x)|^2 dx = \sqrt{\pi}. \quad (3.18)$$

The normalised form of this function is

$$\frac{1}{(\pi)^{1/4}} e^{-x^2/2}. \quad (3.19)$$

We need to know a bit more about the structure of the solution of the Schrödinger equation – boundary conditions and such. Here I shall postulate the boundary conditions, without any derivation.

1.  $\phi(x)$  is a continuous function, and is single valued.
2.  $\int_{-\infty}^{\infty} |\phi(x)|^2 dx$  must be finite, so that

$$P(x) = \frac{|\phi(x)|^2}{\int_{-\infty}^{\infty} |\psi(x)|^2 dx} \quad (3.20)$$

is a probability density.

3.  $\partial\phi(x)/\partial x$  is continuous except where  $V(x)$  has an infinite discontinuity.



## Chapter 4

# Bound states of the square well

One of the simplest potentials to study the properties of is the so-called square well potential,

$$V = \begin{cases} 0 & |x| > a \\ -V_0 & |x| < a \end{cases} . \quad (4.1)$$

We define three areas, from left to right I, II and III. In areas I and III we have the Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E\psi(x) \quad (4.2)$$

whereas in area II we have the equation

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = (E + V_0)\psi(x) \quad (4.3)$$

---

### Solution to a few ODE's

. In this class we shall quite often encounter the ordinary differential equations

$$\frac{d^2}{dx^2} f(x) = -\alpha^2 f(x) \quad (4.4)$$

which has as solution

$$f(x) = A_1 \cos(\alpha x) + B_1 \sin(\alpha x) = C_1 e^{i\alpha x} + D_1 e^{-i\alpha x}, \quad (4.5)$$

and

$$\frac{d^2}{dx^2} g(x) = +\alpha^2 g(x) \quad (4.6)$$

which has as solution

$$g(x) = A_2 \cosh(\alpha x) + B_2 \sinh(\alpha x) = C_2 e^{\alpha x} + D_2 e^{-\alpha x}. \quad (4.7)$$

---

Let us first look at  $E > 0$ . In that case the equation in regions I and III can be written as

$$\frac{d^2}{dx^2} \psi(x) = -\frac{2m}{\hbar^2} E \psi(x) = -k^2 \psi(x), \quad (4.8)$$

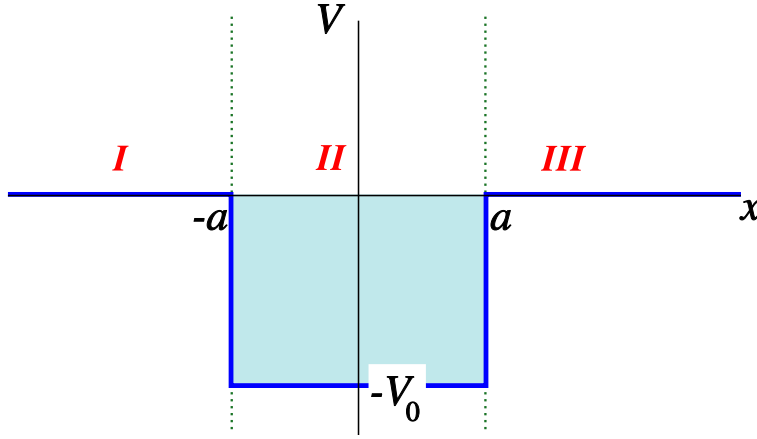


Figure 4.1: The square well potential

where

$$k = \sqrt{\frac{2m}{\hbar^2} E}. \quad (4.9)$$

The solution to this equation is a sum of sines and cosines of  $kx$ , which cannot be normalised: Write  $\psi_{III}(x) = A \cos(kx) + B \sin(kx)$  ( $A, B$ , complex) and calculate the part of the norm originating in region III,

$$\begin{aligned} \int_a^\infty |\psi(x)|^2 dx &= \int_a^\infty |A|^2 \cos^2 kx + |B|^2 \sin^2 kx + 2\Re(AB^*) \sin(kx) \cos(kx) dx \\ &= \lim_{N \rightarrow \infty} N \int_a^{2\pi/k} |A|^2 \cos^2(kx) + |B|^2 \sin^2(kx) \\ &= \lim_{N \rightarrow \infty} N(|A|^2/2 + |B|^2/2) = \infty. \end{aligned} \quad (4.10)$$

We also find that the energy cannot be less than  $-V_0$ , since we cannot construct a solution for that value of the energy. We thus restrict ourselves to  $-V_0 < E < 0$ . We write

$$E = -\frac{\hbar^2 k^2}{2m}, \quad E + V_0 = \frac{\hbar^2 \kappa^2}{2m}. \quad (4.11)$$

The solutions in the areas I and III are of the form ( $i = 1, 3$ )

$$\psi(x) = A_i e^{kx} + B_i e^{-kx}. \quad (4.12)$$

In region II we have the oscillatory solution

$$\psi(x) = A_2 \cos(\kappa x) + B_2 \sin(\kappa x). \quad (4.13)$$

Now we have to impose the conditions on the wave functions we have discussed before, continuity of  $\psi$  and its derivatives. Actually we also have to impose normalisability, which means that  $B_1 = A_3 = 0$  (exponentially growing functions can not be normalised). As we shall see we only have solutions at certain energies. Continuity implies that

$$\begin{aligned} A_1 e^{-ka} + B_1 e^{ka} &= A_2 \cos(\kappa a) - B_2 \sin(\kappa a) \\ A_3 e^{ka} + B_3 e^{-ka} &= A_2 \cos(\kappa a) + B_2 \sin(\kappa a) \\ kA_1 e^{ka} - kB_1 e^{-ka} &= \kappa A_2 \sin(\kappa a) + \kappa B_2 \cos(\kappa a) \\ kA_3 e^{-ka} - kB_3 e^{ka} &= -\kappa A_2 \sin(\kappa a) + \kappa B_2 \cos(\kappa a) \end{aligned} \quad (4.14)$$

**Tactical approach:** We wish to find a relation between  $k$  and  $\kappa$  (why?), removing as many of the constants  $A$  and  $B$ . The trick is to first find an equation that only contains  $A_2$  and  $B_2$ . To this end we take the ratio of the first and third and second and fourth equation:

$$\begin{aligned} k &= \frac{\kappa[A_2 \sin(\kappa a) + B_2 \cos(\kappa a)]}{A_2 \cos(\kappa a) - B_2 \sin(\kappa a)} \\ k &= \frac{\kappa[A_2 \sin(\kappa a) - B_2 \cos(\kappa a)]}{A_2 \cos(\kappa a) + B_2 \sin(\kappa a)} \end{aligned} \quad (4.15)$$

We can combine these two equations to a single one by equating the right-hand sides. After deleting the common factor  $\kappa$ , and multiplying with the denominators we find

$$\begin{aligned} [A_2 \cos(\kappa a) + B_2 \sin(\kappa a)][A_2 \sin(\kappa a) - B_2 \cos(\kappa a)] \\ = [A_2 \sin(\kappa a) + B_2 \cos(\kappa a)][A_2 \cos(\kappa a) - B_2 \sin(\kappa a)], \end{aligned} \quad (4.16)$$

which simplifies to

$$A_2 B_2 = 0 \quad (4.17)$$

We thus have two families of solutions, those characterised by  $B_2 = 0$  and those that have  $A_2 = 0$ .

## 4.1 $B_2 = 0$

In the first case we read off that  $A_1 = B_3$ , and we find that  $k$  and  $\kappa$  are related by

$$ka = \kappa a \tan \kappa a. \quad (4.18)$$

This equation can be solved graphically. Use  $k = \sqrt{-\kappa^2 + \kappa_0^2}$ , with  $\kappa_0^2 = \frac{2m}{\hbar^2} V_0$ , and find that there is always at least one solution of this kind, no matter how small  $V_0$ ! In the middle region all these solutions behave like sines, and you will be asked to show that the solutions are invariant when  $x$  goes to  $-x$ . (We say that these functions are even.)

## 4.2 $A_2 = 0$

In this case  $A_1 = -B_3$ , and the relation between  $k$  and  $\kappa$  is modified to

$$ka = -\kappa a \cot \kappa a. \quad (4.19)$$

From the graphical solution, in Fig. 4.3 we see that this type of solution only occurs for  $\kappa_0 a$  greater than  $\pi/2$ . In the middle region all these solutions behave like sines, and you will be asked to show that the solutions turn into minus themselves when  $x$  goes to  $-x$ . (We say that these functions are odd.)

## 4.3 Some consequences

There are a few good reasons why the dependence in the solution is on  $ka$ ,  $\kappa a$  and  $\kappa_0 a$ : These are all dimensionless numbers, and mathematical relations can *never* depend on parameters that have a dimension! For the case of the even solutions, the ones with  $B_2 = 0$ , we find that the number of bound states is determined by how many times we can fit  $2\pi$  into  $\kappa_0 a$ . Since  $\kappa_0$  is proportional to (the square root of)  $V_0$ , we find that increasing  $V_0$  increases the number bound states, and the same happens when we increase the width  $a$ . Rewriting  $\kappa_0 a$  slightly we find that the governing parameter is  $\sqrt{\frac{2m}{\hbar^2} V_0 a^2}$ , so that a factor of two change in  $a$  is the same as a factor four change in  $V_0$ .

If we put the two sets of solutions on top of one another we see that after every even solution we get an odd solution, and vice versa.

There is always at least one solution (the lowest even one), but the first odd solution only occurs when  $\kappa_0 a = \pi$

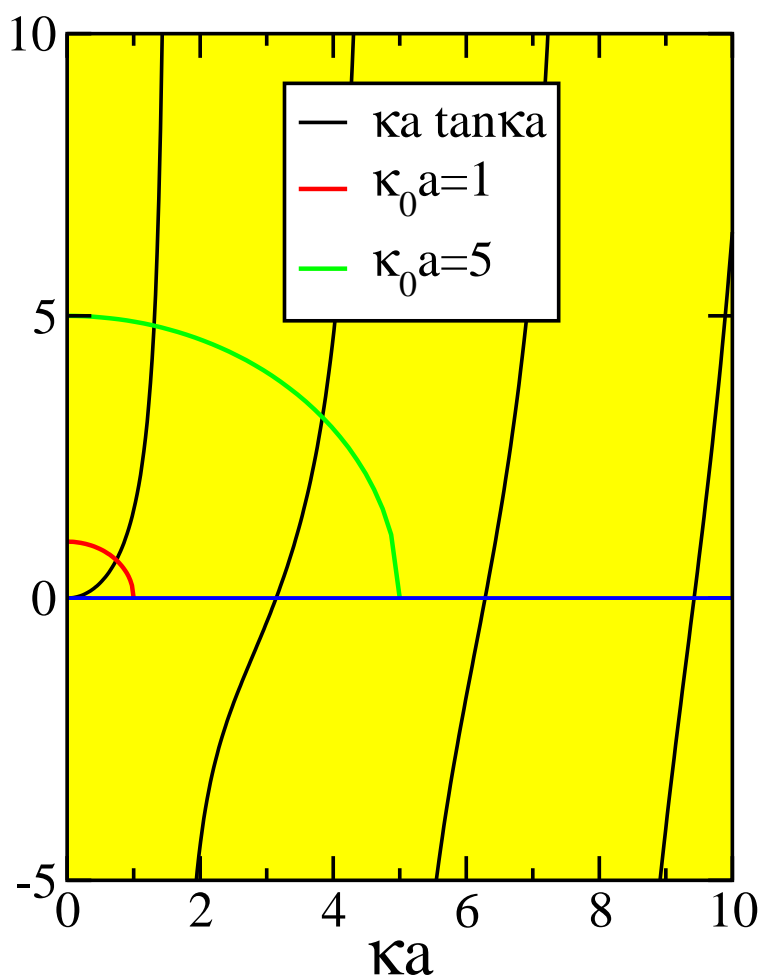


Figure 4.2: The graphical solution for the even states of the square well.

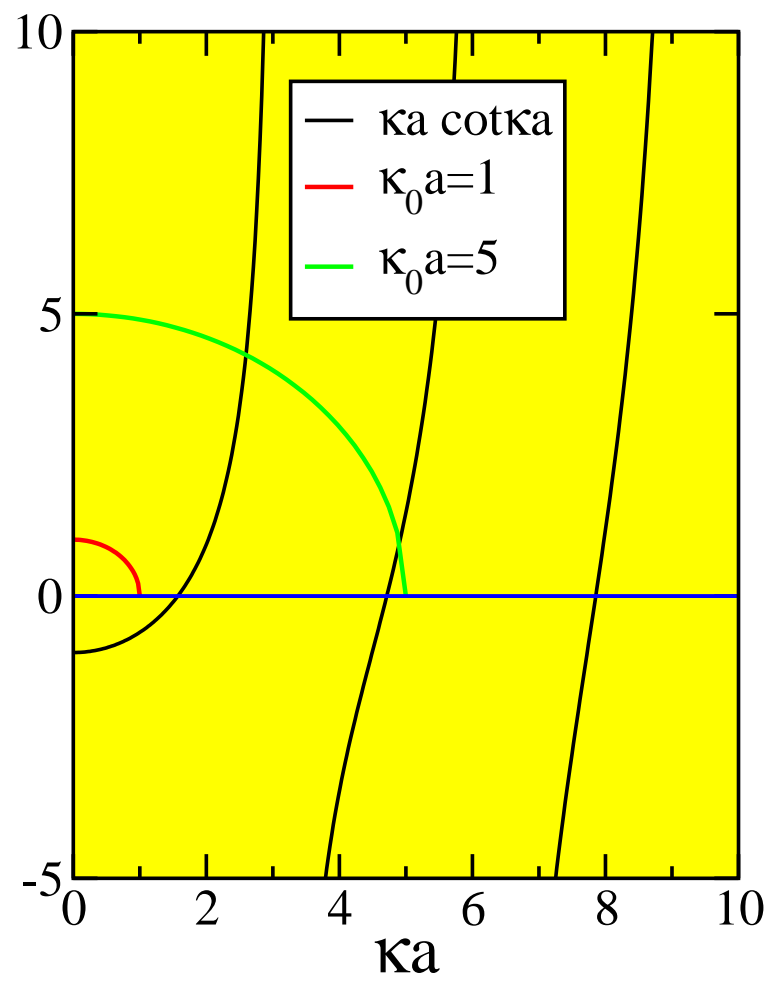


Figure 4.3: The graphical solution for the odd states of the square well.

## 4.4 Lessons from the square well

The computer demonstration showed the following features:

1. If we drop the requirement of normalisability, we have a solution to the TISE at every energy. Only at a few discrete values of the energy do we have normalisable states.
2. The energy of the lowest state is always higher than the depth of the well (uncertainty principle).
3. Effect of depth and width of well. Making the well deeper gives more eigen functions, and decreases the extent of the tail in the classically forbidden region.
4. Wave functions are oscillatory in classically allowed, exponentially decaying in classically forbidden region.
5. The lowest state has no zeroes, the second one has one, etc. Normally we say that the  $n$ th state has  $n - 1$  “nodes”.
6. Eigen states (normalisable solutions) for different eigen values (energies) are orthogonal.

## 4.5 A physical system (approximately) described by a square well

After all this tedious algebra, let us look at a possible physical realisation of such a system. In order to do that, I shall have to talk a little bit about semi-conductors. A semiconductor is a quantum system where the so-called valence electrons completely fill a valence band, and are separated by a gap from a set of free states in a conduction band. These can both be thought of a continuous set of quantum states. The energy difference between the valence and conduction bands is different for different semi-conductors. This can be used in so-called quantum-well structures, where we sandwich a thin layer of, e.g., GaAs between very thick layers of GaAlAs.

Since the gap energy is a lot smaller for GaAs than for GaAlAs, we get the effect of a small square well (in both valence and conduction bands). The fact that we can have a few occupied additional levels in the valence, and a few empty levels in the conduction band can be measured.

The best way to do this, is to shine light on these systems, and see for which frequency we can create a transition (just like in atoms). Phil Dawson has been so kind to provide me with a few slides of such experiments.



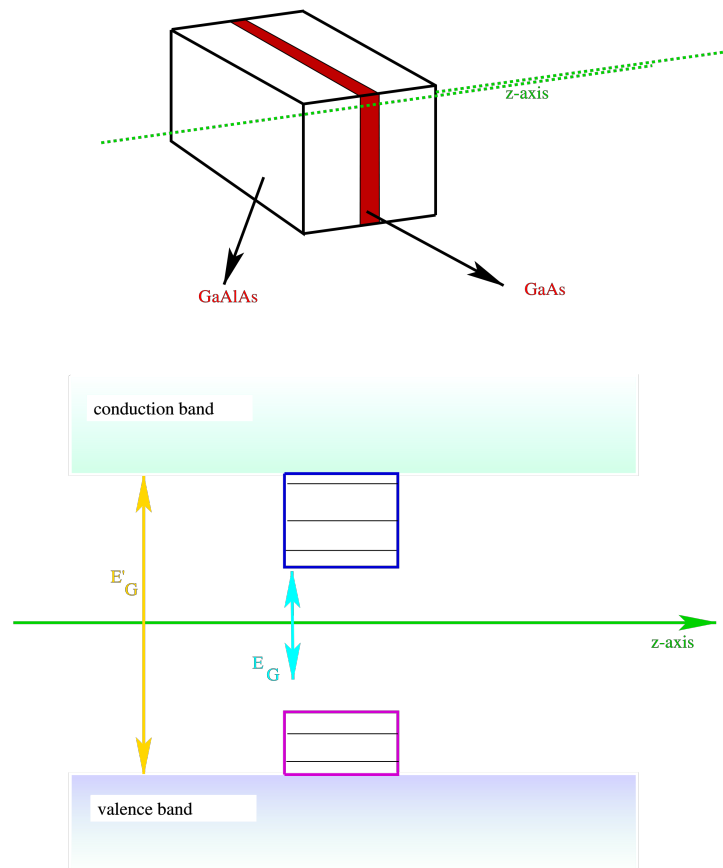


Figure 4.4: A schematic representation of a quantum well



## Chapter 5

# Infinite well

### 5.1 Zero of energy is arbitrary

The normal definition of a potential energy is somewhat arbitrary. Consider where a potential comes from: It appears when the total energy (potential plus kinetic) is constant. But if something is constant, we can add a number to it, and it is still constant! Thus whether we define the gravitational potential at the surface of the earth to be 0 or 100 J does not matter. Only differences in potential energies play a rôle. It is customary to define the potential “far away”, as  $|x| \rightarrow \infty$  to be zero. That is a very workable definition, except in one case: if we take a square well and make it deeper and deeper, the energy of the lowest state decreases with the bottom of the well. As the well depth goes to infinity, the energy of the lowest bound state reaches  $-\infty$ , and so does the second, third etc. state. It makes much more physical sense to define the bottom of the well to have zero energy, and the potential outside to have value  $V_0$ , which goes to infinity.

### 5.2 Solution

As stated before the continuity arguments for the derivative of the wave function do not apply for an infinite jump in the potential energy. This is easy to understand as we look at the behaviour of a low energy solution in one of the two outside regions (I or III). In this case the wave function can be approximated as

$$e^{\pm kr}, \quad k = \sqrt{\frac{2m}{\hbar^2} V_0}, \quad (5.1)$$

which decreases to zero faster and faster as  $V_0$  becomes larger and larger. In the end the wave function can no longer penetrate the region of infinite potential energy. Continuity of the wave function now implies that  $\phi(a) = \phi(-a) = 0$ .

Defining

$$\kappa = \sqrt{\frac{2m}{\hbar^2} E}, \quad (5.2)$$

we find that there are two types of solutions that satisfy the boundary condition:

$$\phi_{2n+1}(x) = \cos(\kappa_{2n+1}x), \quad \phi_{2n}(x) = \sin(\kappa_{2n}x). \quad (5.3)$$

Here

$$\kappa_l = \frac{\pi l}{2a}. \quad (5.4)$$

We thus have a series of eigen states  $\phi_l(x)$ ,  $l = 1, \dots, \infty$ . The energies are

$$E_l = \frac{\hbar^2 \pi^2 l^2}{8a^2}. \quad (5.5)$$

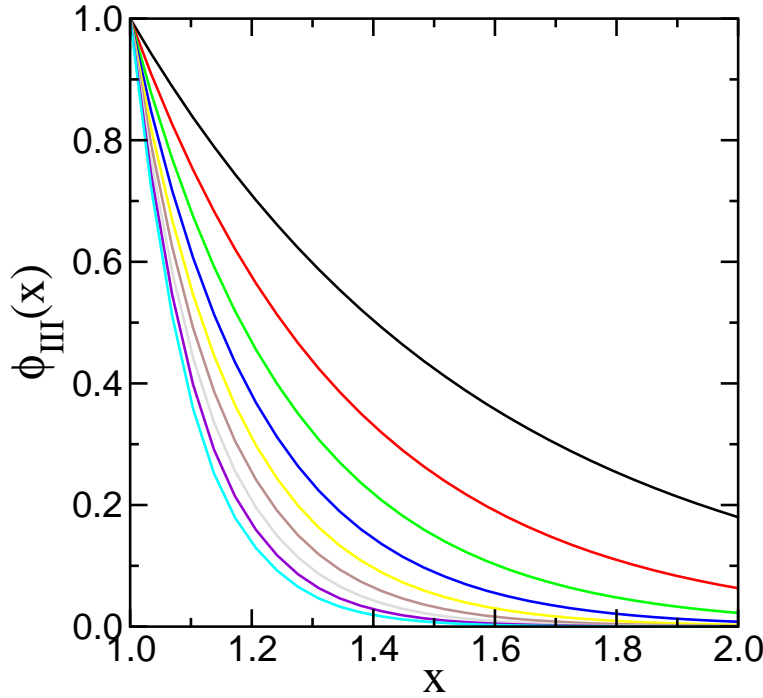


Figure 5.1: The change in the wave function in region III, for the lowest state, as we increase the depth of the potential well. We have used  $a = 10^{-10}$  m, and  $k_0 a = 2, 3, 4, 5, 6, 7, 8, 9$  and  $10$ .

These wave functions are very good to illustrate the idea of normalisation. Let me look at the normalisation of the ground state (the lowest state), which is

$$\phi_0(x) = A_1 \cos\left(\frac{\pi x}{2a}\right) \quad (5.6)$$

for  $-a < x < a$ , and 0 elsewhere.

We need to require

$$\int_{-\infty}^{\infty} |\phi_0(x)|^2 dx = 1, \quad (5.7)$$

where we need to consider the absolute value since  $A_1$  can be complex. We only have to integrate from  $-a$  to  $a$ , since the rest of the integral is zero, and we have

$$\begin{aligned} & \int_{-\infty}^{\infty} |\phi_0(x)|^2 dx \\ &= |A|^2 \int_{-a}^a \cos^2\left(\frac{\pi x}{2a}\right) dx \\ &= |A|^2 \frac{2a}{\pi} \int_{-\pi/2}^{\pi/2} \cos^2(y) dy \\ &= |A|^2 \frac{2a}{\pi} \int_{-\pi/2}^{\pi/2} \frac{1}{2}(1 + \cos(2y)) dy \\ &= |A|^2 \frac{2a}{\pi} \pi. \end{aligned} \quad (5.8)$$

Here we have changed variables from  $x$  to  $y = \frac{\pi x}{2a}$ . We thus conclude that the choice

$$A = \sqrt{\frac{1}{2a}} \quad (5.9)$$

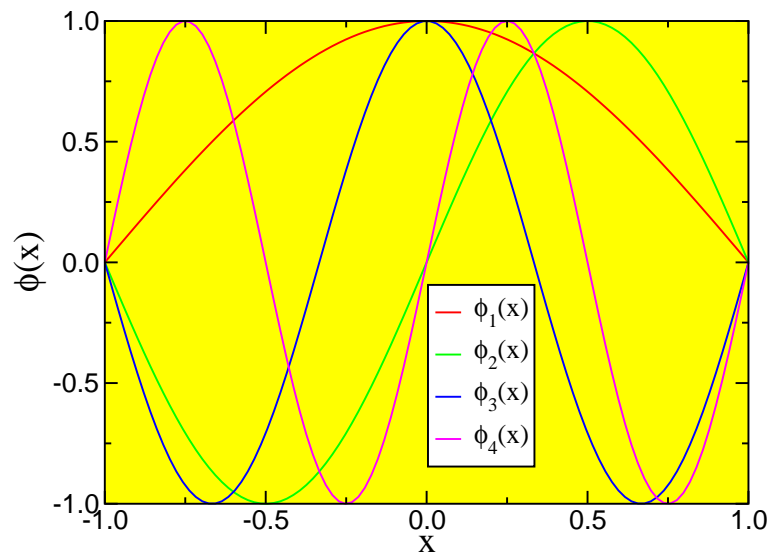


Figure 5.2: A few wave functions of the infinite square well.

leads to a normalised wave function.



## Chapter 6

# Scattering from potential steps and square barriers, etc.

### 6.1 Non-normalisable wave functions

I have argued that solutions to the time-independent Schrödinger equation must be normalised, in order to have a the total probability for finding a particle of one. This makes sense if we think about describing a single Hydrogen atom, where only a single electron can be found. But if we use an accelerator to send a beam of electrons at a metal surface, this is no longer a requirement: What we wish to describe is the flux of electrons, the number of electrons coming through a given volume element in a given time.

Let me first consider solutions to the “free” Schrödinger equation, i.e., without potential, as discussed before. They take the form

$$\phi(x) = Ae^{ikx} + Be^{-ikx}. \quad (6.1)$$

Let us investigate the two functions. Remembering that  $p = \frac{\hbar}{i} \frac{\partial}{\partial x}$  we find that this represents the sum of two states, one with momentum  $\hbar k$ , and the other with momentum  $-\hbar k$ . The first one describes a beam of particles going to the right, and the other term a beam of particles traveling to the left.

Let me concentrate on the first term, that describes a beam of particles going to the right. We need to define a probability current density. Since current is the number of particles times their velocity, a sensible definition is the probability density times the velocity,

$$|\phi(x)|^2 \frac{\hbar k}{m} = |A|^2 \frac{\hbar k}{m}. \quad (6.2)$$

This concept only makes sense for states that are not bound, and thus behave totally different from those I discussed previously.

### 6.2 Potential step

Consider a potential step

$$V(x) = \begin{cases} V_0 & x < 0 \\ V_1 & x > 0 \end{cases} \quad (6.3)$$

Let me define

$$k_0 = \sqrt{\frac{2m}{\hbar^2}(E - V_0)}, \quad (6.4)$$

$$k_1 = \sqrt{\frac{2m}{\hbar^2}(E - V_1)}. \quad (6.5)$$

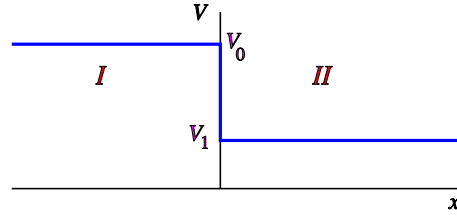


Figure 6.1: The step potential discussed in the text

I assume a beam of particles comes in from the left,

$$\phi(x) = A_0 e^{ik_0 x}, \quad x < 0. \quad (6.6)$$

At the potential step the particles either get reflected back to region I, or are transmitted to region II. There can thus only be a wave moving to the right in region II, but in region I we have both the incoming and a reflected wave,

$$\phi_I(x) = A_0 e^{ik_0 x} + B_0 e^{-ik_0 x}, \quad (6.7)$$

$$\phi_{II}(x) = A_1 e^{ik_1 x}. \quad (6.8)$$

We define a transmission and reflection coefficient as the ratio of currents between reflected or transmitted wave and the incoming wave, where we have canceled a common factor

$$R = \frac{|B_0|^2}{|A_0|^2} \quad T = \frac{k_1 |A_1|^2}{k_0 |A_0|^2}. \quad (6.9)$$

Even though we have given up normalisability, we still have the two continuity conditions. At  $x = 0$  these imply, using continuity of  $\phi$  and  $\frac{d}{dx}\phi$ ,

$$A_0 + B_0 = A_1, \quad (6.10)$$

$$ik_0(A_0 - B_0) = ik_1 A_1. \quad (6.11)$$

We thus find

$$A_1 = \frac{2k_0}{k_0 + k_1} A_0, \quad (6.12)$$

$$B_0 = \frac{k_0 - k_1}{k_0 + k_1} A_0, \quad (6.13)$$

and the reflection and transmission coefficients can thus be expressed as

$$R = \left( \frac{k_0 - k_1}{k_0 + k_1} \right)^2, \quad (6.14)$$

$$T = \frac{4k_1 k_0}{(k_0 + k_1)^2}. \quad (6.15)$$

Notice that  $R + T = 1$ !

In Fig. 6.2 we have plotted the behaviour of the transmission and reflection of a beam of Hydrogen atoms impinging on a barrier of height 2 meV.



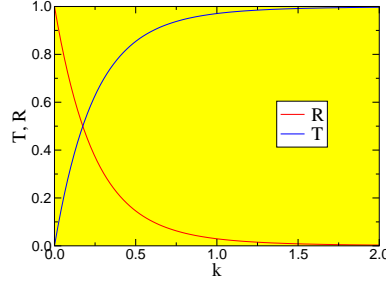


Figure 6.2: The transmission and reflection coefficients for a square barrier.

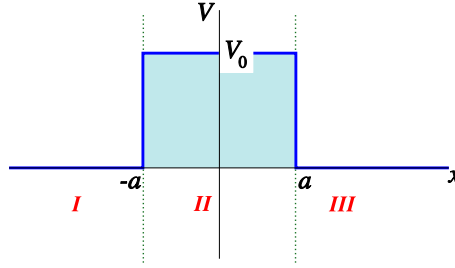


Figure 6.3: The square barrier.

### 6.3 Square barrier

A slightly more involved example is the square potential barrier, an inverted square well, see Fig. 6.3.

We are interested in the case that the energy is below the barrier height,  $0 < E < V_0$ . If we once again assume an incoming beam of particles from the right, it is clear that the solutions in the three regions are

$$\begin{aligned}\phi_I(x) &= A_1 e^{ikx} + B_1 e^{-ikx}, \\ \phi_{II}(x) &= A_2 \cosh(\kappa x) + B_2 \sinh(\kappa x), \\ \phi_{III}(x) &= A_3 e^{ikx}.\end{aligned}\tag{6.16}$$

Here

$$k = \sqrt{\frac{2m}{\hbar^2} E}, \quad \kappa = \sqrt{\frac{2m}{\hbar^2} (V_0 - E)}.\tag{6.17}$$

Matching at  $x = -a$  and  $x = a$  gives (use  $\sinh(-x) = -\sinh x$  and  $\cosh(-x) = \cosh x$ )

$$A_1 e^{-ika} + B_1 e^{ika} = A_2 \cosh \kappa a - B_2 \sinh \kappa a\tag{6.18}$$

$$ik(A_1 e^{-ika} - B_1 e^{ika}) = \kappa(-A_2 \sinh \kappa a + B_2 \cosh \kappa a)\tag{6.19}$$

$$A_3 e^{ika} = A_2 \cosh \kappa a + B_2 \sinh \kappa a\tag{6.20}$$

$$ik(A_3 e^{ika}) = \kappa(A_2 \sinh \kappa a + B_2 \cosh \kappa a)\tag{6.21}$$

These are four equations with five unknowns. We can thus express four of the unknown quantities in one other. Let us choose that one to be  $A_1$ , since that describes the intensity of the incoming beam. We are not interested in  $A_2$  and  $B_2$ , which describe the wave function in the middle. We can combine the equation above so that they either have  $A_2$  or  $B_2$  on the right hand side, which allows us to eliminate these two variables, leading to two equations with the three interesting unknowns  $A_3$ ,  $B_1$  and  $A_1$ . These can then be solved for  $A_3$  and  $B_1$  in terms of  $A_1$ :

The way we proceed is to add eqs. (6.18) and (6.20), subtract eqs. (6.19) from (6.21), subtract (6.20) from (6.18), and add (6.19) and (6.21). We find

$$A_1 e^{-ika} + B_1 e^{ika} + A_3 e^{ika} = 2A_2 \cosh \kappa a \quad (6.22)$$

$$ik(-A_1 e^{-ika} + B_1 e^{ika} + A_3 e^{ika}) = 2\kappa A_2 \sinh \kappa a \quad (6.23)$$

$$A_1 e^{-ika} + B_1 e^{ika} - A_3 e^{ika} = -2B_2 \sinh \kappa a \quad (6.24)$$

$$ik(A_1 e^{-ika} - B_1 e^{ika} + A_3 e^{ika}) = 2\kappa B_2 \cosh \kappa a \quad (6.25)$$

We now take the ratio of equations (6.22) and (6.23) and of (6.24) and (6.25), and find (i.e., we take ratios of left- and right hand sides, and equate those)

$$\frac{A_1 e^{-ika} + B_1 e^{ika} + A_3 e^{ika}}{ik(-A_1 e^{-ika} + B_1 e^{ika} + A_3 e^{ika})} = \frac{1}{\kappa \tanh \kappa a} \quad (6.26)$$

$$\frac{A_1 e^{-ika} + B_1 e^{ika} - A_3 e^{ika}}{ik(-A_1 e^{-ika} + B_1 e^{ika} + A_3 e^{ika})} = -\frac{\tanh \kappa a}{\kappa} \quad (6.27)$$

These equations can be rewritten as (multiplying out the denominators, and collecting terms with  $A_1$ ,  $B_3$  and  $A_3$ )

$$A_1 e^{-ika}(\kappa \tanh \kappa a + ik) + B_1 e^{ika}(\kappa \tanh \kappa a - ik) + A_3 e^{ika}(\kappa \tanh \kappa a - ik) = 0 \quad (6.28)$$

$$A_1 e^{-ika}(\kappa - ik \tanh \kappa a) + B_1 e^{ika}(\kappa + ik \tanh \kappa a) + A_3 e^{ika}(-\kappa + ik \tanh \kappa a) = 0 \quad (6.29)$$

Now eliminate  $A_3$ , add (6.28)( $\kappa - ik \tanh \kappa a$ ) and (6.29)( $\kappa \tanh \kappa a - ik$ ), and find

$$\begin{aligned} & A_1 e^{-ika} [(\kappa - ik \tanh \kappa a)(\kappa \tanh \kappa a + ik) + (\kappa \tanh \kappa a - ik)(\kappa - ik \tanh \kappa a)] \\ & + B_1 e^{ika} [(\kappa - ik \tanh \kappa a)(\kappa \tanh \kappa a - ik) + (\kappa \tanh \kappa a - ik)(\kappa + ik \tanh \kappa a)] = 0 \end{aligned} \quad (6.30)$$

Thus we find

$$B_1 = -A_1 e^{-2ika} \frac{\tanh \kappa a (\kappa^2 + \kappa^2)}{(\kappa - ik \tanh \kappa a)(\kappa \tanh \kappa a - ik)} \quad (6.31)$$

and we find, after using some of the angle-doubling formulas for hyperbolic functions, that the absolute value squared, i.e., the reflection coefficient, is

$$R = \frac{\sinh^2 2\kappa a (\kappa^2 + k^2)^2}{4\kappa^2 k^2 + (\kappa^2 - k^2)^2 \sinh^2 2\kappa a} \quad (6.32)$$

In a similar way we can express  $A_3$  in terms of  $A_1$  (add (6.28) ( $\kappa + ik \tanh \kappa a$ ) and (6.29) ( $-\kappa \tanh \kappa a + ik$ )), or use  $T = 1 - R$ !

---

#### Alternative approach

The equation can be given in matrix form as

$$\begin{pmatrix} e^{-ika} & e^{ika} \\ ike^{-ika} & -ike^{ika} \end{pmatrix} \begin{pmatrix} A_1 \\ B_1 \end{pmatrix} = \begin{pmatrix} \cosh \kappa a & -\sinh \kappa a \\ -\kappa \sinh \kappa a & \kappa \cosh \kappa a \end{pmatrix} \begin{pmatrix} A_2 \\ B_2 \end{pmatrix} \quad (6.33)$$

$$\begin{pmatrix} e^{ika} & e^{-ika} \\ ike^{ika} & -ike^{-ika} \end{pmatrix} \begin{pmatrix} A_3 \\ 0 \end{pmatrix} = \begin{pmatrix} \cosh \kappa a & \sinh \kappa a \\ \kappa \sinh \kappa a & \kappa \cosh \kappa a \end{pmatrix} \begin{pmatrix} A_2 \\ B_2 \end{pmatrix}. \quad (6.34)$$

**Question:** Can you invert the matrices and find the same answer as before?

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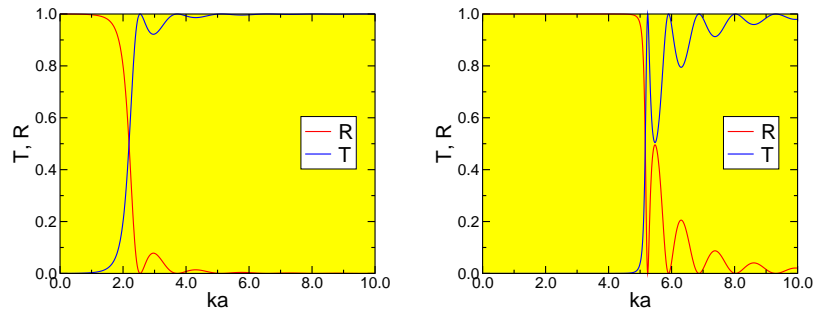


Figure 6.4: The reflection and transmission coefficients for a square barrier of height 4 meV (left) and 50 meV (right) and width  $10^{-10}$  m.

We now consider a particle of the mass of a hydrogen atom,  $m = 1.67 \times 10^{-27}$  kg, and use a barrier of height 4 meV and of width  $10^{-10}$  m. The picture for reflection and transmission coefficients can be seen in Fig. 6.4a. We have also evaluated  $R$  and  $T$  for energies larger than the height of the barrier (the evaluation is straightforward).

If we heighten the barrier to 50 meV, we find a slightly different picture, see Fig. 6.4b.

Notice the oscillations (resonances) in the reflection. These are related to an integer number of oscillations fitting exactly in the width of the barrier,  $\sin 2\kappa a = 0$ .



## Chapter 7

# The Harmonic oscillator

You may be familiar with several examples of harmonic oscillators from classical mechanics, such as particles on a spring or the pendulum for small deviation from equilibrium, etc.

Let me look at the characteristics of one such example, a particle of mass  $m$  on a spring. When the particle moves a distance  $x$  away from the equilibrium position  $x_0$ , there will be a restoring force  $-kx$  pushing the particle back ( $x > 0$  right of equilibrium, and  $x < 0$  on the left). This can be derived from a potential

$$V(x) = \frac{1}{2}kx^2. \quad (7.1)$$

Actually we shall write  $k = m\omega^2$ . The equation of motion

$$m\ddot{x} = -m\omega^2x \quad (7.2)$$

has the solution

$$x(t) = A \cos(\omega t) + B \sin(\omega t). \quad (7.3)$$

We now consider how this system behaves quantum-mechanically.

### 7.1 Dimensionless coordinates

The classical energy (Hamiltonian) is

$$E = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}m\omega^2x^2 = \frac{1}{2m}p^2 + \frac{1}{2}m\omega^2x^2 \quad (7.4)$$

The quantum Hamiltonian operator is thus

$$\hat{H} = \frac{1}{2m}\hat{p}^2 + \frac{1}{2}m\omega^2x^2 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2x^2. \quad (7.5)$$

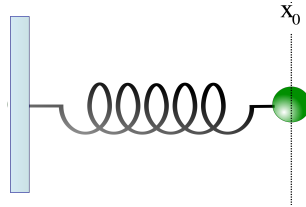


Figure 7.1: The mass on the spring and its equilibrium position

And we thus have to solve Schrödinger's equation

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \phi(x) + \frac{1}{2} m \omega^2 x^2 \phi(x) = E \phi(x). \quad (7.6)$$

In order to treat this equation it is better to remove all the physical constants, and go over to dimensionless coordinates

$$y = \sqrt{\frac{m\omega}{\hbar}} x, \quad \epsilon = \frac{E}{\hbar\omega}. \quad (7.7)$$

**Quiz** What is the dimension of  $\frac{m\omega}{\hbar}$ ? and of  $\hbar\omega$ ? (The dimension of  $\hbar$  is  $[\hbar] = \text{mass} \times \text{length}^2 / \text{time}$ .)  
When we substitute these new variables into the Schrödinger equation we get, using

$$\frac{d}{dx} f(y) = \frac{dy}{dx} \frac{d}{dy} f(y) = \sqrt{\frac{m\omega}{\hbar}} \frac{d}{dy} f(y), \quad (7.8)$$

that  $(\phi(x) = u(y))$

$$-\frac{\hbar^2}{2m} \frac{m\omega}{\hbar} \frac{d^2}{dy^2} u(y) + \frac{1}{2} m \omega^2 \frac{\hbar}{m\omega} y^2 u(y) = \epsilon \hbar \omega u(y). \quad (7.9)$$

Cancelling the common factor  $\hbar\omega$  we find

$$\frac{d^2}{dy^2} u(y) + (2\epsilon - y^2) u(y) = 0 \quad (7.10)$$

## 7.2 Behaviour for large $|y|$

Before solving the equation we are going to see how the solutions behave at large  $|y|$  (and also large  $|x|$ , since these variable are proportional!). For  $|y|$  very large, whatever the value of  $\epsilon$ ,  $\epsilon \ll y^2$ , and thus we have to solve

$$\frac{d^2 u}{dy^2} = y^2 u(y). \quad (7.11)$$

This has two type of solutions, one proportional to  $e^{y^2/2}$  and one to  $e^{-y^2/2}$ . We reject the first one as being not normalisable.

**Question:** Check that these are the solutions. Why doesn't it matter that they don't exactly solve the equations?

Substitute  $u(y) = H(y)e^{-y^2/2}$ . We find

$$\frac{d^2 u}{dy^2} = \left( H''(y) - 2yH'(y) + y^2 H(y) \right) e^{-y^2/2} \quad (7.12)$$

so we can obtain a differential equation for  $H(y)$  in the form

$$H''(y) - 2yH'(y) + (2\epsilon - 1)H(y) = 0. \quad (7.13)$$

This equation will be solved by a substitution and infinite series (Taylor series!), and showing that it will have to terminates somewhere, i.e.,  $H(y)$  is a polynomial!

## 7.3 Taylor series solution

Let us substitute a Taylor series for  $H(y)$ ,

$$H(y) = \sum_{p=0}^{\infty} a_p y^p. \quad (7.14)$$

This leads to

$$\begin{aligned} H'(y) &= \sum_{p=0}^{\infty} p a_p y^{p-1} = \sum_{q=0}^{\infty} (q+1) a_{q+1} y^q \\ H''(y) &= \sum_{p=0}^{\infty} p(p-1) a_p y^{p-2} = \sum_{r=0}^{\infty} (r+1)(r+2) a_{r+2} y^r \end{aligned} \quad (7.15)$$

---

**How to deal with equations involving polynomials.**

If I ask you when is  $a + by + cy^2 = 0$  for all  $y$ , I hope you will answer when  $a = b = c = 0$ . In other words a polynomial is zero when all its coefficients are zero. In the same vein two polynomials are equal when all their coefficients are equal. So what happens for infinite polynomials? They are zero when all coefficients are zero, and they are equal when all coefficients are equal.

---

So let's deal with the equation, and collect terms of the same order in  $y$ .

$$\begin{aligned} y^0 : \quad & 2a_2 + (2\epsilon - 1)a_0 = 0, \\ y^1 : \quad & 6a_3 - 2a_1 + (2\epsilon - 1)a_1 = 0, \\ y^s : \quad & (s+1)(s+2)a_{s+2} - (2s+1-2\epsilon)a_s = 0. \end{aligned} \quad (7.16)$$

These equations can be used to determine  $a_{s+2}$  if we know  $a_s$ . The only thing we do not want of our solutions is that they diverge at infinity. Notice that if there is an integer such that

$$2\epsilon = 2n + 1, \quad (7.17)$$

that  $a_{n+2} = 0$ , and  $a_{n+4} = 0$ , etc. These solutions are normalisable, and will be investigated later. If the series does not terminate, we just look at the behaviour of the coefficients for large  $s$ , using the following

**Theorem**

The behaviour of the coefficients  $a_s$  of a Taylor series  $u(y) = \sum_s a_s y^s$  for large index  $s$  describes the behaviour of the function  $u(y)$  for large value of  $y$ .

Now for large  $s$ ,

$$a_{s+2} = \frac{2}{s} a_s, \quad (7.18)$$

which behaves the same as the Taylor coefficients of  $e^{y^2}$ :

$$e^{y^2} = \sum_{s \text{ even}} b_s y^s = \sum_{s \text{ even}} \frac{1}{\frac{s}{2}!} y^s, \quad (7.19)$$

and we find

$$b_{s+2} = \frac{2}{s+2} b_s, \quad (7.20)$$

which for large  $s$  is the same as the relation for  $a_s$ . Now  $e^{y^2} e^{-y^2/2} = e^{y^2/2}$ , and this diverges....

## 7.4 A few solutions

The polynomial solutions occur for

$$\epsilon_n = (n + \frac{1}{2}). \quad (7.21)$$

The terminating solutions are the ones that contains only even coefficients for even  $n$  and odd coefficients for odd  $n$ . Let me construct a few, using the relation (7.16). For  $n$  even I start with  $a_0 = 1, a_1 = 0$ , and for  $n$  odd I start with  $a_0 = 0, a_1 = 1$ ,

$$H_0(y) = 1, \quad (7.22)$$

$$H_1(y) = y, \quad (7.23)$$

$$H_2(y) = 1 - 2y^2, \quad (7.24)$$

$$H_3(y) = y - \frac{2}{3}y^3. \quad (7.25)$$

**Question:** Can you reproduce these results? What happens if I start with  $a_0 = 0, a_1 = 1$  for, e.g.,  $H_0$ ?

In summary: The solutions of the Schrödinger equation occur for energies  $(n + \frac{1}{2})\hbar\omega$ , and the wavefunctions are

$$\phi_n(x) \propto H_n \left( \sqrt{\frac{m\omega}{\hbar}} x \right) \exp \left( -\frac{m\omega}{\hbar} x^2 \right) \quad (7.26)$$

(In analogy with matrix diagonalisation one often speaks of eigenvalues or eigenenergies for  $E$ , and eigenfunctions for  $\phi$ .)

Once again it is relatively straightforward to show how to normalise these solutions. This can be done explicitly for the first few polynomials, and we can also show that

$$\int_{-\infty}^{\infty} \phi_{n_1}(x) \phi_{n_2}(x) dx = 0 \quad \text{if } n_1 \neq n_2. \quad (7.27)$$

This defines the *orthogonality* of the wave functions. From a more formal theory of the polynomials  $H_n(y)$  it can be shown that the normalised form of  $\phi_n(x)$  is

$$\phi_n(x) = 2^{-n/2} (n!)^{-1/2} \left( \frac{m\omega}{\hbar\pi} \right)^{1/4} \exp \left( -\frac{m\omega}{2\hbar} x^2 \right) H_n \left( \sqrt{\frac{m\omega}{\hbar}} x \right) \quad (7.28)$$

## 7.5 Quantum-Classical Correspondence

One of the interesting questions raised by the fact that we can solve both the quantum and the classical problem exactly for the harmonic oscillator, is “Can we compare the Classical and Quantum Solutions?”

In order to do that we have to construct a probability for the classical solution. The variable over which we must average to get such a distribution must be time, the only one that remains in the solution. For simplicity look at a cosine solution, a sum of sine and cosines behaves exactly the same (**check!**). We thus have, classically,

$$x = A \cos(\omega t), \quad v = -A\omega \sin(\omega t). \quad (7.29)$$

If we substitute this in the energy expression,  $E = \frac{1}{2}mv^2 + \frac{1}{2}m\omega^2 x^2$ , we find that the energy depends on the amplitude  $A$  and  $\omega$ ,

$$E(A) = \frac{1}{2}mA^2\omega^2 \sin^2(\omega t) + \frac{1}{2}m\omega^2 A^2 \cos^2(\omega t) = \frac{1}{2}m\omega^2 A^2 \quad (7.30)$$

Now the probability to find the particle at position  $x$ , where  $-A < x < A$  is proportional to the time spent in an area  $dx$  around  $x$ . The time spent in its turn is inversely proportional to the velocity  $v$

$$\mathcal{P}_{\text{class}}(x) dx \propto \frac{1}{|v(x)|} dx \quad (7.31)$$



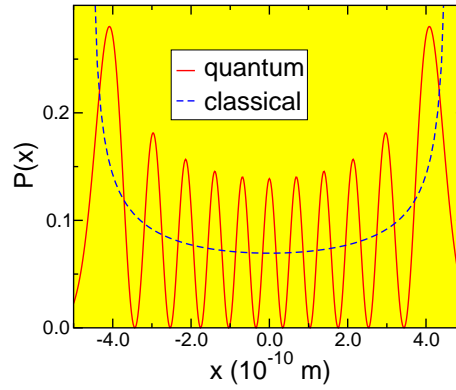


Figure 7.2: The correspondence between quantum and classical probabilities

Solving  $v$  in terms of  $x$  we find

$$|v(x)| = \omega \sqrt{A^2 - x^2} \quad (7.32)$$

Doing the integration of  $1/v(x)$  over  $x$  from  $-A$  to  $A$  we find that the normalised probability is

$$\mathcal{P}_{\text{class}}(x)dx = \frac{1}{\pi \sqrt{A^2 - x^2}} dx. \quad (7.33)$$

We now would like to compare this to the quantum solution. In order to do that we should consider the probabilities at the same energy,

$$\frac{1}{2} m \omega^2 A^2 = \hbar \omega (n + \frac{1}{2}), \quad (7.34)$$

which tells us what  $A$  to use for each  $n$ ,

$$A(n) = \sqrt{\frac{\hbar}{m\omega}} (2n + 1). \quad (7.35)$$

So let us look at an example for  $n = 10$ . Suppose we choose  $m$  and  $\omega$  such that  $\sqrt{\frac{\hbar}{m\omega}} = 10^{-10}$  m. We then get the results shown in Fig. 7.2, where we see the correspondence between the two functions.



## Chapter 8

# The formalism underlying QM

Now we have worked a bit with wave functions, we do have to consider some of the underlying interpretation. This can be most easily captured in some formal statements. Note, however, that even though there is no problem with calculations of quantum processes, the interpretation of QM and the measurement process is a complicated and partially unsolved problem. The problem is probably more philosophical than physical!

### 8.1 Key postulates

1. Every single system has a wave function  $\psi(x, t)$ .
2. Every observable is represented by a Hermitean operator  $\hat{O}$ .
3. The expectation value (average outcome of a measurement) is given by  $\int \phi(x)^* [\hat{O}\phi(x)] dx$
4. The outcome of an individual experiment can be any of the eigenvalues of  $\hat{O}$ .

Let me take each of these in turn.

#### 8.1.1 Wavefunction

The detailed statement is that: for every physical system there exists a wave function, a function of the parameters of the system (coordinates and such) and time, from which the outcome of any experiment can be predicted.

In these lectures I will not touch on systems that depend on other parameters than coordinates, but examples are known, such as the spin of an electron, which can be up or down, and is not like a coordinate at all.

#### 8.1.2 Observables

In classical mechanics “observables” (the technical term for anything that can be measured) are represented by numbers. Think e.g., of  $x, y, z, p_x, p_y, p_z, E, \dots$ . In quantum mechanics “observables” are often quantised, they cannot take on all possible values: how to represent such quantities?

We have already seen that energy and momentum are represented by operators,

$$\hat{p} = -i\hbar\nabla = -i\hbar\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right). \quad (8.1)$$

and

$$\hat{H} = -\frac{\hbar^2 d^2}{2mdx^2} + V(x) \quad (8.2)$$

Let me look at the Hamiltonian, the energy operator. We know that its normalisable solutions (eigenvalues) are discrete.

$$\hat{H}\phi_n(x) = E_n\phi_n(x). \quad (8.3)$$

The numbers  $E_n$  are called the eigenvalues, and the functions  $\phi_n(x)$  the eigenfunctions of the operator  $\hat{H}$ . Our postulate says that the only possible outcomes of any experiment where we measure energy are the values  $E_n$ !

### 8.1.3 Hermitean operators

Hermitean operators are those where the outcome of any measurement is always real, as they should be (complex position?). This means that both its eigenvalues are real, and that the average outcome of any experiment is real. The mathematical definition of a Hermitean operator can be given as

$$\int_{\text{all space}} \psi_1^*(x) [\hat{O}\psi_2(x)] dx = \int_{\text{all space}} [\hat{O}\psi_1(x)]^* \psi_2(x) dx. \quad (8.4)$$

**Quiz** show that  $\hat{x}$  and  $\hat{p}$  (in 1 dimension) are Hermitean.

### 8.1.4 Eigenvalues of Hermitean operators

Eigenvalues and eigen vectors of Hermitean operators are defined as for matrices, i.e., where there is a matrix-vector product we get an operator acting on a function, and the eigenvalue/function equation becomes

$$\hat{O}f(x) = o_n f(x), \quad (8.5)$$

where  $o_n$  is a number (the “eigenvalue”) and  $f(x)$  is the “eigenfunction”.

A list of important properties of the eigenvalue-eigenfunction pairs for Hermitean operators are:

1. The eigenvalues of an Hermitean operator are all real.
  2. The eigenfunctions for different eigenvalues are orthogonal.
  3. The set of all eigenfunction is complete.
- Ad 1. Let  $\phi_n(x)$  be an eigenfunction of  $\hat{O}$ . Use

$$o_n = \int dx \phi_n(x)^* [\hat{O}\phi_n(x)] = \int dx [\hat{O}\phi_n(x)]^* \phi_n(x) = o_n^* \quad (8.6)$$

- Ad 2. Let  $\phi_n(x)$  and  $\phi_m(x)$  be eigenfunctions of  $\hat{O}$ . Use

$$o_n \int dx \phi_n(x)^* \phi_n(x) = \int dx \phi_n(x)^* [\hat{O}\phi_n(x)] = \int dx [\hat{O}\phi_n(x)]^* \phi_n(x) = o_m \int dx \phi_n(x)^* \phi_n(x). \quad (8.7)$$

This leads to

$$(o_n - o_m) \int dx \phi_n(x)^* \phi_n(x) = 0, \quad (8.8)$$

and if  $o_n \neq o_m$   $\int dx \phi_n(x)^* \phi_n(x) = 0$ , which is the definition of two orthogonal functions.

- Ad 3. This is more complex, and no proof will be given. It means that any function can be written as a sum of eigenfunctions of  $\hat{O}$ ,

$$f(x) = \sum_{n=0}^{\infty} c_n \phi_n(x) \quad (8.9)$$

(A good example of such a sum is the Fourier series.)

### 8.1.5 Outcome of a single experiment

The outcome of a measurement of any quantity can only be the set of natural values of such a quantity. These are just the eigenvalues of  $\hat{O}$

$$\hat{O}f_n(x) = o_n f_n(x). \quad (8.10)$$

Is this immediately obvious from the formalism? The short answer is no, but suppose we measure the value of the observable for a wave function known to be an eigenstate. The outcome of a measurement better be this eigenvalue and nothing else. This leads us to surmise that this rule holds for any wave function, and we get the answer we are looking for. This also agrees with the experimentally observed quantisation of observables such as energy.

### 8.1.6 Eigenfunctions of $\hat{x}$

The operator  $\hat{x}$  multiplies with  $x$ . Solving the equation

$$\hat{x}\phi(x) = x_0\phi(x) \quad (8.11)$$

we find that the solution must be exactly localised at  $x = x_0$ . The function that does that is called a Dirac  $\delta$  function  $\delta(x - x_0)$ . This is defined through integration,

$$\int_{-\infty}^{\infty} \delta(x - x_0)g(x) dx = g(x_0), \quad (8.12)$$

and is not normalisable,

$$\int \delta(x - x_0)^2 dx = \infty. \quad (8.13)$$

### 8.1.7 Eigenfunctions of $\hat{p}$

The operator  $\hat{p}$  is  $-i\hbar \frac{\partial}{\partial x}$ . Solving the equation

$$-i\hbar \frac{d}{dx}\phi(x) = p_0\phi(x), \quad (8.14)$$

we get

$$\frac{d}{dx}\phi(x) = ip_0/\hbar\phi(x), \quad (8.15)$$

with solution

$$\phi(x) = e^{ip_0x/\hbar} \quad (8.16)$$

a “plane wave”. As we have seen before these states aren’t normalised either!

## 8.2 Expectation value of $\hat{x}^2$ and $\hat{p}^2$ for the harmonic oscillator

As an example of all we have discussed let us look at the harmonic oscillator. Suppose we measure the average deviation from equilibrium for a harmonic oscillator in its ground state. This corresponds to measuring  $\hat{x}$ . Using

$$\phi_0(x) = \left(\frac{m\omega}{\hbar\pi}\right)^{1/4} \exp\left(-\frac{m\omega}{2\hbar}x^2\right) \quad (8.17)$$

we find that

$$\langle x \rangle = \int_{-\infty}^{\infty} \left(\frac{m\omega}{\hbar\pi}\right)^{1/2} x \exp\left(-\frac{m\omega}{\hbar}x^2\right) dx = 0. \quad (8.18)$$

Qn Why is it 0? Similarly, using  $\hat{p} = -i\hbar \frac{d}{dx}$  and

$$\hat{p} \left( \frac{m\omega}{\hbar\pi} \right)^{1/4} \exp \left( -\frac{m\omega}{2\hbar} x^2 \right) = im\omega x \left( \frac{m\omega}{\hbar\pi} \right)^{1/4} \exp \left( -\frac{m\omega}{2\hbar} x^2 \right), \quad (8.19)$$

we find

$$\langle p \rangle = 0. \quad (8.20)$$

More challenging are the expectation values of  $x^2$  and  $p^2$ . Let me look at the first one first:

$$\begin{aligned} \langle x^2 \rangle &= \int_{-\infty}^{\infty} \left( \frac{m\omega}{\hbar\pi} \right)^{1/2} x^2 \exp \left( -\frac{m\omega}{\hbar} x^2 \right) dx \\ &= \left( \frac{\hbar}{m\omega} \right) \pi^{-1/2} \int_{-\infty}^{\infty} y^2 \exp \left( -y^2 \right) dy \\ &= \left( \frac{\hbar}{m\omega} \right) \frac{1}{2}. \end{aligned} \quad (8.21)$$

Now for  $\hat{p}^2$ ,

$$\hat{p}^2 \exp \left( -\frac{m\omega}{2\hbar} x^2 \right) = [-(m\omega x)^2 + \hbar m\omega] \exp \left( -\frac{m\omega}{2\hbar} x^2 \right). \quad (8.22)$$

Thus,

$$\begin{aligned} \langle \hat{p}^2 \rangle &= \int_{-\infty}^{\infty} \left( \frac{m\omega}{\hbar\pi} \right)^{1/2} [-(m\omega x)^2 + \hbar m\omega] \exp \left( -\frac{m\omega}{\hbar} x^2 \right) dx \\ &= \hbar m\omega \pi^{-1/2} \int_{-\infty}^{\infty} [1 - y^2] \exp \left( -y^2 \right) dy \\ &= \hbar m\omega \frac{1}{2}. \end{aligned} \quad (8.23)$$

This is actually a form of the uncertainty relation, and shows that

$$\Delta x \Delta p \geq \frac{1}{2} \hbar! \quad (8.24)$$

### 8.3 The measurement process

Suppose I know my wave function at time  $t = 0$  is the sum of the two lowest-energy harmonic oscillator wave functions,

$$\psi(x, 0) = \frac{1}{\sqrt{2}} [\phi_0(x) + \phi_1(x)]. \quad (8.25)$$

The introduction of the time independent wave function was through the separation  $\psi_n(x, t) = e^{-iE_n/\hbar t} \phi_n(x)$ . Together with the superposition for time-dependent wave functions, we find

$$\psi(x, t) = \frac{1}{\sqrt{2}} \left[ \phi_0(x) e^{-i\frac{1}{2}\omega t} + \phi_1(x) e^{-i\frac{3}{2}\omega t} \right]. \quad (8.26)$$

The expectation value of  $\hat{H}$ , i.e., the expectation value of the energy is

$$\langle \hat{H} \rangle = \frac{1}{2} (E_0 + E_1) = \hbar\omega. \quad (8.27)$$

The interpretation of probabilities now gets more complicated. If we measure the energy, we don't expect an outcome  $E_3$ , since there is no  $\phi_3$  component in the wave function. We do expect  $E_0 = \frac{1}{2}\hbar\omega$  or  $E_1 = \frac{3}{2}\hbar\omega$  with 50 % probability, which leads to the right average. Actually simple mathematics shows that the result for the expectation value was just that,  $\langle E \rangle = \frac{1}{2}E_0 + \frac{1}{2}E_1$ .

We can generalise this result to stating that if

$$\psi(x, t) = \sum_{n=0}^{\infty} c_n(t) \phi_n(x), \quad (8.28)$$

where  $\phi_n(x)$  are the eigenfunctions of an (Hermitean) operator  $\hat{O}$ ,

$$\hat{O}\phi_n(x) = o_n\phi_n(x), \quad (8.29)$$

then

$$\langle \hat{O} \rangle = \sum_{n=0}^{\infty} |c_n(t)|^2 o_n, \quad (8.30)$$

and the probability that the outcome of a measurement of  $\hat{O}$  at time  $t_0$  is  $o_n$  is  $|c_n(t)|^2$ . Here we use orthogonality and completeness of the eigenfunctions of Hermitean operators.

### 8.3.1 Repeated measurements

If we measure  $E$  once and we find  $E_i$  as outcome we know that the system is in the  $i$ th eigenstate of the Hamiltonian. That certainty means that if we measure the energy again we must find  $E_i$  again. This is called the “collapse of the wave function”: before the first measurement we couldn’t predict the outcome of the experiment, but the first measurement prepares the wave function of the system in one particular state, and there is only one component left!

Now what happens if we measure two different observables? Say, at 12 o’clock we measure the position of a particle, and a little later its momentum. How do these measurements relate? Measuring  $\hat{x}$  to be  $x_0$  makes the wavefunction collapse to  $\delta(x - x_0)$ , *whatever it was before*. Now mathematically it can be shown that

$$\delta(x - x_0) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ik(x-x_0)} dk. \quad (8.31)$$

Since  $e^{ikx}$  is an eigenstate of the momentum operator, the coordinate eigen function is a superposition of all momentum eigen functions with equal weight. Thus the spread in possible outcomes of a measurement of  $p$  is infinite!

---

**incompatible operators**

The reason is that  $\hat{x}$  and  $\hat{p}$  are so-called incompatible operators, where

$$\hat{p}\hat{x} \neq \hat{x}\hat{p}! \quad (8.32)$$

The way to show this is to calculate

$$(\hat{p}\hat{x} - \hat{x}\hat{p})f(x) \equiv [\hat{p}, \hat{x}]f(x) \quad (8.33)$$

for arbitrary  $f(x)$ . A little algebra shows that

$$\begin{aligned} [\hat{p}, \hat{x}]f(x) &= \frac{\hbar}{i} \left( \frac{d}{dx} x \right) f(x) \\ &= \frac{\hbar}{i} f(x). \end{aligned} \quad (8.34)$$

In operatorial notation,

$$[\hat{p}, \hat{x}] = \frac{\hbar}{i} \hat{1}, \quad (8.35)$$

where the operator  $\hat{1}$ , which multiplies by 1, i.e., changes  $f(x)$  into itself, is usually not written.

The reason these are now called “incompatible operators” is that an eigenfunction of one operator is not one of the other: if  $\hat{x}\phi(x) = x_0\phi(x)$ , then

$$\hat{x}\hat{p}\phi(x) = x_0\hat{p}\phi(x) - \frac{\hbar}{i}\phi(x) \quad (8.36)$$

If  $\phi(x)$  was also an eigenstate of  $\hat{p}$  with eigenvalue  $p_0$  we find the contradiction  $x_0 p_0 = x_0 p_0 - \frac{\hbar}{i}$ .

---

Now what happens if we initially measure  $\hat{x} = x_0$  with finite accuracy  $\Delta x$ ? This means that the wave function collapses to a Gaussian form,

$$\phi(x) \propto \exp(-(x - x_0)^2 / \Delta x^2) \quad (8.37)$$

It can be shown that

$$\exp(-(x - x_0)^2 / \Delta x^2) = \int_{-\infty}^{\infty} dk e^{ikx} e^{-ikx_0} \exp(-1/4k^2 \Delta x^2), \quad (8.38)$$

from which we read off that  $\Delta p = \hbar / (2\Delta x)$ , and thus we conclude that at best

$$\Delta x \Delta p = \hbar / 2 \quad (8.39)$$

which is the celebrated Heisenberg uncertainty relation.



## Chapter 9

# Ladder operators

### 9.1 Harmonic oscillators

One of the major playing fields for operatorial methods is the harmonic oscillator. Even though they look very artificial, harmonic potentials play an extremely important rôle in many areas of physics. This is due to the fact that around an equilibrium point, where the forces vanish, any potential behaves as an harmonic one (plus small corrections). This can best be seen by making a Taylor series expansion about such a point,

$$V(x) = V_0 + \frac{1}{2}m\omega^2 x^2 + \mathcal{O}(x^3). \quad (9.1)$$

**Question:** Why is there no linear term?

For small enough  $x$  the quadratic term dominates, and we can ignore other terms. Such situations occur in many physical problems, and make the harmonic oscillator such an important problem.

As explained in our first discussion of harmonic oscillators, we scale to dimensionless variables (“pure numbers”)

$$y = \sqrt{\frac{m\omega}{\hbar}} x, \quad \epsilon = E / (\hbar\omega). \quad (9.2)$$

In these new variables the Schrödinger equation becomes

$$\frac{1}{2} \left( \frac{-d^2}{dy^2} + y^2 \right) u(y) = \epsilon u(y). \quad (9.3)$$

### 9.2 The operators $\hat{a}$ and $\hat{a}^\dagger$ .

In a previous chapter I have discussed a solution by a power series expansion. Here I shall look at a different technique, and define two operators  $\hat{a}$  and  $\hat{a}^\dagger$ ,

$$\hat{a} = \frac{1}{\sqrt{2}} \left( y + \frac{d}{dy} \right), \quad \hat{a}^\dagger = \frac{1}{\sqrt{2}} \left( y - \frac{d}{dy} \right). \quad (9.4)$$

Since

$$\frac{d}{dy}(yf(y)) = y \frac{d}{dy}f(y) + f(y), \quad (9.5)$$

or in operator notation

$$\frac{d}{dy}\hat{y} = \hat{y} \frac{d}{dy} + \hat{1}, \quad (9.6)$$

(the last term is usually written as just 1) we find

$$\begin{aligned}\hat{a}\hat{a}^\dagger &= \frac{1}{2} \left( \hat{y}^2 - \frac{d^2}{d\hat{y}^2} + \hat{1} \right), \\ \hat{a}^\dagger\hat{a} &= \frac{1}{2} \left( \hat{y}^2 - \frac{d^2}{d\hat{y}^2} - \hat{1} \right).\end{aligned}\tag{9.7}$$

If we define the *commutator*

$$[\hat{f}, \hat{g}] = \hat{f}\hat{g} - \hat{g}\hat{f},\tag{9.8}$$

we have

$$[\hat{a}, \hat{a}^\dagger] = \hat{1}.\tag{9.9}$$

Now we see that we can replace the eigenvalue problem for the scaled Hamiltonian by either of

$$\begin{aligned}\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)u(y) &= \epsilon u(y), \\ \left(\hat{a}\hat{a}^\dagger - \frac{1}{2}\right)u(y) &= \epsilon u(y).\end{aligned}\tag{9.10}$$

By multiplying the first of these equations by  $\hat{a}$  we get

$$\left(\hat{a}\hat{a}^\dagger\hat{a} + \frac{1}{2}\hat{a}\right)u(y) = \epsilon\hat{a}u(y).\tag{9.11}$$

If we just rearrange some brackets, we find

$$\left(\hat{a}\hat{a}^\dagger + \frac{1}{2}\right)\hat{a}u(y) = \epsilon\hat{a}u(y).\tag{9.12}$$

If we now use

$$\hat{a}\hat{a}^\dagger = \hat{a}^\dagger\hat{a} - \hat{1},\tag{9.13}$$

we see that

$$\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)\hat{a}u(y) = (\epsilon - 1)\hat{a}u(y).\tag{9.14}$$

**Question:** Show that

$$\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)\hat{a}^\dagger u(y) = (\epsilon + 1)\hat{a}^\dagger u(y).\tag{9.15}$$

We thus conclude that (we use the notation  $u_n(y)$  for the eigenfunction corresponding to the eigenvalue  $\epsilon_n$ )

$$\begin{aligned}\hat{a}u_n(y) &\propto u_{n-1}(y), \\ \hat{a}^\dagger u_n(y) &\propto u_{n+1}(y).\end{aligned}\tag{9.16}$$

So using  $\hat{a}$  we can go down in eigenvalues, using  $\hat{a}^\dagger$  we can go up. This leads to the name lowering and raising operators (guess which is which?).

We also see from (9.15) that the eigenvalues differ by integers only!

### 9.3 Eigenfunctions of $\hat{H}$ through ladder operations

If we start with the ground state we would expect that we can't go any lower,

$$\hat{a}u_0(y) = 0.\tag{9.17}$$

This can of course be checked explicitly,

$$\begin{aligned}
 \hat{a}e^{-y^2/2} &= \frac{1}{\sqrt{2}} \left( \hat{y} + \frac{d}{dy} \right) e^{-y^2/2} \\
 &= \frac{1}{\sqrt{2}} \left( ye^{-y^2/2} - ye^{-y^2/2} \right) \\
 &= 0
 \end{aligned} \tag{9.18}$$

**Quiz** Can you show that  $\epsilon_0 = 1/2$  using the operators  $\hat{a}^\dagger$ ?

Once we know that  $\epsilon_0 = 1/2$ , repeated application of Eq. (9.15) shows that  $\epsilon_n = n + 1/2$ , which we know to be correct from our previous treatment.

Actually, once we know the ground state, we can now easily determine all the Hermite polynomials up to a normalisation constant:

$$\begin{aligned}
 u_1(y) &\propto \hat{a}^\dagger e^{-y^2/2} \\
 &= \frac{1}{\sqrt{2}} \left( \hat{y} - \frac{d}{dy} \right) e^{-y^2/2} \\
 &= \frac{1}{\sqrt{2}} \left( ye^{-y^2/2} + ye^{-y^2/2} \right) \\
 &= \sqrt{2}ye^{-y^2/2}.
 \end{aligned} \tag{9.19}$$

Indeed  $H_1(y) \propto y$ .

From math books we can learn that the standard definition of the Hermite polynomials corresponds to

$$H_n(y)e^{-y^2/2} = (\sqrt{2})^n (\hat{a}^\dagger)^n e^{-y^2/2}. \tag{9.20}$$

We thus learn  $H_1(y) = 2y$  and  $H_2(y) = (4y^2 - 2)$ .

**Question:** Prove this last relation.

## 9.4 Normalisation and Hermitean conjugates

If you look at the expression  $\int_{-\infty}^{\infty} f(y)^* \hat{a}^\dagger g(y) dy$  and use the explicit form  $\hat{a}^\dagger = \frac{1}{\sqrt{2}} \left( y - \frac{d}{dy} \right)$ , you may guess that we can use partial integration to get the operator acting on  $f$ ,

$$\begin{aligned}
 &\int_{-\infty}^{\infty} f(y)^* \hat{a}^\dagger g(y) dy \\
 &= \int_{-\infty}^{\infty} f(y)^* \frac{1}{\sqrt{2}} \left( y - \frac{d}{dy} \right) g(y) dy \\
 &= \int_{-\infty}^{\infty} \frac{1}{\sqrt{2}} \left( y + \frac{d}{dy} \right) f(y)^* g(y) dy \\
 &= \int_{-\infty}^{\infty} [\hat{a}f(y)]^* g(y) dy \quad .
 \end{aligned} \tag{9.21}$$

This is the first example of an operator that is clearly not Hermitean, but we see that  $\hat{a}$  and  $\hat{a}^\dagger$  are related by ‘‘Hermitean conjugation’’. We can actually use this to normalise the wave function! Let us look at

$$\begin{aligned}
 O_n &= \int_{-\infty}^{\infty} \left[ (\hat{a}^\dagger)^n e^{-y^2/2} \right]^* (\hat{a}^\dagger)^n e^{-y^2/2} dy \\
 &= \int_{-\infty}^{\infty} \left[ \hat{a} (\hat{a}^\dagger)^n e^{-y^2/2} \right]^* (\hat{a}^\dagger)^{n-1} e^{-y^2/2} dy
 \end{aligned} \tag{9.22}$$

If we now use  $\hat{a}\hat{a}^\dagger = \hat{a}^\dagger\hat{a} + \hat{1}$  repeatedly until the operator  $\hat{a}$  acts on  $u_0(y)$ , we find

$$O_n = nO_{n-1}. \quad (9.23)$$

Since  $O_0 = \sqrt{\pi}$ , we find that

$$u_n(y) = \frac{1}{\sqrt{n!\sqrt{\pi}}} \left(\hat{a}^\dagger\right)^n e^{-y^2/2} \quad (9.24)$$

**Question:** Show that this agrees with the normalisation proposed in the previous study of the harmonic oscillator!

**Question:** Show that the states  $u_n$  for different  $n$  are orthogonal, using the techniques sketched above.

## Chapter 10

# Time dependent wave functions

Up till now I have ignored time dependence. I cannot always do that, which is what these notes are about!

### 10.1 correspondence between time-dependent and time-independent solutions

The time dependent Schrödinger equation is

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x, t) + V(x) \psi(x, t) = \frac{\hbar i \partial}{\partial t} \psi(x, t). \quad (10.1)$$

As we remember, a solution of the form

$$\psi(x, t) = \phi(x) e^{-iEt/\hbar} \quad (10.2)$$

leads to a solution of the time-independent Schrödinger equation of the form

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \phi(x) + V(x) \phi(x) = E \phi(x). \quad (10.3)$$

### 10.2 Superposition of time-dependent solutions

There has been an example problem, where I asked you to show “that if  $\psi_1(x, t)$  and  $\psi_2(x, t)$  are both solutions of the time-dependent Schrödinger equation, then  $\psi_1(x, t) + \psi_2(x, t)$  is a solution as well.” Let me review this problem

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi_1(x, t) + V(x) \psi_1(x, t) &= \frac{\hbar i \partial}{\partial t} \psi_1(x, t) \\ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi_2(x, t) + V(x) \psi_2(x, t) &= \frac{\hbar i \partial}{\partial t} \psi_2(x, t) \\ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} [\psi_1(x, t) + \psi_2(x, t)] + V(x) [\psi_1(x, t) + \psi_2(x, t)] &= \frac{\hbar i \partial}{\partial t} [\psi_1(x, t) + \psi_2(x, t)], \end{aligned} \quad (10.4)$$

where in the last line I have use the sum rule for derivatives. This is called the superposition of solutions, and holds for any two solutions to the *same* Schrödinger equation!

**Question:** Why doesn't it work for the time-independent Schrödinger equation?

### 10.3 Completeness and time-dependence

In the discussion on formal aspects of quantum mechanics I have shown that the eigenfunctions to the Hamiltonian are complete, i.e., for any  $\psi(x, t)$

$$\psi(x, t) = \sum_{n=1}^{\infty} c_n(t) \phi_n(x), \quad (10.5)$$

where

$$\hat{H}\phi_n(x) = E_n\phi_n(x). \quad (10.6)$$

We know, from the superposition principle, that

$$\psi(x, t) = \sum_{n=1}^{\infty} c_n(0) e^{-iEt/\hbar} \phi_n(x), \quad (10.7)$$

so that the time dependence is completely fixed by knowing  $c(0)$  at time  $t = 0$  only! In other words if we know how the wave function at time  $t = 0$  can be written as a sum over eigenfunctions of the Hamiltonian, we can then determine the wave function for all times.

### 10.4 Simple example

The best way to clarify this abstract discussion is to consider the quantum mechanics of the Harmonic oscillator of mass  $m$  and frequency  $\omega$ ,

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2. \quad (10.8)$$

If we assume that the wave function at time  $t = 0$  is a linear superposition of the first two eigenfunctions,

$$\begin{aligned} \psi(x, t = 0) &= \sqrt{\frac{1}{2}} \phi_0(x) - \sqrt{\frac{1}{2}} \phi_1(x), \\ \phi_0(x) &= \left( \frac{m\omega}{\pi\hbar} \right)^{1/4} \exp\left(-\frac{m\omega}{2\hbar} x^2\right), \\ \phi_1(x) &= \left( \frac{m\omega}{\pi\hbar} \right)^{1/4} \exp\left(-\frac{m\omega}{2\hbar} x^2\right) \sqrt{\frac{m\omega}{\hbar}} x. \end{aligned} \quad (10.9)$$

(The functions  $\phi_0$  and  $\phi_1$  are the *normalised* first and second states of the harmonic oscillator, with energies  $E_0 = \frac{1}{2}\hbar\omega$  and  $E_1 = \frac{3}{2}\hbar\omega$ .) Thus we now know the wave function for all time:

$$\psi(x, t) = \sqrt{\frac{1}{2}} \phi_0(x) e^{-\frac{1}{2}i\omega t} - \sqrt{\frac{1}{2}} \phi_1(x) e^{-\frac{3}{2}i\omega t}. \quad (10.10)$$

In figure 10.1 we plot this quantity for a few times.

The best way to visualize what is happening is to look at the probability density,

$$\begin{aligned} \mathcal{P}(x, t) &= \psi(x, t)^* \psi(x, t) \\ &= \frac{1}{2} \left( \phi_0(x)^2 + \phi_1(x)^2 - 2\phi_0(x)\phi_1(x) \cos \omega t \right). \end{aligned} \quad (10.11)$$

This clearly oscillates with frequency  $\omega$ .

**Question:** Show that  $\int_{-\infty}^{\infty} \mathcal{P}(x, t) dx = 1$ .

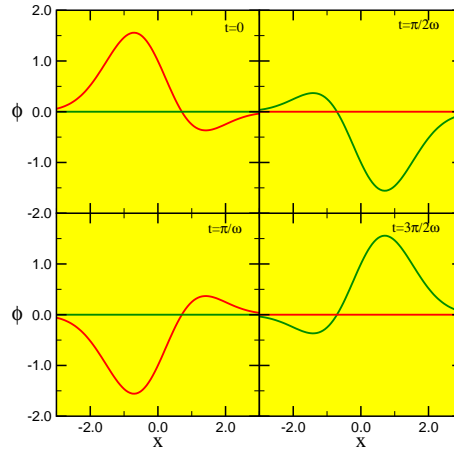


Figure 10.1: The wave function (10.10) for a few values of the time  $t$ . The solid line is the real part, and the dashed line the imaginary part.

Another way to look at that is to calculate the expectation value of  $\hat{x}$ :

$$\begin{aligned}
 \langle \hat{x} \rangle &= \int_{-\infty}^{\infty} \mathcal{P}(x, t) dx \\
 &= \underbrace{\frac{1}{2} \int_{-\infty}^{\infty} \phi_0(x)^2 x dx}_{=0} + \underbrace{\frac{1}{2} \int_{-\infty}^{\infty} \phi_1(x)^2 x dx}_{=0} - \cos \omega t \int_{-\infty}^{\infty} \phi_0(x) \phi_1(x) x dx \\
 &= -\cos \omega t \sqrt{\frac{\hbar}{m\omega}} \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} y^2 e^{-y^2} dy \\
 &= -\frac{1}{2} \sqrt{\frac{\hbar}{m\omega}} \cos \omega t.
 \end{aligned} \tag{10.12}$$

This once again exhibits oscillatory behaviour!

## 10.5 Wave packets (states of minimal uncertainty)

One of the questions of some physical interest is “how can we create a quantum-mechanical state that behaves as much as a classical particle as possible?” From the uncertainty principle,

$$\Delta x \Delta p \geq \frac{1}{2} \hbar, \tag{10.13}$$

this must be a state where  $\Delta x$  and  $\Delta p$  are both as small as possible. Such a state is known as a “wavepacket”. We shall see below (and by using a computer demo) that its behavior depends on the Hamiltonian governing the system that we are studying!

Let us start with the uncertainty in  $x$ . A state with width  $\Delta x = \sigma$  should probably be a Gaussian, of the form

$$\psi(x, t) = \exp\left(-\frac{(x - x_0)^2}{2\sigma^2}\right) A(x). \tag{10.14}$$

In order for  $\psi$  to be normalised, we need to require

$$|A(x)|^2 = \sqrt{\frac{1}{\sigma^2 \pi}}. \tag{10.15}$$

Actually, I shall show below that with

$$A(x) = \sqrt[4]{\frac{1}{\sigma^2 \pi}} e^{ip_0 x / \hbar}, \quad (10.16)$$

we have

$$\langle \hat{x} \rangle = x_0, \quad \langle \hat{p} \rangle = p_0, \quad \Delta x = \sigma, \quad \Delta p = \hbar / \sigma \quad (10.17)$$

The algebra behind this is relatively straightforward, but I shall just assume the first two, and only do the last two in all gory details.

$$\hat{p} \exp \left( -\frac{(x-x_0)^2}{2\sigma^2} \right) A(x) = (p_0 + i\hbar \frac{(x-x_0)}{\sigma^2}) \exp \left( -\frac{(x-x_0)^2}{2\sigma^2} \right) A(x). \quad (10.18)$$

Thus

$$\langle p \rangle = \sqrt{\frac{1}{\sigma^2 \pi}} \int_{-\infty}^{\infty} (p_0 + i\hbar \frac{(x-x_0)}{\sigma^2}) \exp \left( -\frac{(x-x_0)^2}{2\sigma^2} \right) = p_0. \quad (10.19)$$

Let  $\hat{p}$  act twice,

$$\begin{aligned} \hat{p}^2 \exp \left( -\frac{(x-x_0)^2}{2\sigma^2} \right) A(x) &= \left( p_0^2 + 2i\hbar p_0 \frac{(x-x_0)}{\sigma^2} - \hbar^2 \left[ \frac{(x-x_0)^2}{\sigma^4} - \frac{1}{\sigma^2} \right] \right) \times \\ &\quad \exp \left( -\frac{(x-x_0)^2}{2\sigma^2} \right) A(x). \end{aligned} \quad (10.20)$$

Doing all the integrals we conclude that

$$\langle p^2 \rangle = p_0^2 + \frac{\hbar^2}{2\sigma^2}. \quad (10.21)$$

Thus, finally,

$$\Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} = \frac{\hbar}{\sigma} \quad (10.22)$$

This is just the initial state, which clearly has minimal uncertainty. We shall now investigate how the state evolves in time by using a numerical simulation. What we need to do is to decompose our state of minimal uncertainty in a sum over eigenstates of the Hamiltonian which describes our system!

## 10.6 computer demonstration



## Chapter 11

# 3D Schrödinger equation

Up till now we have been studying (very) artificial systems, where space is one dimensional. Of course the real world is three dimensional, and even the Schrödinger equation will have to take this into account. So how do we go about doing this?

### 11.1 The momentum operator as a vector

First of all we know from classical mechanics that velocity and momentum, as well as position, are represented by vectors. Thus we need to represent the momentum operator by a vector of operators as well,

$$\hat{\mathbf{p}} = \left( \frac{\hbar}{i} \frac{\partial}{\partial x}, \frac{\hbar}{i} \frac{\partial}{\partial y}, \frac{\hbar}{i} \frac{\partial}{\partial z} \right). \quad (11.1)$$

There exists a special notation for the vector of partial derivatives, which is usually called the gradient, and one writes

$$\hat{\mathbf{p}} = \frac{\hbar}{i} \nabla. \quad (11.2)$$

We now that the energy, and Hamiltonian, can be written in classical mechanics as

$$E = \frac{1}{2} m v^2 + V(\mathbf{x}) = \frac{1}{2m} \mathbf{p}^2 + V(\mathbf{x}), \quad (11.3)$$

where the square of a vector is defined as the sum of the squares of the components,

$$(v_1, v_2, v_3)^2 = v_1^2 + v_2^2 + v_3^2. \quad (11.4)$$

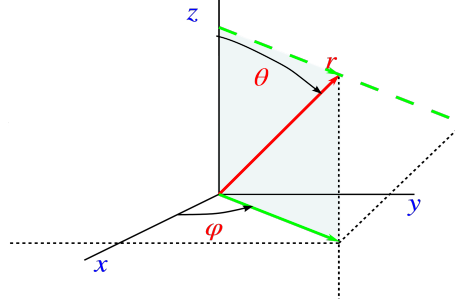
The Hamiltonian *operator* in quantum mechanics can now be read of from the classical one,

$$\hat{H} = \frac{1}{2m} \hat{\mathbf{p}}^2 + V(\mathbf{x}) = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(\mathbf{x}). \quad (11.5)$$

Let me introduce one more piece of notation: the square of the gradient operator is called the Laplacian, and is denoted by  $\Delta$ .

### 11.2 Spherical coordinates

The solution to Schrödinger's equation in three dimensions is quite complicated in general. Fortunately, nature lends us a hand, since most physical systems are "rotationally invariant", i.e.,  $V(\mathbf{x})$  depends on

Figure 11.1: The spherical coordinates  $r, \theta, \varphi$ .

the size of  $x$ , but not its direction! In that case it helps to introduce spherical coordinates, as denoted in Fig. 11.1.

The coordinates  $r, \theta$  and  $\varphi$  are related to the standard ones by

$$\begin{aligned} x &= r \cos \varphi \sin \theta \\ y &= r \sin \varphi \sin \theta \\ &= r \cos \theta \end{aligned} \quad (11.6)$$

where  $0 < r < \infty$ ,  $0 < \theta < \pi$  and  $0 < \varphi < 2\pi$ . In these new coordinates we have

$$\Delta f(r, \theta, \varphi) = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} f(r, \theta, \varphi) \right) - \frac{1}{r^2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} f(r, \theta, \varphi) \right) + \frac{\partial^2}{\partial \varphi^2} f(r, \theta, \varphi) \right]. \quad (11.7)$$

### 11.3 Solutions independent of $\theta$ and $\varphi$

Initially we shall just restrict ourselves to those cases where the wave function is independent of  $\theta$  and  $\varphi$ , i.e.,

$$\phi(r, \theta, \varphi) = R(r). \quad (11.8)$$

In that case the Schrödinger equation becomes (why?)

$$-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} R(r) \right) + V(r)R(r) = ER(r). \quad (11.9)$$

One often simplifies life even further by substituting  $u(r)/r = R(r)$ , and multiplying the equation by  $r$  at the same time,

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} u(r) + V(r)u(r) = Eu(r). \quad (11.10)$$

Of course we shall need to normalise solutions of this type. Even though the solution are independent of  $\theta$  and  $\varphi$ , we shall have to integrate over these variables. Here a geometric picture comes in handy. For each value of  $r$ , the allowed values of  $x$  range over the surface of a sphere of radius  $r$ . The area of such a sphere is  $4\pi r^2$ . Thus the integration over  $r, \theta, \varphi$  can be reduced to

$$\int_{\text{all space}} f(r) dx dy dz = \int_0^\infty f(r) 4\pi r^2 dr. \quad (11.11)$$

Especially, the normalisation condition translates to

$$\int_0^\infty |R(r)|^2 4\pi r^2 dr = \int_0^\infty |u(r)|^2 4\pi dr = 1 \quad (11.12)$$

## 11.4 The hydrogen atom

For the hydrogen atom we have a Coulomb force exerted by the proton forcing the electron to orbit around it. Since the proton is 1837 heavier than the electron, we can ignore the reverse action. The potential is thus

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}. \quad (11.13)$$

If we substitute this in the Schrödinger equation for  $u(r)$ , we find

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} u(r) - \frac{e^2}{4\pi\epsilon_0 r} u(r) = Eu(r). \quad (11.14)$$

The way to attack this problem is once again to combine physical quantities to set the scale of length, and see what emerges. From a dimensional analysis we find that the length scale is set by the Bohr radius  $a_0$ ,

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2} = 0.53 \times 10^{-10} \text{ m}. \quad (11.15)$$

The scale of energy is set by these same parameters to be

$$\frac{e^2}{4\pi\epsilon_0 a_0} = 2 \text{ Ry}, \quad (11.16)$$

and one Ry (Rydberg) is 13.6 eV. Solutions can be found by a complicated argument similar to the one for the Harmonic oscillator, but (without proof) we have

$$E_n = -\frac{1}{2} \left( \frac{e^2}{4\pi\epsilon_0 a_0} \right) \frac{1}{n^2} = -13.6 \frac{1}{n^2} \text{ eV}. \quad (11.17)$$

and

$$R_n = e^{-r/(na_0)} (c_0 + c_1 r + \dots + c_{n-1} r^{n-1}) \quad (11.18)$$

The explicit, and normalised, forms of a few of these states are

$$R_1(r) = \frac{1}{\sqrt{4\pi}} 2a_0^{-3/2} e^{-r/a_0}, \quad (11.19)$$

$$R_2(r) = \frac{1}{\sqrt{4\pi}} 2(2a_0)^{-3/2} \left( 1 - \frac{r}{2a_0} \right) e^{-r/(2a_0)}. \quad (11.20)$$

Remember these are normalised to

$$\int_0^\infty R_n(r)^* R_m(r) dr = \delta_{nm}. \quad (11.21)$$

Notice that there are solution that do depend on  $\theta$  and  $\varphi$  as well, and that we have not looked at such solutions here!

## 11.5 Now where does the probability peak?

Clearly the probability density to find an electron at point  $x$  is

$$\mathcal{P}(x) = R(r)^* R(r), \quad (11.22)$$

but what is the probability to find the electron at a distance  $r$  from the proton? The key point to realise is that for each value of  $r$  the electron can be anywhere on the surface of a sphere of radius  $r$ , so that

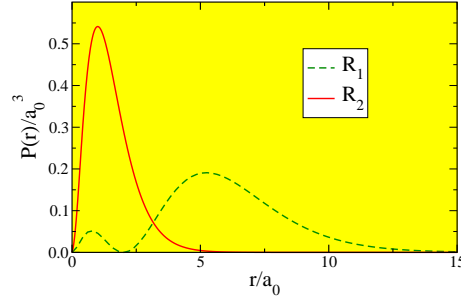


Figure 11.2: The probability to find a certain value of  $r$  for the first two Harmonic oscillator wave functions.

for larger  $r$  more points contribute than for smaller  $r$ . This is exactly the source of the factor  $4\pi r^2$  in the normalisation integral. The probability to find a certain value of  $r$  is thus

$$\mathcal{P}(r) = 4\pi r^2 R(r)^* R(r). \quad (11.23)$$

These probabilities are sketched in Fig. 11.2. The peaks are of some interest, since they show where the electrons are most likely to be found. Let's investigate this mathematically:

$$\mathcal{P}_1 = 4r^2/a_0^3 e^{-2r/a_0}. \quad (11.24)$$

if we differentiate with respect to  $r$ , we get

$$\frac{d}{dr} \mathcal{P}_1 = \frac{4}{a_0^3} (2r e^{-2r/a_0} - 2r^2/a_0 e^{-2r/a_0}). \quad (11.25)$$

This is zero at  $r = a_0$ . For the first excited state this gets a little more complicated, and we will have to work harder to find the answer.

## 11.6 Spherical harmonics

The key issue about three-dimensional motion in a spherical potential is angular momentum. This is true classically as well as in quantum theories. The angular momentum in classical mechanics is defined as the vector (outer) product of  $\mathbf{r}$  and  $\mathbf{p}$ ,

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}. \quad (11.26)$$

This has an easy quantum analog that can be written as

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}. \quad (11.27)$$

After expansion we find

$$\hat{\mathbf{L}} = -i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y}, z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z}, x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \quad (11.28)$$

This operator has some very interesting properties:

$$[\hat{\mathbf{L}}, \hat{\mathbf{r}}] = 0. \quad (11.29)$$

Thus

$$[\hat{\mathbf{L}}, \hat{H}] = 0! \quad (11.30)$$

And even more surprising,

$$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z. \quad (11.31)$$

Thus the different components of  $L$  are not compatible (i.e., can't be determined at the same time). Since  $L$  commutes with  $H$  we can diagonalise one of the components of  $L$  at the same time as  $H$ . Actually, we diagonalise  $\hat{L}^2$ ,  $\hat{L}_z$  and  $H$  at the same time!

The solutions to the equation

$$\hat{L}^2 Y_{LM}(\theta, \phi) = \hbar^2 L(L+1) Y_{LM}(\theta, \phi) \quad (11.32)$$

are called the spherical harmonics.

**Question:** check that  $\hat{L}^2$  is independent of  $r$ !

The label  $M$  corresponds to the operator  $\hat{L}_z$ ,

$$\hat{L}_z Y_{LM}(\theta, \phi) = \hbar M Y_{LM}(\theta, \phi). \quad (11.33)$$

## 11.7 General solutions

One of the reasons for playing such game is that we can rewrite the kinetic energy as

$$-\frac{\hbar^2}{2m} \hat{p}^2 f(\mathbf{r}) = -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} f(\mathbf{r}) \right) + \frac{1}{r^2} \hat{L}^2 f(\mathbf{r}). \quad (11.34)$$