Quantentheorie I und II
Vorlesungsnotizen
HS21/FS22

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Chapter 1

Introduction

The experiments we are going to briefly describe in this introductory chapter were mostly performed at the end of the 19th century and represented a challenge to the physicists of that time because an interpretation of them in the framework of classical physics did not seem to be possible – and indeed it wasn't. After many small steps in the right direction and ad hoc intepretations, the solution of all the puzzles was provided by the formulation of Quantum Mechanics. Surprisingly (or maybe not, see later), the laws of Nature take a different form if one makes experiments which probe matter at microscopic, atomic scales. Actually, once we have established what the microscopic laws of Nature are, we have to conclude that these are the truly fundamental ones, whereas those of classical mechanics are approximate versions of the quantum laws, valid only in the limit of macroscopic bodies. The fact that depending on the size of a physical system the quantum laws get simplified into the classical ones means that we can define what is "big" and what is "small" in absolute terms. This fact is related to the existence in Nature of a fundamental, dimensional constant, the Planck constant $h = 6.63 \cdot 10^{-34}$ J s.

For example, in quantum mechanics angular momentum is quantized and can only take values equal to multiples of $\hbar/2$ ($\hbar = h/2\pi$). If one has to deal with a system whose typical size of angular momentum is orders of magnitude larger than $\hbar$, then it is understandable that he will not notice that angular momentum is quantized and will treat it as a quantity which can vary continuously, as in classical mechanics. The Planck constant is not the only dimensional fundamental constant of Nature: another one is c, the velocity of light and of any other massless particle. In fact it is the maximal velocity allowed in Nature. The existence of this constant implies that we can define in absolute terms whether a velocity is big or small. If we deal with small velocities, then we can take certain approximations (which again correspond to the classical mechanics) and forget about the special theory of relativity. The third fundamental constant of Nature is Newton's gravitational constant G_N. If you are intrigued by the concept of fundamental dimensional costants in Nature and by the fact that they define big and small in absolute terms, I suggest you to read Ref. [1]. Three well known

physicists present their different views on this subject and claim that the number of fundamental dimensional constants in Nature is a) three, b) two, c) zero[1]. From what I wrote is clear that I symphatize with answer a), but you may end up with a different answer after reading this paper.

One of the founders of quantum mechanics, P.A.M. Dirac writes in the introduction of his book that a change in the laws of Nature that would allow us to define big and small in absolute terms is to be expected. He writes [2]:
"The necessity to depart from classical ideas when one wishes to account for the ultimate structure of matter may be seen, not only from experimentally established facts, but also from general philosophical grounds. In a classical explanation of the constitution of matter, one would assume it to be made up of a large number of small constituent parts and one would postulate laws for the behaviour of these parts, from which the laws of the matter in bulk could be deduced. This would not complete the explanation, however, since the question of the structure and stability of the constituent parts is left untouched. To go into this question, it becomes necessary to postulate that each constituent part is itself made up of smaller parts, in terms of which its behaviour is to be explained. There is clearly no end to this procedure, so that one can never arrive at the ultimate structure of matter on these lines. So long as *big* and *small* are merely relative concepts, it is of no help to explain the big in terms of the small. It is therefore necessary to modify classical ideas in such a way as to give meaning to size."

In closing this introduction I will also warn you (as many books and lecture notes on quantum mechanics do), that because we are macroscopic bodies and have experience of the physics of other macroscopic bodies, we have developed an intuition (at least some) for classical physics and not for quantum mechanics. Understanding quantum mechanics is therefore difficult – some very famous physicists claim that nobody truly understands it and the best you can hope is to be able to use it. This is by no means meant to discourage you: trying to understand it is a wonderful challenge on which you should not give up. Still, you should first learn how to use it, and for this I hope that these notes will be helpful.

In the rest of this introduction I will discuss a few of the crucial experiments which paved the way to the formulation of quantum mechanics: first those which showed that light consists of single quanta, called photons, which behave like particles and then a Gedankenexperiment which shows that electrons behave like waves, like light.

[1] At a summer school some years ago I heard C. Tsallis argue that the number of fundamental constants is actually four, the fourth being Boltzmann's constant. Unfortunately I do not have a reference where you can read arguments in favour of this point of view

1.1 Black body radiation

Let us consider a cavity in thermal equilibrium, at a certain temperature T. The walls of the cavity will absorb and emit radiation with a certain probability which depends on the temperature. Inside the cavity there are photons in thermal equilibrium and the energy density of photons of frequency ν depends on the temperature – it will be given by a function $u(\nu, T)$. This energy density can be measured if one looks at the radiation coming out of a little hole in the cavity. It can be shown that the emissive power (energy emitted per frequency per unit area, per unit time) of this cavity is directly proportional to the energy density $u(\nu, T)$. Measurements and theoretical work on the properties of the black body radiation were performed at the end of the 19th century.

In 1894 Wien showed that the energy density divided by the cube of the temperature had to be a function of one variable only, ν/T:

$$\frac{u(\nu, T)}{T^3} = f\left(\frac{\nu}{T}\right) , \tag{1.1.1}$$

as was confirmed by measurements. With the help of a model he then predicted the form of the function to be

$$u(\nu, T) = C\nu^3 e^{-\beta\nu/T} . \tag{1.1.2}$$

This function has two free parameters, and by appropriately adjusting these, would indeed reproduce the measurements of the function u, but only as far as the high frequency part of the spectrum was concerned. In 1900 Rayleigh showed that classical physics arguments required an energy distribution of the form (this formula goes under the name of Rayleigh-Jeans law, after Jeans corrected a minor mistake in Rayleigh's original formula)

$$u(\nu, T) = \frac{8\pi\nu^2}{c^3} k_B T , \tag{1.1.3}$$

where $k_B = 1.38 \cdot 10^{-23}$ J/K is Boltzmann's constant. What goes into this formula is the density of modes of frequency ν, which is equal to $8\pi\nu^2/c^3$ as we will see below, and the average energy of each mode, which is taken to be equal to $k_B T$. Such a formula cannot be correct at high frequencies, because the quadratic dependence on the frequency prevents the integral over all frequencies (giving the total energy contained in the cavity) from converging. On the other hand it described the low frequency part of the spectrum quite well.

In 1900 Planck proposed a formula which interpolated between the successful formula at low and at high frequencies, namely

$$u(\nu, T) = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{h\nu/k_B T} - 1} , \tag{1.1.4}$$

and could indeed describe the data over the whole spectrum. The only adjustable parameter appearing in his formula, h, was determined by fitting experimental data and later became known as the Planck constant, which we have introduced already. Although Planck originally derived his formula as a simple interpolation between two successful ones, he later provided an interpretation of it as a distribution of photons in thermal equilibrium.

His derivation was as follows: assume that the energy associated with the allowed modes of the electromagnetic field in the cavity could not vary continuously, but had to be the multiple of a minimum energy ϵ. Then the average energy associated with each mode can be derived using Boltzmann's probability distribution[2]

$$P(E) = \frac{e^{-E/k_B T}}{\mathcal{N}} \, . \tag{1.1.5}$$

The calculation of the average energy gives

$$\bar{E} = \sum_E E P(E) = \frac{1}{\mathcal{N}} \sum_{n=0}^{\infty} n\epsilon e^{-n\epsilon/k_B T} = \frac{\epsilon}{e^{\epsilon/k_B T} - 1} \, . \tag{1.1.6}$$

The correct result is then obtained by identifying[3] $\epsilon = h\nu$.

In order to get the energy density in the cavity we still have to count how many modes of frequency ν per unit volume we have. If we consider a square cavity of finite size and assume periodic boundary conditions at the walls, the allowed momenta for the photons are discrete

$$\vec{k} = \frac{2\pi}{L} \vec{m} \tag{1.1.7}$$

where $\vec{m}$ is a vector with integer components. For every momentum we have two possible polarization states for the photons, and so have to count every $\vec{m}$ twice. We now consider a very large volume and instead of summing over all vectors $\vec{m}$ we integrate over d^3k. The average energy is then given by

$$\langle E \rangle = 2 \left(\frac{L}{2\pi} \right)^3 \int d^3k \bar{E} = L^3 \frac{1}{\pi^2} \int k^2 dk \frac{h\nu}{e^{h\nu/k_B T} - 1} \, . \tag{1.1.8}$$

Making a variable transformation from k to $\nu = k/2\pi c$ and dividing the result by the volume L^3 we can read off the formula for the energy density $u(\nu, T)$ and see that it agrees with Planck formula (1.1.4).

[2] $\mathcal{N} = \sum_E e^{-E/k_B T}$ ensures that the distribution is correctly normalized.

[3] Or $\epsilon = \hbar\omega$ if one prefers to use the angular frequency $\omega \equiv 2\pi\nu$. Warning: sometimes ω is also called "frequency" – confusion, however, does not usually arise, because the context makes clear which one is meant.

1.2 The photoelectric effect

In classical electrodynamics – the theory which describes the behaviour of electromagnetic radiation and its interaction with macroscopic bodies – moving charges can emit or absorb electromagnetic waves. The emitted energy per unit time depends on some continuously varying quantities, like the charge and the acceleration (cf. for example the Larmor formula). Macroscopic bodies can emit any amount of energy in electromagnetic radiation. Like for angular momentum, this statement is only an approximation which is valid when the amount of emitted energy is "large". If one makes experiments which are sensitive to the behaviour of microscopic entities (like electrons) as they emit or absorb radiation, one soon discovers that the classical picture does not hold and that radiation is absorbed and emitted in quanta (photons). One such experiment is the one measuring the photoelectric effect, which was discovered by Hertz in 1887: if light is shone onto a metal, this may extract electrons out of the metal.

In order for this to happen, the electromagnetic radiation has to provide single electrons enough energy to overcome the binding force which keeps them inside the metal. In classical electrodynamics the energy of electromagnetic radiation is given by the modulus squared of the fields. One would have expected that in order to make the effect happen and then to increase the number of electrons extracted from the metal one simply had to increase the intensity of the electromagnetic radiation.

The surprising experimental facts which contradicted the classical expectations were the following:

1. the photoelectric effect happens if the electromagnetic radiation shone onto the metal has a frequency which is higher than a certain threshold ν_0. This threshold varies from metal to metal. If the light has a frequency smaller than ν_0 the effect does not take place, independently of the intensity;

2. the number of electrons extracted from the metal (photoelectrons) is proportional to the intensity of the light source (provided its frequency is higher than ν_0);

3. the kinetic energy of the photoelectrons is independent of the intensity of the light source but varies linearly with the difference $\nu - \nu_0$, where ν is the frequency of the incoming light.

An explanation of all these experimental facts (in fact the latter of them was a prediction later verified by the experiments of Millikan) was provided by Einstein, who postulated that light of frequency ν consisted of quanta, each of which carries an energy $h\nu$. Electrons would then be able to absorb a single one of these quanta and correspondingly increase their energy by $h\nu$. Assuming that for each metal there is a different minimal binding energy $W = h\nu_0$ (also called

work function) for the electrons contained in it, the extraction of electrons can happen only if $h\nu > W$. The excess of energy will stay with the electron in form of kinetic energy:

$$\frac{1}{2}m_e v^2 = h\nu - W = h(\nu - \nu_0) \ .$$

This formula directly displays also the threshold in frequency. It is also obvious that if the light has a high enough frequency, the higher the intensity, the higher the number of photons which hit the metal and therefore the higher the number of extracted electrons.

1.3 The Compton Effect

The effect discovered by Arthur H. Compton in 1923 also showed unmistakably that radiation in certain circumstances behaves like particles. He shot X rays through a thin metallic foil and measured the scattered radiation after the foil. In classical electrodynamics a free particle (electrons in this case – we will ignore the binding force inside the metal) which is subject to an oscillating electromagnetic field of frequency ν, oscillates with the same frequency. In turn, a charged particle oscillating with frequency ν will emit radiation of the same frequency. This means that the expectations based on classical physics are that the scattered radiation after the foil would have the same frequency as the incoming radiation. The angular dependence of the intensity of the scattered radiation can also be calculated and reads $(1 + \cos^2\theta)$.

The measurement of Compton showed that the outgoing radiation had both a component with the same frequency and a component with a shifted frequency. In order to interpret the result of his experiment, Compton assumed that radiation consists of photons, which behave as normal particles. The energy of a photon is $h\nu$ (as already postulated by Einstein) and its momentum $p = h\nu/c$. A simple calculation of relativistic kinematics shows that the energy of the outgoing photon depends on the scattering angle according to the formula (we have assumed that the electron off which the photon scatters is at rest)

$$\nu' = \frac{\nu}{1 + \frac{h\nu}{m_e c^2}(1 - \cos\theta)} \ . \tag{1.3.1}$$

1.4 The double slit experiment

The experiments we have discussed so far show that electromagnetic radiation is actually made of quanta, photons, which behave like particles, if one looks at them with the appropriate tool. Electrons were discovered as particles, but the experiment we are going to discuss now shows that they also behave like waves. We first discuss the experiment for macroscopic particles (bullets, say), then for waves and finally for electrons.

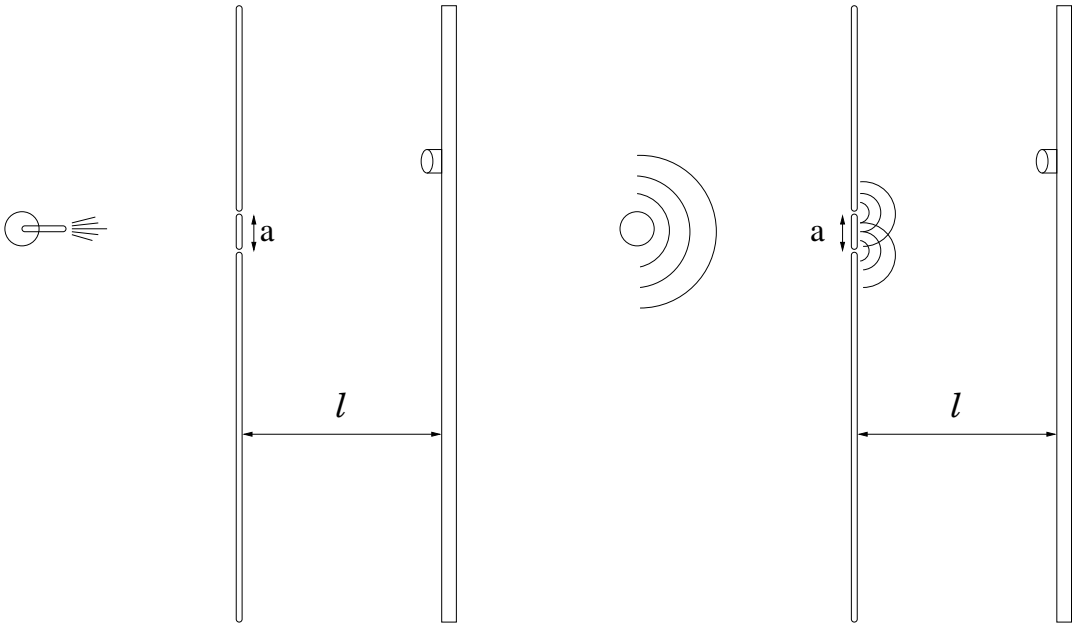

Figure 1.1: Schematic view of the double-slit experiment in case of bullets (left) and waves (right).

The setup is as follows: we have a source of bullets, a gun which shoots them in a certain direction but not quite precisely, so that each shot comes out with a random angle around the central direction. At a certain distance from the source we have a screen, a wall which stops the bullets. The wall has two slits, and behind it we have a second wall where we can place our detectors, which tell us where the bullets have hit the wall. The setup is schematically drawn on Fig. 1.1. Note that not only the bullets which can go exactly through the slits will hit the second wall (this would mean that all bullets would concentrate in a very small spot). We assume that the borders of the slit will deflect the bullets which hit them: as a consequence the distribution of the bullets on the second wall will be rather broad. We can do the experiment and measure how many bullets hit the wall at a distance y from the center, first keeping slit 2 closed, and then slit 1 closed. The bullets going through slit 1 (2) have a distribution $I_{1(2)}$ which has a maximum shifted somewhat to the right (left) with respect to the center of the wall ($y = 0$), as illustrated in Fig. 1.2. If we now repeat the experiment with both slits open, the outcome is shown on the right panel of Fig. 1.2 and is simply the sum of the two distributions. Actually we do not need to first close one slit at the time and then open both of them: if we do directly the experiment with both slits open, we can simply check through which slit each bullet goes, and measure at once both distributions. If we do things this way it is then obvious that the distribution I_{12} that we measure with both slits open is

$$I_{12} = I_1 + I_2 \ .$$

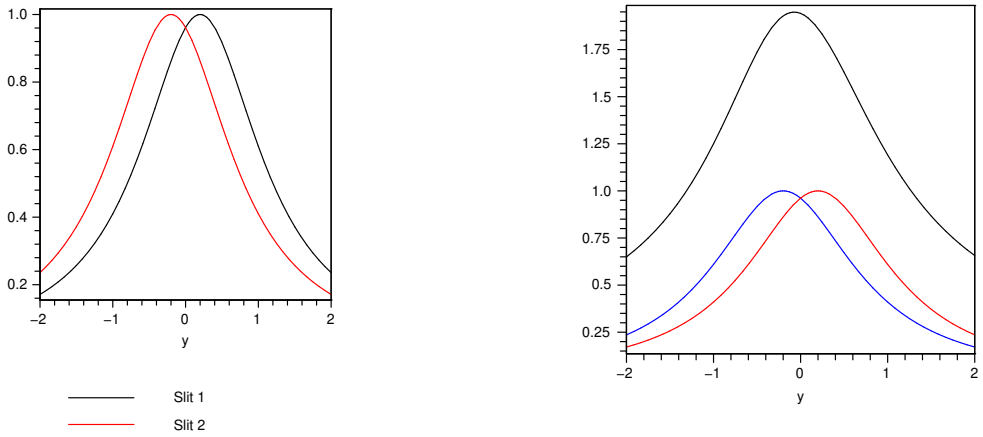

Figure 1.2: Distribution of the bullets going through slit 1 or 2 (left), and total distribution (right). The latter is the sum of the two.

There is another rather obvious remark to be made at this point. Each bullet goes through slit 1 or 2 and hits the wall only at one place. In other words, if we cover the wall with detectors, it will hit only one of them, while all the others will give no signal. This is how particles behave: they are in a well defined point in space at any time.

If we arrange a similar experiment with waves, the situation and the results will be rather different as illustrated schematically in Fig. 1.1. A wave is a nonlocal object and for none of the questions we already asked for bullets we get a sharp, yes-or-no kind of answer. For example when a wave hits the first wall it does get stopped by the wall, but only in part. In part it goes through slit 1 and in part through slit 2. If we then want to measure where the wave hits the second wall, we have first to formulate the question differently, because the wave hits the wall everywhere. One way to ask the question, for example, is how much energy is carried by the wave at each point where it reaches the wall. If the amplitude of the wave is ϕ, the energy is proportional to $|\phi|^2$, and so to answer the question we need a detector that measures $|\phi|^2$.

Each of the two slits acts as a source of a spherical wave. The amplitudes of the two waves have the form

$$\phi_i(\vec{x}, t) = A(r_i)e^{i(kr_i - \omega t)} \tag{1.4.1}$$

where $k = 2\pi/\lambda$ is the wave vector, $r_i = |\vec{x} - \vec{x_i}|$ the distance from the center of the slit $\vec{x}_i$, and $\omega = kv$ the angular frequency, with v the velocity of the wave. If we measure how much energy is deposited on the wall as a function of y and open the two slits one at a time, we will find a shape similar to the one observed for the bullets, cf. Fig. 1.2 – the exact form being given by $|A(r_i)|^2$ (on the second wall, r_i is a function of y only). The big difference among bullets and waves will

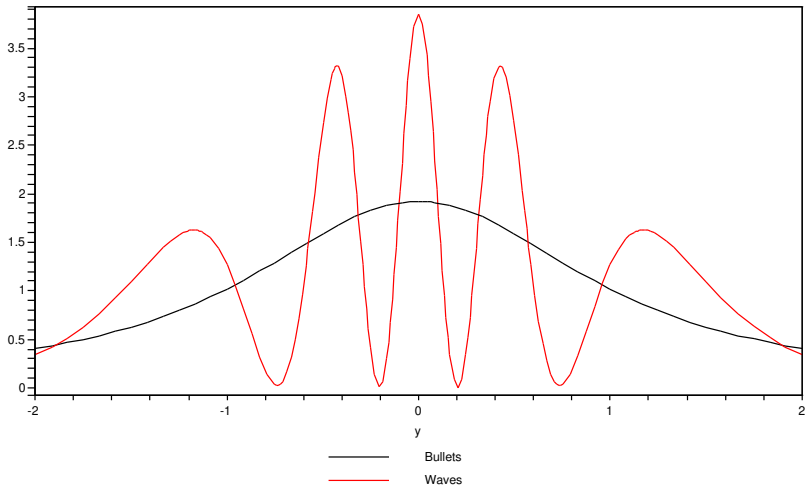

Figure 1.3: Distribution of the energy of the waves as they arrive on the wall when both slits are open, compared to the distribution of bullets in the same case.

be apparent as we open both slits and measure the energy which arrives on the wall. In this case we get:

$$\begin{aligned} I_{12}(y) &= |\phi_1+\phi_2|^2 = |A(r_1)|^2 \left|1+\frac{A(r_2)}{A(r_1)}e^{ik(r_2-r_1)}\right|^2 \\ &\sim |A(r_1)|^2 \left|1+e^{ik(r_2-r_1)}\right|^2 \quad , \end{aligned} \tag{1.4.2}$$

where in the last step we have neglected the different size of $A(r_1)$ and $A(r_2)$. A plot of this distribution (for a certain value of k) is shown in Fig. 1.3 and compared to the same distribution in case of bullets. The new feature is the appearance of several maxima and minima which are higher or lower than the sum of the two intensities. The maxima occur when $k(r_2 - r_1) = 2\pi n$ and the minima when $k(r_2-r_1) = (2n+1)\pi$. Translated in a condition on the wavelength, one sees more than just one maximum provided the wavelength is smaller than twice the distance between the two slits: $\lambda < 2a$. The presence of both waves implies an interference among them – in this case the energy is distributed very differently from the energy distribution of each of them and of the sum. This shows the different nature of particles and waves: if a particle which goes through slit 1 hits the wall in a certain place, it does not care whether at the same time slit 2 was open or closed. For a wave this is different: a wave going through slit 1 does notice if at the same time there is another way propagating in the same region of space, because the way in which the medium gets deformed (if we are talking, e.g., of waves on the surface of water) changes.

If we do the experiment with electrons[4], the whole setup looks very much like the one for bullets: an electron gun can shoot electrons one by one, and when the electrons hit the detectors on the second wall, only one detector at a time gives a signal. As for bullets we then expect that the electrons go either through slit 1 or 2 and that if we do the experiment with both slits open, what we get is the sum of the two distributions. Surprisingly, this is not true. If we count the electrons which hit each detector and make an histogram which shows us the distribution of the events as a function of y, we see the interference pattern just like for waves. Clearly we are facing a contradiction because if the electrons go through either of the two slits, keeping both slits open at the same time cannot generate anywhere a depletion of the counts of electrons with respect to the case when only one slit is open.

We can try to solve the contradiction experimentally and find a way to detect which of the slits each electron went through. For example we can place a source of light just behind the first wall and use the interaction of photons and electrons in order to see where the electron went through. We will need to place extra detectors sensitive to photons, that allow us to see a flash of light and identify whether it comes from slit 1 or 2. If we do this and are indeed able to see which slit the electrons went through something even more surprising happens: the interference patterns disappear. This may actually not be very surprising, after all – because this source of light has made the old experiment into a new one, and the same things do not have to necessarily happen. Maybe this was not quite the right thing to do. We may try next to reduce the intensity of the light so that the electrons get disturbed less. Below a certain intensity we will realize that the flash of light does not happen with each electron. In this case, the electrons which are not detected at the slits do generate an interference pattern, but those which are detected not. The total distribution is then the sum of these two components.

A second attempt may be to reduce the frequency of the light which should detect the electrons. A photon of frequency ν carries energy $h\nu$ and if ν is too high so is the energy of the photon and this must disturb substantially the electrons which get detected. As we reduce the frequency nothing really happens and we do not see the interference patterns reappear (provided all electrons are seen as they go through the slits) – well, unless the wavelength of the photons becomes of the same order of a, the distance between the two slits. In this case the photons do not allow us to identify the slit through which the electrons are going: the resolving power of this photons is of the order of their wavelength, and the two slits are not distinguishable by these photons. In this case the interference patterns reappear.

One may try other ways to see the electrons go through the slits without

[4]This experiment has actually been carried out by a few different groups. More details can be found in the following web pages:
`http://physicsworld.com/cws/article/print/9745` and
`http://www.hqrd.hitachi.co.jp/em/doubleslit.cfm` .

destroying the interference patterns, but they are all going to fail. The contradiction we have discussed above is a real one: if we know through which slit the electrons go, then there cannot be interference, and indeed there isn't. When interference happens this is because we have not determined whether the electron went through slit 1 or 2. More importantly, the contradiction would be there even if we were not able to detect the electrons, but they would indeed go through either slit 1 or 2. We have to conclude that if we do not detect the electrons at the slits, they **do not** go either through slit 1 or 2, but in some sense through both.

This is one of the first disturbing encounters we have with quantum mechanics, and will probably give you a lot to think, and make you try to find alternative explanations to these astonishing facts. Many people have tried and the only successful explanation of this experiment is that electrons are described by wave functions, $\Psi(\vec{x}, t)$ and that the modulus squared of the wave function gives us the probability per unit volume to find an electron in a small region around $\vec{x}$ at time t. If I do the experiment with slit 1 (2) open, I describe the electrons with a wave function $\Psi_{1(2)}(\vec{x}, t)$ and see a distribution on the second wall equal to $I_{1(2)}(y) = |\Psi_{1(2)}(l, y, t)|^2$, where l, as shown in Fig. 1.1 is the distance between the first and the second wall. If I now do the experiment with both slits open, each electron will have the same probability to go through slit 1 as to go through slit 2 and its state will be described by the wave function $\Psi_1 + \Psi_2$[5]. The distribution at the second wall in this case will be given by $|\Psi_1 + \Psi_2|^2$ and will show the typical interference pattern of waves.

Why do we not see these phenomena with macroscopic object like bullets? If the laws of quantum mechanics are more fundamental than those of classical mechanics, then they must be valid even for small pieces of matter – should we not see interference patterns for them too? In order to answer this question we can rely on the concept of de Broglie waves. He postulated that just like photons, also particles (like electrons) behave like waves, and that their wave parameters are related to the particle properties in the same way as for photons. A photon of momentum $\vec{p}$ has wave vector $\vec{k} = \vec{p}/\hbar$. According to de Broglie this is also true for particles. If we consider a macroscopic object, say with a mass of a fraction of a gram, which moves slowly, with a speed of a fraction of a centimeter per second, and calculate its de Broglie wavelength, we obtain something several orders of magnitude smaller than the size of a proton – it would be quite difficult to make two slits separated by a distance larger but comparable to this one! In any case the distance between the maxima and minima of the interference pattern would be of the order of the de Broglie wavelength, and therefore undetectable. This is the reason why we never see such phenomena with macroscopic objects.

[5]There is a normalization of the wave function to worry about, but we ignore it for the moment and will discuss it in detail later.

1.5 Quantum mechanics: timeline

We close the chapter with the quantum mechanics timeline. The reader interested in historical aspects of the developments of this beautiful theory is referred to the vast literature on the subject (for a compact account, see, *e.g.* Ref. [3]).

Year	Discoverer	Event
1897	Thomson(41)	Discovery of the electron
1900	Planck(42)	Explanation of the blackbody spectrum
1905	Einstein(26)	Explanation of the photoelectric effect
1911	Rutherford(40)	Discovery of the nucleus
1913	Bohr(28)	Atomic model, angular momentum quantization
1922	Stern(34), Gerlach(23)	Deflection of particles with angular momentum going through a magnetic field
1923	De Broglie(28)	Particle-wave duality
1924	Pauli(24)	Formulation of the exclusion principle
1925	Heisenberg(23)	Matrix mechanics
	Born(41), Jordan(22)	(further developed the theory with Heisenberg)
	Uhlenbeck(25)	Hypothesis of the existence of
	& Goudsmit(23)	intrinsic angular momentum (spin)
1926	Schrödinger(38)	Wave mechanics – formulation of his equation
	Dirac(24)	Formal aspects of quantum mechanics (correspondence Poisson brackets–commutators)
1927	Pauli	Theory of spin
1928	Dirac	Relativistic quantum mechanics: Dirac equation
1932	von Neumann(29)	Axiomatization of quantum mechanics
1935	Einstein, Podolsky(39)	EPR paradox
	& Rosen(26)	
1941	Feynman (23)	Path-integral formulation of quantum mechanics
1964	Bell (36)	Formulates his famous inequalities
1982	Aspect (35)	Experimental proof that Bell's inequalities are violated

Table 1.1: Chronology of the main events which marked the developments of quantum mechanics. The numbers in parentheses close to the names, indicate the age of the people at the time of their discoveries.

Chapter 2

The wave function

2.1 The Schrödinger equation

In quantum mechanics the state of a particle is fully specified by its wave function $\Psi(x,t)$, which only allows us to calculate the probability to find the particle in a given region of space, and never to answer the question "where will the particle be at time t?". This is a lot less than in classical mechanics where, in principle, one is able to predict the position of a particle $x(t)$ at any later time if the initial conditions for the position $x(t_0)$ and velocity $\dot{x}(t_0)$ of the particle are known. As we have seen, physicists have been forced to become infinitely less ambitious by a number of experiments which could not be explained within classical physics – Nature really gave us no choice.

Although less ambitious, the goal of quantum mechanics is still to predict the future evolution of a physical system based on the knowledge of the dynamics of that system. This is done through a differential equation which conceptually plays the role of the Newton equation in classical mechanics. Such an equation was first formulated by Schrödinger in 1925 and has the following form

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2M}\frac{\partial^2\Psi}{\partial x^2} + V\Psi \quad . \tag{2.1.1}$$

Given a potential energy V, and appropriate initial conditions $\Psi(x,t_0)$ the solution of the equation predicts the state of the system in the form of the wave function at any time $t > t_0$. Notice that in contrast to Newton's equation, this is of first order, and that instead of the force, the potential energy appears – the relation among potential energy and force is $F = -\partial V/\partial x$.

2.2 A heuristic derivation

A good way to convince oneself that the Schrödinger equation is the right one is the following. We start from the idea that particles also behave (and can

therefore be described) like waves. According to De Broglie (1923) it is reasonable to assume that the relations between energy and frequency, and momentum and wavelength which one has established for photons should also be valid for particles. These read:

$$p = \frac{h}{\lambda} , \qquad E = h\nu \ . \tag{2.2.1}$$

For a nonrelativistic particle energy and momentum are also related by $E = p^2/2M$. This implies a relation between frequency and wavelength for particles, which is different from the one valid for photons, $\nu = c/\lambda$.

When we consider waves, we never deal with exactly monochromatic ones, but rather have to do with a superposition of plane waves of different wavelengths. Something of the form

$$f(x,t) = \int dk \; g(k) \; e^{i(kx-\omega t)} \ , \tag{2.2.2}$$

where ω is usually a function of k (which is related to the wavelength by $k = 2\pi/\lambda$) – for photons, $\omega = ck$. The same will happen with the function describing quantum particles, and if we use p instead of k and E instead of ω, a wave function will look like:

$$\Psi(x,t) = \int dp \; \phi(p) \; e^{i(px-Et)/\hbar} \ . \tag{2.2.3}$$

The nonrelativistic relation between E and p has to be required for the integrand, because that contains the contributions of fixed momentum and energy. The relation $E = p^2/2M$ is equivalent to the equation

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2M} \frac{\partial^2 \Psi}{\partial x^2} \tag{2.2.4}$$

as can be easily seen by bringing the derivatives inside the integrals in Eq. (2.2.3). This is the Schrödinger equation for a free particle, in the absence of a potential. If the particle of interest is submitted to a force, its energy is shifted by the potential energy (assuming the force is not dissipative, *i.e.* that it can be written as $F = -dV/dx$). If we do this and add a term of the form $V(x)\Psi(x,t)$ to the right-hand side of Eq. (2.2.4), we obtain exactly the Schrödinger equation (2.1.1).

2.3 Normalization, probability

The wave function represents the probability amplitude and its modulus squared gives the probability density – the probability to find the particle in the volume dx around the point x at the time t is given by $|\Psi(x,t)|^2 dx$. If we now integrate this over a finite interval (a,b) we get

$$P(a,b) = \int_a^b dx |\Psi(x,t)|^2 \ , \tag{2.3.1}$$

the probability that an experiment will detect a particle in that interval. If we now extend the integration limits to infinity, we must get $P(-\infty, \infty) = 1$, because it is certain that the particle will be detected somewhere. This implies that the functions which can represent physically meaningful solutions of the Schrödinger equation must have a square which is integrable. Moreover, they have to be normalized such that

$$\int_{-\infty}^{\infty} dx |\Psi(x,t)|^2 = 1 \quad . \tag{2.3.2}$$

Even if we restrict our search for solutions of the Schrödinger equation to functions which have an integrable modulus squared, and choose the initial conditions such that Eq. (2.3.2) is satisfied at $t = t_0$ nothing guarantees a priori that the normalization condition stays constant in time. If that were not the case we would be in serious trouble, because in order to make sense of the solution of the Schrödinger equation as a properly defined probability amplitude, we would have to multiply it with a time-dependent normalization. The predictive power of the Schrödinger equation would be lost.

It is therefore important to check that the normalization of any solution of the Schrödinger equation is a constant:

$$\frac{d}{dt}\int_{-\infty}^{\infty} dx |\Psi(x,t)|^2 = \int_{-\infty}^{\infty} dx \left(\frac{\partial \Psi^*}{\partial t}\Psi + \Psi^* \frac{\partial \Psi}{\partial t} \right) \quad . \tag{2.3.3}$$

We can now use Eq. (2.1.1) substitute the time derivatives of Ψ and Ψ^* with the right-hand side of the Schrödinger equation. It is easy to see that the term with the potential energy drops out and what we are left with is

$$\frac{\partial}{\partial t}|\Psi|^2 = \frac{i\hbar}{2M}\left(\Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \frac{\partial^2 \Psi^*}{\partial x^2}\Psi \right) = \frac{i\hbar}{2M}\frac{\partial}{\partial x}\left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x}\Psi \right) \quad . \tag{2.3.4}$$

Since the integrand is a derivative, the integral is trivial

$$\frac{d}{dt}\int_{-\infty}^{\infty} dx |\Psi(x,t)|^2 = \frac{i\hbar}{2M}\left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x}\Psi \right)\Big|_{-\infty}^{\infty} = 0 \quad . \tag{2.3.5}$$

The result is zero because, as we have seen, the wave function has an integrable square modulus, and therefore has to vanish at infinity faster than $x^{-1/2}$.

2.3.1 Probability current

In Eq. (2.3.5) we have seen that the total probability is conserved. On the other hand, if we consider the probability to find a particle inside a given interval (a, b) on the real axis, this changes in time. The change is given by the value of a function (the integrand in Eq. (2.3.5)) at the two endpoints of the interval, a and b:

$$\frac{d}{dt}P(a,b,t) \equiv \frac{d}{dt}\int_a^b dx |\Psi(x,t)|^2 = \frac{i\hbar}{2M}\left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x}\Psi \right)\Big|_a^b \quad . \tag{2.3.6}$$

By working in one space dimension we make this relation not particularly illuminating, but with a little imagination we can view the right-hand side of Eq. (2.3.6) as the flux of a current $j(x,t)$ through the boundaries of an interval, the current being

$$j(x,t) \equiv -\frac{i\hbar}{2M}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right) \quad . \tag{2.3.7}$$

What requires a little imagination in the one-dimensional case is completely obvious in three spatial dimensions, and to illustrate our statement that we indeed have found the probability current we briefly discuss the latter case. The Schrödinger equation in three dimensions reads

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2M}\triangle\Psi + V\Psi \quad , \tag{2.3.8}$$

where $\triangle \equiv \partial_x^2+\partial_y^2+\partial_z^2$ is the Laplace operator. The probability to find a particle inside a volume V is then given by the volume integral

$$P(V,t) = \int_V d^3x|\Psi|^2 \quad , \tag{2.3.9}$$

and its derivative in time is

$$\frac{d}{dt}P(V,t) = \frac{i\hbar}{2M}\int_V d^3x\nabla\cdot(\Psi^*\nabla\Psi - \nabla\Psi^*\Psi) = -\int_{\partial V} d\vec{S}\cdot\vec{J} \quad , \tag{2.3.10}$$

where $\vec{J} \equiv -i\hbar/2M(\Psi^*\nabla\Psi - \nabla\Psi^*\Psi)$ is the probability current, now a vector, in three dimensions. If we define the modulus square of the wave function as the probability density, then Eq. (2.3.10) can be rewritten as

$$\int_V d^3x\left[\dot{\rho} + \nabla\cdot\vec{J}\right] = 0 \quad , \tag{2.3.11}$$

and since this is valid for any volume, it is the integrand which has to vanish:

$$\dot{\rho} + \nabla\cdot\vec{J} = 0 \quad . \tag{2.3.12}$$

Eq. (2.3.12) is the continuity equation for probability in quantum mechanics and gives sense to calling $\vec{J}$ the probability current. In one spatial dimension the equation becomes

$$\frac{\partial\rho}{\partial t} + \frac{\partial j}{\partial x} = 0 \quad , \tag{2.3.13}$$

with $j(x,t)$ as defined in Eq. (2.3.7), the one-dimensional probability current.

2.4 Position

Given the state of a particle, as described by its wave function, where is its position? As we have learned, this question does not make sense in quantum mechanics, where one can only answer with which probability one will find the particle in a certain position. This is, however, not the only answer that we can get from the wave function. Since the latter provides a probability distribution, we can define some usual quantities which characterize the latter.

The median position is the position for which the probability that the particle is to its left is equal to the pobability that it is to its right:

$$\int_{-\infty}^{x_{\text{median}}} dx|\Psi|^2 = \frac{1}{2} \ . \tag{2.4.1}$$

The average position, often called expectation value, is the average of the values of x – obtained weighing each value of x with the probability distribution

$$\langle x \rangle = \int_{-\infty}^{\infty} dx x|\Psi|^2 \ . \tag{2.4.2}$$

The average squared position (or any other power) is given by

$$\langle x^n \rangle = \int_{-\infty}^{\infty} dx x^n|\Psi|^2 \ . \tag{2.4.3}$$

The standard deviation σ_x is defined as the square root of the average of $(x - \langle x \rangle)^2$:

$$\sigma_x^2 = \int_{-\infty}^{\infty} dx \left(x - \langle x \rangle\right)^2 |\Psi|^2 = \langle x^2 \rangle - \langle x \rangle^2 \ , \tag{2.4.4}$$

and provides a measure of how peaked around the expectation value a distribution is.

2.5 Velocity and momentum

The wave function tells us with what probability one finds a particle in a certain region of space as a function of time. Schrödinger's equation prescribes the evolution in time of this probability and tells us how fast this changes and with which sign. Although we can speak of time evolution in quantum mechanics, it is far from obvious whether a concept like velocity makes any sense. At the very least we have to define what we mean by "velocity". Let us imagine that a wave function of a particle is rather well peaked around a certain point x_0 at time t_0. At a later time $t_0 + dt$ the peak will have moved a little and will be at $x_0 + dx$ – in this case it would be natural to take dx/dt as a measure of the velocity of this particle. But what if the wave function is not peaked at all? Also, if we speak

of a peak and its movement in time, what do we mean exactly? The position of the maximum? The average value of x, the median value? We have to specify how exactly we want to define the concept of velocity in this case, and there is certainly more than way of doing this.

One rather natural way is to define the expectation value of the velocity as the derivative in time of the expectation value of the position:

$$\langle v \rangle = \frac{d\langle x \rangle}{dt} \quad . \tag{2.5.1}$$

Using the definition of $\langle x \rangle$ and again the Schrödinger equation we can rewrite this as follows

$$\frac{d\langle x \rangle}{dt} = -\int_{-\infty}^{\infty} dx x \frac{i\hbar}{2M} \frac{\partial}{\partial x} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) \quad . \tag{2.5.2}$$

Because of the factor x in the integrand we cannot immediately solve the integral, as we did when evaluating the time dependence of the normalization. In the present case we can, however, apply a partial integration (the wave function goes to zero fast enough at infinity such that $x(\partial\Psi^*/\partial x \Psi - \Psi^* \partial\Psi/\partial x)$ also vanishes there) to get

$$\langle v \rangle = -\frac{i\hbar}{2M} \int_{-\infty}^{\infty} dx \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) = -\frac{i\hbar}{M} \int_{-\infty}^{\infty} dx \Psi^* \frac{\partial \Psi}{\partial x} \quad . \tag{2.5.3}$$

Having an expression for the velocity (its expectation value) we can immediately get the one for the momentum, obtained by simply multiplying the velocity by the mass

$$\langle p \rangle = \int_{-\infty}^{\infty} dx \Psi^* \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi \quad . \tag{2.5.4}$$

This way of writing emphasizes the similarity to the expression for the expectation value of the position. The factor x in Eq. (2.4.2) is substituted with the derivative with respect to x, multiplied with the factor $-i\hbar$. As we will see later such an expression is very general in quantum mechanics – the expectation value of any physical quantity is obtained through an integral of the type Eq. (2.4.2) or (2.5.4). What stays between brackets is the quantum mechanical representation of the physical quantity – in general this is given by an operator in the space of the wave functions. Indeed both x (the multiplication with) and the derivative in x are operators on wave functions. We will formalize these concepts later, but we can now already anticipate that, if we can write a quantity as a function of x and p in classical mechanics, $Q(x, p)$, the quantum mechanical representation generalizes this function to the corresponding operators:

$$\hat{Q}(x, p) = Q(\hat{x}, \hat{p}) = Q\left(x, \frac{\hbar}{i} \frac{\partial}{\partial x} \right) \quad , \tag{2.5.5}$$

where with the hat on any symbol we indicate the operator that corresponds to the physical quantity identified by that symbol. As an example we mention the kinetic energy which, in classical mechanics, is given by $T = p^2/2M$. In quantum mechanics we then have

$$\hat{T} = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x^2} \ , \qquad \langle T \rangle = -\frac{\hbar^2}{2M}\int_{-\infty}^{\infty} dx \ \Psi^* \frac{\partial^2 \Psi}{\partial x^2} \ . \tag{2.5.6}$$

2.6 The uncertainty principle: a qualitative discussion

Now that we have discussed how to evaluate both the expectation value as well as the standard deviation of position and momentum, it is hard to resist to discuss at a qualitative level what the uncertainty principle is. Quantitatively, the principle takes the form of the following inequality

$$\sigma_x \sigma_p \geq \frac{\hbar}{2} \ . \tag{2.6.1}$$

For any wave function which is a solution of the Schrödinger equation, the product of the standard deviation of position and of momentum has to be larger than half the reduced Planck constant. The inequality holds independently from the specific form of the potential. Where does such a general result come from? It is a mathematical result in the theory of Fourier transformations – the only physics input which enters the formula and which is specific of quantum mechanics is the relation among wavelength and momentum:

$$p = \hbar k = \hbar \frac{2\pi}{\lambda} \ . \tag{2.6.2}$$

If we substitute p with the wave vector k (or the wavelength λ), then $\hbar$ disappears from the formula and we see the purely mathematical result. This can be explained as follows. If we look at any wave phenomenon, it is impossible to construct a wave which has a well defined wavelength and which is at the same time sharply localized in space. Per definition, a wave of a definite wavelength extends everywhere in space. On the other hand, if we observe a wave which is well localized in space, and make its Fourier transformation, i.e. we describe it as a superposition of plane waves, we need the contribution of very many plane waves with very different wavelengths. Such a wave has no definite wavelength – if we evaluate the average value of the wavelength and the corresponding standard deviation, we are going to find that the latter is very large. Intuitively, it is quite well understandable. As we will see later, one can give this discussion full mathematical rigour and prove the inequality (2.6.1), as was first done by Heisenberg.

Chapter 3

Time-independent Schrödinger equation

3.1 Eigenvalue equation for the energy

In this chapter we are going to solve the Schrödinger equation for a few simple potentials, and in one spatial dimension. In order to do this we will first look for solutions of a very special form. We separate the time and space variables and write the wave function as a product of two functions, each of a single variable:

$$\Psi(x,t) = \psi(x)\phi(t) \ . \tag{3.1.1}$$

At this point this may look like a rather restrictive choice, which may actually hinder us in getting any far in our search for solutions. As we will see very soon, this is not the case – for the moment let us just proceed and derive the equations for the two separate functions. The Schrödinger equation now looks as follows:

$$i\hbar\psi\frac{d\phi}{dt} = -\frac{\hbar^2}{2M}\frac{d^2\psi}{dx^2}\phi + V\psi\phi \ , \tag{3.1.2}$$

and this is already quite interesting, because if we divide it by $\psi\phi$ we notice that on the left-hand side only ϕ appears and on the right-hand side only ψ:

$$i\hbar\frac{1}{\phi}\frac{d\phi}{dt} = -\frac{\hbar^2}{2M}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + V \ . \tag{3.1.3}$$

Assuming that V is time-independent (in other words, we are considering isolated systems), the left-hand side is only a function of t and the right-hand side of x. Such an equation admits solutions only if both sides are constants:

$$i\hbar\frac{d\phi}{dt} = E\phi \ , \qquad -\frac{\hbar^2}{2M}\frac{d^2\psi}{dx^2} + V\psi = E\psi \ . \tag{3.1.4}$$

The equation for ϕ is trivial to solve: $\phi = C\exp(-iEt/\hbar)$. The constant C is relevant for the normalization of the wave function – this, however, only matters

for the product $\phi\psi$, and so when we discuss ϕ we can simply drop the constant C:

$$\phi = e^{-i\frac{Et}{\hbar}} \quad . \tag{3.1.5}$$

For this class of solutions the time dependence turns out to be particularly simple and is just an overall phase. This means, in particular, that the probability density is equal to

$$|\Psi(x,t)|^2 = |\phi(t)|^2|\psi(x)|^2 = |\psi(x)|^2 \quad , \tag{3.1.6}$$

and therefore time-independent. The expected value of any function of x is also time independent, and the same is true for expected values of any function of p – this means that any physical quantity, which can be expressed as a function of x and p in classical mechanics (basically all physical quantities), has a time-independent expectation value. The probability of any measurement of such a state is constant in time: such states are therefore called stationary.

We discover another remarkable property of these states if we look at the operator corresponding to the total energy. We have seen above that in quantum mechanics the operator for the kinetic energy is given by $(\hbar^2/2M)\partial^2/\partial x^2$. If we add to this the potential energy, $V(x)$ we get the operator for the total energy – the corresponding function is called Hamiltonian in classical mechanics, and therefore Hamiltonian operator in quantum mechanics:

$$H(p,x) = \frac{p^2}{2M} + V(x) \quad \Rightarrow \quad \hat{H} = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x^2} + V(x) \quad . \tag{3.1.7}$$

This is exactly the differential operator which acts on ψ in the second equation in (3.1.4), which can in fact be written as

$$\hat{H}\psi = E\psi \quad ,$$

i.e. as an eigenvalue equation for the Hamiltonian. The latter is also called the time-independent Schrödinger equation. We can look for solutions of this equation only if we specify the form of the potential energy $V(x)$, and this we will do in the following sections of this chapter for a few simple cases. The fact that the solutions of the time-independent Schrödinger equation are eigenvalues of the Hamiltonian implies that if we act on ψ with any power of $\hat{H}$ we always get $E^n\psi$ – if we evaluate the expectation value of any power of the energy, we get as result E to the same power:

$$\langle \hat{H}^n \rangle = \int dx \Psi^* \hat{H}^n \Psi = \int dx \psi^* \hat{H}^n \psi = \int dx \psi^* E^n \psi = E^n \quad . \tag{3.1.8}$$

The measurement of the energy of these states gives E with probability 1. The stationary states have a definite energy.

While all these are very interesting properties of these special solutions of the Schrödinger equation, we are still left with the question whether it is at all useful to consider these states in detail if our final goal is to solve the time-dependent Schrödinger equation. The answer is yes, because any solution of the Schrödinger equation can be written as a superposition (in general an infinite sum) of stationary states:

$$\Psi(x,t) = \sum_n c_n e^{-i\frac{E_n t}{\hbar}} \psi_n(x) \quad . \tag{3.1.9}$$

Obviously, as soon as one has more than one term in the sum (and two different energies $E_{n_1} \neq E_{n_2}$), the state is not stationary anymore, and the corresponding probability density is no longer time independent. From expression (3.1.9) one also sees that specifying the initial conditions, $\Psi(x,0)$ is equivalent to providing the coefficients c_n – once this is done, one immediately has the wave function at any later time, as the time dependence is fully given by the exponentials of time. This shows that if one has solved the time-independent Schrödinger equation (and therefore determined all eigenvalues E_n and all corresponding eigenfunctions ψ_n), the solution of the time-independent equation is obtained very easily.

3.2 The infinite square well

As a first example of a potential for which we solve the Schrödinger equation we consider a very simple one: it is zero in a finite interval and infinite everywhere else

$$V(x) = \begin{cases} 0 & 0 \leq x \leq a \\ \infty & \text{otherwise} \end{cases} \quad . \tag{3.2.1}$$

The wave function must then be confined to the same interval and is zero for $x < 0$ or $x > a$. The time-independent Schrödinger equation for this potential is a free-particle equation in this interval:

$$-\frac{\hbar^2}{2M}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \qquad 0 \leq x \leq a \quad . \tag{3.2.2}$$

This is a simple, ordinary differential equation,

$$\frac{d^2\psi(x)}{dx^2} = -k^2\psi(x) \quad , \qquad k = \frac{\sqrt{2ME}}{\hbar} \quad , \tag{3.2.3}$$

whose solution is well known:

$$\psi(x) = A\sin(kx) + B\cos(kx) \quad . \tag{3.2.4}$$

We assume that the solution (but not its derivative) is continuous at the borders of the interval:

$$\psi(0) = \psi(a) = 0 \quad \Rightarrow B = 0 \; , \quad A\sin(ka) = 0 \quad . \tag{3.2.5}$$

The latter condition has one trivial solution, $A = 0$, and an infinite number of nontrivial ones which are independent of A, but constrain k:

$$ka = n\pi \quad , n \in \mathbb{Z} \quad . \tag{3.2.6}$$

The value $k = 0$ gives the trivial solution $\psi(x) = 0$, whereas all negative values are equivalent to the positive ones, because the minus sign in the argument of the sine function can be reabsorbed in the sign of A, which is an irrelevant overall phase. We will therefore consider only positive values of n. The boundary conditions restrict the allowed k (and energy!) values to a discrete set, but leave the value of A still undetermined – we can now pin it down with the help of the normalization condition

$$\int_0^a dx|\psi(x)|^2 = 1 \quad . \tag{3.2.7}$$

The integral is easy to evaluate and gives

$$\int_0^a dx \sin^2\left(\frac{n\pi x}{a}\right) = \frac{a}{2} \qquad \Rightarrow \qquad A = \sqrt{\frac{2}{a}} \quad , \tag{3.2.8}$$

where we have arbitrarily chosen A to be positive exploiting our freedom in fixing its phase.

In this manner we have determined all eigenfunctions of the Hamiltonian – and also the eigenvalues, because the allowed values of k, which we obtained imposing the boundary conditions, provide us with the eigenvalues of the energy (cf. Eq. (3.2.3)):

$$E_n = \frac{n^2\pi^2\hbar^2}{2Ma^2} \quad . \tag{3.2.9}$$

We see here again that the sign of n does not matter, and that the eigenvalues of the energy are all positive. This is in accordance to a general result which is easy to prove[1]: the minimum eigenvalue of the energy is larger than the minimum of the potential. The corresponding eigenfunctions are

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \quad . \tag{3.2.10}$$

These eigenfunctions have a number of interesting properties which are worth listing here:

1. They all have a definite parity under inversions around the middle point of the interval $[0, a]$. The functions with an odd n are even and viceversa:

$$\psi_{2n+1}(x) = \psi_{2n+1}(a - x) \; , \qquad \psi_{2n}(x) = -\psi_{2n}(a - x) \quad . \tag{3.2.11}$$

[1]Rewrite the time-independent Schrödinger equation as $d^2\psi/dx^2 = 2M/\hbar^2(V - E)\psi$. If $E < V_{\min}$ then the right-hand side of the equation is a positive coefficient times ψ. This implies that such a solution does not approach zero at infinity and is therefore not normalizable. (This is just a hint, prove it!)

2. The n-th eigenfunction has $n-1$ zeros.

3. The eigenfunctions are mutually orthogonal

$$\int_0^a dx\psi_m^*(x)\psi_n(x) = 0 \quad \forall m \neq n \ . \tag{3.2.12}$$

(Evaluate the integral and show it!). Together with the normalization condition, we can express these relations in the following compact form

$$\int_0^a dx\psi_m^*(x)\psi_n(x) = \delta_{mn} \ . \tag{3.2.13}$$

4. The infinite set of all eigenfunctions $\psi_n(x)$ form a basis in the space of functions which satisfy the boundary conditions $f(0) = f(a) = 0$ and are continuous. This is a result of Fourier analysis. It means that any function $f(x)$ with these properties can be written as

$$f(x) = \sum_{n=1}^{\infty} c_n\psi_n(x) = \sqrt{\frac{2}{a}}\sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi x}{a}\right) \ , \tag{3.2.14}$$

and that the coefficients c_n are all zero if and only if the function itself is zero.

Given a function $f(x)$ the corresponding coefficients c_n can be obtained with the help of the following observation: Eq. (3.2.13) implies that if we multiply the function $f(x)$ with $\psi_n^*(x)$ and integrate in the interval $[0, a]$ we get the n-th coefficient

$$\int_0^a dx\psi_n^*(x)f(x) = \sum_{m=1}^{\infty} c_m \int_0^a dx\psi_n^*(x)\psi_m(x) = \sum_{m=1}^{\infty} c_m\delta_{mn} = c_n \ . \tag{3.2.15}$$

All the information about the function $f(x)$ is contained in the coefficients c_n. Indeed one can translate any property of the function itself into a property of the set of Fourier coefficients. The normalization property, e.g., becomes

$$\begin{aligned}\int_0^a dx f^*(x)f(x) &= \int_0^a dx \left(\sum_{m=1}^{\infty} c_m^*\psi_m^*(x)\right)\left(\sum_{n=1}^{\infty} c_n\psi_n(x)\right) \\ &= \sum_{m,n=1}^{\infty} c_m^* c_n \int_0^a dx\psi_m^*(x)\psi_n(x) = \sum_{n=1}^{\infty} |c_n|^2 = 1 \ .\end{aligned} \tag{3.2.16}$$

Analogously one can calculate the expectation value of the energy and express this as an infinite sum over the Fourier coefficients:

$$\langle H\rangle = \sum_{n=1}^{\infty} |c_n|^2 E_n = \frac{\pi^2\hbar^2}{2Ma^2}\sum_{n=1}^{\infty} n^2|c_n|^2 \ . \tag{3.2.17}$$

3.3 The harmonic oscillator

The second example of potential that we discuss here is that of the harmonic oscillator. The potential is quadratic in the displacement from the rest position x_0:

$$V(x) = \frac{1}{2}k(x - x_0)^2 \ . \tag{3.3.1}$$

In classical mechanics the solution of the equation of motion for this potential is given by an oscillatory movement with a fixed frequency $\omega = \sqrt{k/M}$. In order to simplify our discussion we choose the origin at x_0 and replace k with ω:

$$V(x) = \frac{1}{2}M\omega^2 x^2 \ . \tag{3.3.2}$$

The eigenvalue equation for the energy looks as follows:

$$\frac{1}{2M}\left[-\hbar^2\frac{d^2}{dx^2} + (M\omega x)^2\right]\psi(x) = E\psi(x) \ . \tag{3.3.3}$$

3.3.1 Solution by the analytical method

In order to solve the equation we first clean up the notation and multiply the equation by $2/\hbar\omega$:

$$-\frac{\hbar}{M\omega}\frac{d^2\psi}{dx^2} + \frac{M\omega}{\hbar}x^2\psi = \frac{2E}{\hbar\omega}\psi \ . \tag{3.3.4}$$

We then change the variable x for ξ, defined as

$$\xi \equiv \sqrt{\frac{M\omega}{\hbar}}x \tag{3.3.5}$$

and rewrite the equation as

$$\frac{d^2\psi}{d\xi^2} = \left(\xi^2 - K\right)\psi \tag{3.3.6}$$

where $K = 2E/\hbar\omega$. To solve this equation we need to make several steps, and start by looking at the behaviour of the function for large ξ.

Step 1 For large ξ we can neglect K with respect to ξ^2 and get the equation:

$$\xi \to \infty \quad \Rightarrow \quad \frac{d^2\psi}{d\xi^2} = \xi^2\psi \tag{3.3.7}$$

which is solved by[2] $e^{\pm\xi^2/2}$ – the exponential with the plus sign cannot be normalized and should be disregarded: $\psi \sim e^{-\xi^2/2}$. We are looking for the exact

[2]Not quite, but again neglecting small terms compared to ξ^2 yes.

solution, however, and are not yet satisfied with an approximate solution giving the leading behaviour for large ξ. We therefore write:

$$\psi(\xi) \equiv h(\xi) e^{-\xi^2/2} \ , \tag{3.3.8}$$

and proceed further looking for ways to determine h.

Step 2 If we insert Eq. (3.3.8) into Eq. (3.3.6) we obtain an equation for $h(\xi)$, namely:

$$h''(\xi) - 2\xi h'(\xi) + (K-1)h(\xi) = 0 \ . \tag{3.3.9}$$

At this stage, it almost looks like we made our life more complicated than it was with the equation for ψ, but we will later see that this is not the case.

Step 3 We write the function h as a power series:

$$h(\xi) = \sum_{l=1}^{\infty} a_l \xi^l \tag{3.3.10}$$

and look for the solution in this form. Inserting the power series in Eq. (3.3.9) we get

$$\sum_{l=0}^{\infty} \left[l(l-1) a_l \xi^{l-2} - 2l a_l \xi^l + (K-1) a_l \xi^l \right] = 0 \ , \tag{3.3.11}$$

which we can rewrite as

$$\sum_{l=0}^{\infty} \left[(l+2)(l+1) a_{l+2} + (K-1-2l) a_l \right] \xi^l = 0 \ . \tag{3.3.12}$$

Since the power series expansion is unique, it vanishes only if all the coefficients of all the powers of ξ vanish, *i.e.* if

$$(l+2)(l+1)a_{l+2} + (K-1-2l)a_l = 0 \quad \Rightarrow \quad a_{l+2} = \frac{2l+1-K}{(l+2)(l+1)} a_l \tag{3.3.13}$$

which is a recursive determination of all the coefficients in terms of the first one. Actually, given the coefficient a_0, all the coefficients with even index get determined, but not the odd ones. These are determined in terms of a_1, so that all in all the function is fixed by two constants, a_0 and a_1. In turn, at least one of the two we would have to determine through the normalization condition.

Step 4 Indeed, the question arises whether the solution we have found can be at all normalized. In order to answer this question we look at the behaviour of our power series for large values of ξ. This will be determined by the coefficients with large values of l, and so we simplify Eq. (3.3.13) in this limit:

$$l \to \infty \quad \Rightarrow \quad a_{l+2} = \frac{2}{l} a_l \ . \tag{3.3.14}$$

Inserting this back into the power series, we can resum it and get:

$$\xi \to \infty \quad \Rightarrow \quad h(\xi) \sim C \sum_{l=2k} \frac{1}{(l/2)!} \xi^l = C \sum_k \frac{1}{k!} \xi^{2k} = C e^{\xi^2} \ , \tag{3.3.15}$$

so when we look back at the behaviour of ψ we find out that we have now destroyed the nice behaviour at infinity:

$$\psi(\xi) = h(\xi) e^{-\xi^2/2} \stackrel{\xi \to \infty}{\longrightarrow} C e^{\xi^2/2} \ . \tag{3.3.16}$$

At first sight it seems that all the work we have done so far is nearly useless, as we cannot interpret these solutions of the differential equation as wave functions...

Step 5 ... unless we require that starting from a certain value of l the coefficients a_l all vanish. This will happen if for $l = n$, one specific integer, the right-hand side of Eq. (3.3.13) vanishes:

$$2n + 1 = K \quad \Rightarrow \quad E_n = \hbar\omega \left(n + \frac{1}{2} \right) \ . \tag{3.3.17}$$

This is a condition on the values of the energy: only for these values we can find a solution of the differential equation for ψ that is integrable and can therefore be interpreted as a wave function.

Step 6 For each positive integer n (and each eigenvalue of energy) we can get the explicit form of the functions $h_n(\xi)$. These are polynomials of degree n, which contain all possible lower powers of ξ with the same parity as n, and whose coefficients are fixed by the recursion relation (3.3.13). They are called the Hermite polynomials and the first few read

$$H_0 = 1 \ , \quad H_1 = 2\xi \ , \quad H_2 = 4\xi^2 - 2 \ , \quad H_3 = 8\xi^3 - 12\xi \ . \tag{3.3.18}$$

In order to get the complete eigenfunctions of $\hat{H}$ we should still normalize $\psi_n = H_n e^{-\xi^2/2}$ – we do this below.

3.3.2 Solution by the algebraic method

After having solved the differential equation by standard, analytical methods, we now show how one can obtain the same solution by the algebraic method, based on the use of raising and lowering operators, which will be useful also in other contexts. Since the Hamiltonian is the sum of two squares, we could factorize it in two factors linear in momentum and position. If we speak of the classical Hamiltonian, this is straightforward:

$$H(p,x) = \frac{1}{2M}\left(p^2 + (M\omega x)^2\right) = \frac{1}{2M}(-ip + M\omega x)(ip + M\omega x) \ . \tag{3.3.19}$$

In quantum mechanics this is not so simple, because both momentum as well as position are operators, and the factorization of operators requires more care, as we have to consider their ordering. Indeed if we write the factorization formula (3.3.19) substituting p with $\hat{p}$, we discover that it does not work, and that we get an extra term besides the Hamiltonian:

$$\frac{1}{2M}(-i\hat{p} + M\omega\hat{x})(i\hat{p} + M\omega\hat{x}) = \hat{H} - \frac{\hbar\omega}{2} \ . \tag{3.3.20}$$

The reason for the appearance of this extra term is that the momentum and position operators do not commute:

$$[\hat{x}, \hat{p}] = i\hbar \ . \tag{3.3.21}$$

This is easy to verify, by letting the product of the two operators act on a test function. When the momentum is to the left of x, the derivative acts both on x and on the test function. The action of the derivative on x is responsible for the non-zero commutator, and in the end also of the extra term in Eq. (3.3.20).

We now give names to the two operators appearing in Eq. (3.3.20)

$$a_\pm = \frac{1}{\sqrt{2\hbar M\omega}}(\mp i\hat{p} + M\omega\hat{x}) \ , \tag{3.3.22}$$

and write the Hamiltonian in terms of these

$$\hat{H} = \hbar\omega\left(a_- a_+ - \frac{1}{2}\right) = \hbar\omega\left(a_+ a_- + \frac{1}{2}\right) \ . \tag{3.3.23}$$

The latter is the form we will use more often but the two are obviously equivalent. The fact that the constant term changes as we change the order of the two operators is a sign of a nonvanishing commutator between a_+ and a_-. Indeed it is easy to verify that

$$[a_-, a_+] = 1 \ . \tag{3.3.24}$$

We now immediately exploit this commutation relation to show that if ψ is an eigenfunction of the Hamiltonian with eigenvalue E, then $a_+\psi$ is also an eigenfunction, and the corresponding eigenvalue is $E + \hbar\omega$:

$$\begin{aligned} \hat{H}a_+\psi &= \hbar\omega\left(a_+a_- + \frac{1}{2}\right)a_+\psi = \hbar\omega a_+\left(a_+a_- + \frac{3}{2}\right)\psi \\ &= a_+(\hat{H} + \hbar\omega)\psi = (E + \hbar\omega)a_+\psi \ . \end{aligned} \tag{3.3.25}$$

Analogously we can show that $a_-\psi$ is an eigenfunction with eigenvalue $E - \hbar\omega$. So, given one single eigenfunction, we can construct an infinite set of them by operating repeatedly with the raising and lowering operators – the name comes precisely from the fact that they increase or decrease the eigenvalue by one unit of $\hbar\omega$.

While increasing the eigenvalues of energy an indefinite number of times is allowed, if we decrease it enough times we get to a point where the eigenvalue would become negative, and we have discussed above that this is impossible – the eigenfunction corresponding to a negative eigenvalue would not be normalizable. What happens is that applying a_- to an eigenfunction whose eigenvalue is smaller than $\hbar\omega$ annihilates the function:

$$\hat{H}\psi_0 = E_0\psi_0 \ , E_0 < \hbar\omega \ , \Rightarrow a_-\psi_0 = 0 \ . \tag{3.3.26}$$

In this case it is very easy to determine E_0, because the nontrivial part of the Hamiltonian applied to ψ_0 gives zero:

$$\hbar\omega\left(a_+a_- + \frac{1}{2}\right)\psi_0 = \frac{1}{2}\hbar\omega\psi_0 \quad \Rightarrow \quad E_0 = \frac{1}{2}\hbar\omega \ . \tag{3.3.27}$$

Starting from this minimum value, we can now climb the whole ladder of the allowed eigenvalues which are given by

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \qquad \forall n \in \mathbb{N} \ . \tag{3.3.28}$$

3.3.3 Determining the eigenfunctions

Now that we have the eigenvalues, we want to get in explicit form the corresponding eigenfunctions. We now determine the lowest eigenfunction, ψ_0 and then obtain all the others by applying repeatedly the raising operator. The relevant equation for determining ψ_0 is

$$a_-\psi_0 = 0 \quad \Rightarrow \quad \frac{d\psi_0}{dx} = -\frac{M\omega}{\hbar}x\psi_0 \ , \tag{3.3.29}$$

and the solution is of the form

$$\psi_0(x) = Ae^{-\frac{M\omega}{2\hbar}x^2} \ . \tag{3.3.30}$$

The constant A can again be pinned down by imposing the normalization condition

$$1 = |A|^2 \int_{-\infty}^{\infty} dx e^{-\frac{M\omega}{\hbar}x^2} = |A|^2 \sqrt{\frac{\hbar}{M\omega}} \int_{-\infty}^{\infty} dx e^{-x^2} = |A|^2 \sqrt{\frac{\hbar\pi}{M\omega}} \ . \qquad (3.3.31)$$

Choosing A to be real and positive, the lowest eigenfunction of the harmonic oscillator is

$$\psi_0(x) = \left(\frac{M\omega}{\hbar\pi}\right)^{1/4} e^{-\frac{M\omega}{2\hbar}x^2} \ . \qquad (3.3.32)$$

Higher eigenfunctions are obtained by applying the raising operator. In general, however, the application of the raising operator will not give automatically the correct normalization. Defining ψ_n to be the properly normalized eigenfunctions, we have

$$A_n \psi_n(x) = a_+ \psi_{n-1}(x) \ , \qquad (3.3.33)$$

and we now determine the constants A_n. We start from the observation that the raising and lowering operators are the hermitian conjugate of each other. The hermitian conjugate is defined as follows: given two function f and g whose square is integrable, and an operator $\hat{O}$, the hermitian conjugate of the latter is defined as[3]

$$\int dx f^*(x) \hat{O} g(x) = \int dx (\hat{O}^\dagger f)^*(x) g(x) \ . \qquad (3.3.34)$$

For $a_\pm$ we have:

$$\begin{aligned} \int dx f^*(x) a_\pm g(x) &= \frac{1}{\sqrt{2\hbar M\omega}} \int dx f^*(x) \left(\mp\hbar\frac{d}{dx} + M\omega x\right) g(x) \\ &= \frac{1}{\sqrt{2\hbar M\omega}} \int dx \left[\left(\pm\hbar\frac{d}{dx} + M\omega x\right) f^*(x)\right] g(x) \\ &= \int dx (a_\mp f)^*(x) g(x) \ , \end{aligned} \qquad (3.3.35)$$

where the shift of the operators from g to f has been made through a partial integration – the only sign affected is the one in front of the derivative. We now look at the normalization of the modulus square of $a_+\psi_n$:

$$|A_{n+1}|^2 = \int dx (a_+\psi_n)^* a_+ \psi_n = \int dx \psi_n^* a_- a_+ \psi_n \ . \qquad (3.3.36)$$

In the last integral the function $a_- a_+ \psi_n$ appears, which is proportional ψ_n. The proportionality factor is easy to determine, by looking at the Hamiltonian and remembering that $\hat{H}\psi_n = \hbar\omega(n+1/2)\psi_n$:

$$a_- a_+ \psi_n = \left[\frac{1}{\hbar\omega}\hat{H} + \frac{1}{2}\right] \psi_n = (n+1)\psi_n \ . \qquad (3.3.37)$$

[3]If we do not explicitly write the integration boundaries, it is meant that the integral goes from $-\infty$ to ∞.

We therefore conclude that

$$|A_{n+1}|^2 = (n+1) \quad \Rightarrow \quad A_n = \sqrt{n} \ . \tag{3.3.38}$$

We are now done with the determination of the normalization coefficient, and have so fully determined the eigenfunctions of the harmonic oscillator. The n-th eigenfunction is obtained by acting n times with the a_+ on ψ_0. Each time we get a factor A_i, with $i = 1, \ldots, n$. All in all we get

$$\psi_n(x) = \frac{1}{\sqrt{n!}} a_+^n \psi_0(x) \ , \tag{3.3.39}$$

which is a fully explicit determination, since we have the explicit expressions of ψ_0 and the operators a_+.

As in the case of the infinite square well, the eigenfunctions of the Hamiltonian form a basis in the space of all possible wave functions; i.e. any wave function $f(x)$ can be written as a superposition of (infinitely many) ψ_n:

$$f(x) = \sum_{n=0}^{\infty} c_n \psi_n(x) \ . \tag{3.3.40}$$

Moreover, they have the orthonormality property as we can easily show:

$$A_{mn} \equiv \int dx \psi_m^* a_+ a_- \psi_n = n \int dx \psi_m^* \psi_n \equiv n I_{mn} \ , \tag{3.3.41}$$

but using the property $a_+^\dagger = a_-$ we also get

$$A_{mn} = \int dx (a_- \psi_m)^* a_- \psi_n = \int dx (a_+ a_- \psi_m)^* \psi_n = m I_{mn} \ , \tag{3.3.42}$$

So if $m \neq n$ the integral I_{mn} must vanish; in general $I_{mn} = \delta_{mn}$. This means that the coefficients c_n can be also determined through the projection

$$\int dx \psi_n^* f(x) = \sum_m c_m \int dx \psi_n^* \psi_m = \sum_m c_m \delta_{mn} = c_n \ . \tag{3.3.43}$$

We now give the explicit form of the first few eigenfunctions ψ_n. In order to do this it is convenient to introduce two new symbols:

$$\alpha \equiv \left(\frac{M\omega}{\pi\hbar} \right)^{1/4} \ , \qquad \xi \equiv \sqrt{\frac{M\omega}{\hbar}} x \ . \tag{3.3.44}$$

We then have

$$\psi_0 = \alpha e^{-\xi^2/2} \ , \quad \psi_1 = \sqrt{2} \alpha \xi e^{-\xi^2/2} \ , \quad \psi_2 = \frac{\alpha}{\sqrt{2}} (2\xi^2 - 1) e^{-\xi^2/2} \ . \tag{3.3.45}$$

In deriving these expressions it is easy to convince oneself that the n-th eigenfunction will be a polynomial of order n times the exponential $\exp(-\xi^2/2)$, and that the polynomial will contain either odd or even powers of ξ, depending whether n is odd or even. These polynomials are the same we already encountered in the previous section. They are called Hermite polynomials and denoted by $H_n(\xi)$ and are well known in the mathematical literature. Using their standard definition the eigenfunctions of the harmonic oscillator can be written as follows

$$\psi_n = \frac{\alpha}{\sqrt{2^n n!}} H_n(\xi) e^{-\xi^2/2} \quad . \tag{3.3.46}$$

There are various ways to derive their form explicitly. We mention here three of them:

Recursion relation:

$$\begin{aligned} H_{n+1}(\xi) &= 2\xi H_n(\xi) - 2n H_{n-1}(\xi) \quad , \\ \text{(Starting point:} \qquad & H_0 = H_{-1} = 1) \end{aligned}$$

Derivative relation:

$$\frac{dH_n}{d\xi} = 2n H_{n-1}(\xi) \quad ,$$

Generating function:

$$e^{-z^2+2z\xi} = \sum_{n=0}^{\infty} \frac{z^n}{n!} H_n(\xi) \quad , \tag{3.3.47}$$

where the latter shows how to obtain the Hermite polynomials from a Taylor expansion around $z = 0$ of an elementary function.

3.3.4 Quantum vs classical solution, coherent states

In classical physics a particle which moves in a quadratic potential has a fixed total energy, but oscillating (time-dependent) position and momentum. The latter implies that the total energy gets constantly transformed among potential and kinetic energy: at $x = 0$ the particle has only kinetic energy $T = mv^2/2$, whereas at its maximal distance from the origin, $|x|_{\max} = v/\omega$ it is at rest (zero kinetic energy) and has maximal potential energy $V = M\omega|x|^2_{\max}/2$.

The quantum states with fixed energy, the eigenfunctions we have just discussed, look rather different. Their probability distribution in space is time independent (the quantum particle does not oscillate in a harmonic oscillator potential):

$$|\Psi_n(x,t)|^2 = \psi_n^*(x) e^{iE_n t/\hbar} e^{-iE_n t/\hbar} \psi_n(x) = |\psi(x)|^2 \quad , \tag{3.3.48}$$

as is the expectation value of any measurable quantity. For example, if we evaluate the expectation value of the potential energy

$$V(x) = \frac{1}{2} M\omega^2 x^2 = \frac{\hbar\omega}{4}(a_+ + a_-)^2 = \frac{\hbar\omega}{4}(a_+^2 + a_-^2 + a_+ a_- + a_- a_+) \tag{3.3.49}$$

we get

$$\begin{aligned}\langle V\rangle &= \int dx\psi_n^* V\psi_n = \frac{\hbar\omega}{4}\int dx\psi_n^*(a_+a_- + a_-a_+)\psi_n \\ &= \frac{\hbar\omega}{4}\int dx\psi_n^*(2n+1)\psi_n = \frac{\hbar\omega}{2}\left(n+\frac{1}{2}\right) = \frac{1}{2}E_n \ , \end{aligned} \tag{3.3.50}$$

where we have used the orthonormality property of the eigenfunctions and the relations:

$$a_+a_-\psi_n = n\psi_n \ , \quad a_-a_+\psi_n = (n+1)\psi_n \ . \tag{3.3.51}$$

The outcome of the calculation is that the expectation value of the potential energy is constant in time and half the total energy. Obviously this means that the expectation value of the kinetic energy is the same:

$$\langle T\rangle = \langle \hat{H} - V\rangle = E_n - E_n/2 = E_n/2 \ . \tag{3.3.52}$$

There is another important difference between the quantum and the classical harmonic oscillator. In the classical case, the particle oscillates between the two extrema $\pm|x|_{\max}$ and cannot move beyond these two points because it does not have enough energy to overcome the potential barrier. The quantum particle in a x^2 potential, on the other hand, has a nonzero probability to be detected even beyond the point where the potential is equal to its total energy. In fact arbitrarily far away from this point. The probability decreases with the distance exponentially fast, but is not zero. This is clearly a quantum effect which disappears in the limit $\hbar \to 0$, but in this limit none of the energy eigenfunctions will look anything like a classical harmonic oscillator. For all of them, in the classical limit the exponential factor $\exp(-\xi^2/2)$ will dominate everything else and will give a zero probability of finding a particle away from the origin.

How can we meaningfully get the classical limit from our quantum solutions? The trick is to construct the appropriate superpositions of the energy eigenfunctions. These are called coherent states and are the eigenfunctions of the a_- operator. Without explaining how one arrives to this idea, we now simply try to derive the form of the eigenfunctions of a_- and then discuss their properties. The eigenvalue equation for a_- is

$$a_-\phi_\lambda = \lambda\phi_\lambda \ . \tag{3.3.53}$$

We assume that such an eigenfunction exists and expand it in the eigenfunctions of the Hamiltonian:

$$\phi_\lambda = \sum_n c_n(\lambda)\psi_n \ . \tag{3.3.54}$$

Applying a_- on these we get:

$$a_-\phi_\lambda = \sum_n c_n(\lambda)a_-\psi_n = \sum_n c_n(\lambda)\sqrt{n}\psi_{n-1} \ , \tag{3.3.55}$$

and the requirement that this be equal to $\lambda\phi_\lambda$ is satisfied if the coefficients $c_n(\lambda)$ satisfy the following recursive equation

$$c_{n+1}(\lambda) = \frac{\lambda}{\sqrt{n+1}} c_n(\lambda) \quad \Rightarrow \quad c_n(\lambda) = \frac{\lambda^n}{\sqrt{n!}} c_0(\lambda) \ . \tag{3.3.56}$$

The function ϕ_λ is therefore proportional to a constant $c_0(\lambda)$, whereas all the rest is fixed. This constant can be pinned down through the normalization condition

$$1 = \int dx \phi_\lambda^* \phi_\lambda = \sum_n |c_n(\lambda)|^2 = |c_0(\lambda)|^2 \sum_n \frac{|\lambda|^{2n}}{n!} = |c_0(\lambda)|^2 e^{|\lambda|^2} \ , \tag{3.3.57}$$

which implies (taking c_0 to be real and positive)

$$c_0(\lambda) = e^{-|\lambda|^2/2} \ . \tag{3.3.58}$$

We now have found the eigenfunctions of a_- in explicit form

$$\phi_\lambda = e^{-|\lambda|^2/2} \sum_n \frac{\lambda^n}{\sqrt{n!}} \psi_n \ , \tag{3.3.59}$$

and seen that there is no restriction on the eigenvalues λ – indeed they can be any complex number.

We now look at the expectation values of the Hamiltonian, x and p and their squares on these states:

$$\langle \hat{H} \rangle = \int dx \phi_\lambda^* \hbar\omega \left(a_+ a_- + \frac{1}{2} \right) \phi_\lambda = \hbar\omega \sum_n |c_n(\lambda)|^2 \left(n + \frac{1}{2} \right) \ , \tag{3.3.60}$$

and inserting the explicit expression of the $c_n(\lambda)$ it is easy to get

$$\langle \hat{H} \rangle = \hbar\omega \left(|\lambda|^2 + \frac{1}{2} \right) \ . \tag{3.3.61}$$

The square of the Hamiltonian gives

$$\langle \hat{H}^2 \rangle = \hbar^2\omega^2 \sum_n |c_n(\lambda)|^2 \left(n^2 + n + \frac{1}{4} \right) = \hbar^2\omega^2 \left(|\lambda|^4 + 2|\lambda|^2 + \frac{1}{2} \right) , \tag{3.3.62}$$

and consequently, the standard deviation of the energy is

$$\sigma_E = \sqrt{\langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2} = \hbar\omega |\lambda| \ . \tag{3.3.63}$$

These coherent states can have all possible values above the minimum allowed $\hbar\omega/2$ for the expectation value of the energy. It is interesting to note that the ratio

$$\frac{\sigma_E}{\langle E \rangle} = \frac{|\lambda|}{|\lambda|^2 + \frac{1}{2}} \ , \tag{3.3.64}$$

vanishes both for very large as for very small $|\lambda|$ and is maximal at $|\lambda| = 1/\sqrt{2}$.

The evaluation of $\langle x \rangle$ and $\langle p \rangle$ is very simple if we write them as linear combinations of the $a_\pm$ operators:

$$\hat{x} = \sqrt{\frac{\hbar}{2M\omega}}(a_+ + a_-) \ , \quad \hat{p} = i\sqrt{\frac{\hbar M\omega}{2}}(a_+ - a_-) \ . \tag{3.3.65}$$

We then have

$$\begin{aligned} \langle x \rangle &= \sqrt{\frac{\hbar}{2M\omega}} \left[\int dx (a_-\phi_\lambda)^* \phi_\lambda + \int dx \phi_\lambda^* a_- \phi_\lambda \right] = \sqrt{\frac{\hbar}{2M\omega}}(\lambda^* + \lambda) \\ \langle p \rangle &= i\sqrt{\frac{\hbar M\omega}{2}} \left[\int dx (a_-\phi_\lambda)^* \phi_\lambda - \int dx \phi_\lambda^* a_- \phi_\lambda \right] = i\sqrt{\frac{\hbar M\omega}{2}}(\lambda^* - \lambda) \ . \end{aligned} \tag{3.3.66}$$

The expectation value of x (p) is proportional to the real (imaginary) part of the eigenvalue λ. Evaluating the expectation values of the squares of x and p is also easy and gives

$$\begin{aligned} \langle x^2 \rangle &= \frac{\hbar}{2M\omega} \left(\lambda^2 + \lambda^{*2} + 2|\lambda|^2 + 1 \right) \ , \\ \langle p^2 \rangle &= -\frac{\hbar M\omega}{2} \left(\lambda^2 + \lambda^{*2} - 2|\lambda|^2 - 1 \right) \ , \end{aligned} \tag{3.3.67}$$

and the corresponding standard deviations are

$$\sigma_x = \sqrt{\frac{\hbar}{2M\omega}} \ , \quad \sigma_p = \sqrt{\frac{\hbar M\omega}{2}} \ \Rightarrow \sigma_p \sigma_x = \frac{\hbar}{2} \ . \tag{3.3.68}$$

For the coherent states the product of the standard deviations in x and p is exactly the minimum allowed by the Heisenberg uncertainty relation. This is indeed a good indication that these states are as close to classical states as it is possible.

To finally convince ourselves we evaluate the corresponding time-dependent solutions:

$$\begin{aligned} \Phi_\lambda(x,t) &= \sum_n c_n(\lambda) \psi_n(x) e^{-iE_n t/\hbar} \\ &= e^{-|\lambda|^2/2} \sum_n \frac{\lambda^n}{\sqrt{n!}} e^{-i\omega(n+1/2)t} \psi_n(x) \\ &= e^{-|\lambda|^2/2 - i\omega t/2} \sum_n \frac{(\lambda e^{-i\omega t})^n}{\sqrt{n!}} \psi_n(x) = e^{-i\omega t/2} \phi_{\lambda(t)}(x) \ , \end{aligned} \tag{3.3.69}$$

where $\lambda(t) \equiv \lambda \exp(-i\omega t)$. In the last step we have written the time-dependent eigenfunction as an irrelevant (time-dependent) phase times the time-independent

one where, however, the eigenvalue λ is taken to be time dependent. And its time dependence is a simple oscillation with frequency ω. So, since the expectation value of x and p in a state ϕ_λ are proportional to the real and imaginary parts of λ, in the time dependent case they will be proportional to the real and imaginary parts of $\lambda(t)$ and will therefore have the oscillatory behaviour of a classical harmonic oscillator. If we choose as eigenvalue $\lambda \propto 1/\sqrt{\hbar}$ we can take the limit $\hbar \to 0$ and nicely recover the behaviour of a classical particle: constant total energy (but time dependent potential and kinetic energies!), oscillating x and p and uncertainties that go to zero.

3.4 The free particle

As a next example we now discuss the free particle. Although it may sound trivial and not really worth discussing, it is a useful (and nontrivial!) example to see what happens if the eigenvalue of the energy is larger than the potential at infinity. So, we take the potential constant everywhere and equal to zero. The time-independent Schrödinger equation then becomes

$$-\frac{\hbar^2}{2M}\frac{d^2\psi}{dx^2} = E\psi \qquad \Rightarrow \qquad \frac{d^2\psi}{dx^2} = -k^2\psi \ , \tag{3.4.1}$$

with $k = \sqrt{2ME}/\hbar$. The general solution of this equation has the form

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \ , \tag{3.4.2}$$

which implies that the time-dependent solution can be written as

$$\Psi(x,t) = Ae^{ik\left(x-\frac{\hbar k}{2M}t\right)} + Be^{-ik\left(x+\frac{\hbar k}{2M}t\right)} \ , \tag{3.4.3}$$

i.e. as a superposition of two plane waves, one travelling in the right direction and the other in the left direction, both with speed $|v| = \hbar k/2M$. Notice that this wave-function describes a free particle with kinetic energy $E = (\hbar k)^2/2M$. Classically, such a kinetic energy would correspond to a velocity $|v_{\rm cl}| = \hbar k/M$, which is two times larger than the quantum velocity. This apparent paradox can be resolved if we consider that something close to a classical particle which moves with a certain speed in a certain direction should also be localized in space – a plane wave, on the other hand, is spread over the whole axis. If we build a superposition of plane waves which is maximally localized both in space as well as in momentum, then we will have a wave-function of the form[4]

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} dk\phi(k)e^{ik\left(x-\frac{\hbar k}{2M}t\right)} \ . \tag{3.4.4}$$

[4]Since we integrate over all momenta, it is not necessary to separate the term with a positive k from the one with a negative one. The square root of 2π in front of the integral is conventional, see below.

It is well known that if such a wave packet is well localized in momentum around a certain momentum k_0, it will move coherently with velocity

$$v = \frac{d}{dk}\frac{\hbar k^2}{2M}_{|k=k_0} = \frac{\hbar k_0}{M} \ , \tag{3.4.5}$$

which coincides with the classical one. The paradox arose because what we looked at was the so-called phase velocity, which describes how fast the individual plane waves move – the group velocity gives however the correct description of the movement of the wave packet.

Actually the introduction of wave packets is necessary not only to understand the relation to the classical free particle. More importantly, we have to introduce them to make sense at all of the solutions of the Schrödinger equations in the quantum theory. If we require that the eigenfunctions of the energy are correctly normalized, we get an unpleasant surprise[5]

$$\int_{-\infty}^{\infty} dx|\Psi(x,t)|^2 = |A|^2 \int_{-\infty}^{\infty} dx = \infty \ , \tag{3.4.6}$$

which is nothing but the statement that a free particle with a fixed momentum is not at all localized in space (a consequence of the uncertainty relation). This is not an acceptable wave function, because it is not normalizable. But although we cannot take the eigenfunctions of the energy as properly defined wave functions, we can still use them as a basis and write a generic wave function as a superposition of plane waves. Since we have no restrictions on the admissible values of the momenta k, instead of having a sum, we will have an integral of the form (3.4.4). Before accepting this as a solution of the Schrödinger equation for a free particle we still have to answer two questions:

1. what is the condition on $\phi(k)$ if we require that $\Psi(x,t)$ is properly normalized?

2. how do we find an explicit solution given the initial condition $\Psi(x,0)$?

The answer to both questions comes from Fourier analysis and we state them without proof:

$$\int_{-\infty}^{\infty} dx|\Psi(x,t)|^2 = \int_{-\infty}^{\infty} dk|\phi(k)|^2 \ , \tag{3.4.7}$$

which is analogous to the condition $\sum_n |c_n|^2 = 1$ in the case of discrete eigenvalues. Concerning the initial condition $\Psi(x,0)$, if I set $t = 0$ in Eq. (3.4.4) I get

$$\Psi(x,0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk\phi(k)e^{ikx} \ , \tag{3.4.8}$$

[5]Again without lack of generality we have dropped the part proportional to B, *i.e.* with negative k.

which is nothing but the statement that $\Psi(x,0)$ is the inverse Fourier transform of $\phi(k)$. But since the Fourier transformation is invertible, this relation can only be true if $\phi(k)$ is the Fourier transform of the initial conditions:

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx \Psi(x,0) e^{-ikx} \quad . \tag{3.4.9}$$

So, if we are given the initial condition $\Psi(x,0)$ we can evaluate its Fourier transform $\phi(k)$. The initial condition must be properly normalized by definition. This implies that $\int dk |\phi(k)|^2 = 1$. Having the explicit form of $\phi(k)$ we can insert it in Eq. (3.4.4) and get explicitly the solution of the Schrödinger equation for the free particle – since $\phi(k)$ is properly normalized $\Psi(x,t)$ will also be so at any later time.

3.5 The finite square well

After having looked at one-dimensional potentials which have either only discrete or only continuous eigenvalues of the energy, we now look at a more realistic case where one has both simultaneously. This is the case of the finite square well:

$$V(x) = \begin{cases} -V_0 & -a < x < a \\ 0 & |x| > a \end{cases} \quad . \tag{3.5.1}$$

3.5.1 Negative eigenvalues

We first consider the eigenfunctions with negative eigenvalues. In this case the Schrödinger equation can be written piecewise in this form

$$\begin{array}{llll} \text{Region I} & (x < -a) & -\frac{\hbar^2}{2M}\frac{d^2}{dx^2}\psi(x) = E\psi(x) & E < 0 \\ \text{Region II} & (|x| < a) & -\frac{\hbar^2}{2M}\frac{d^2}{dx^2}\psi(x) = (E+V_0)\psi(x) & (E+V_0) > 0 \\ \text{Region III} & (x > a) & -\frac{\hbar^2}{2M}\frac{d^2}{dx^2}\psi(x) = E\psi(x) & E < 0 \end{array} \quad . \tag{3.5.2}$$

In regions I and III the solution is a linear combination of exponentials $\exp(\pm\kappa x)$, with $\kappa = \sqrt{-2ME}/\hbar$. In region I the exponential with the minus sign must be discarded, because it would explode when $x \to -\infty$, whereas in region III the exponential with the plus sign has to be discarded:

$$\psi_{\rm I}(x) = Ae^{\kappa x} \ , \qquad \psi_{\rm III}(x) = Fe^{-\kappa x} \quad . \tag{3.5.3}$$

In region II the sign of the constant on the right-hand side of the equation is positive and we can write the solution of the differential equation as a combination of sine and cosine:

$$\psi_{\rm II}(x) = C\sin(lx) + D\cos(lx) \quad , \qquad l = \frac{\sqrt{2M(E+V_0)}}{\hbar} \quad . \tag{3.5.4}$$

Although the differential equation is defined piecewise, the solution should be continuous over the whole real axis. We will now impose the continuity of both the function as well as its first derivative[6] at the two points where the potential has a discontinuity, $x = \pm a$. Before doing this, however, we notice that the potential is even in x – this implies that if $\psi(x)$ is a solution of the equation so is also $\psi(-x)$, and that we can split any solution into an even and an odd part. So without loss of generality we can consider either even or odd solutions. We start with the even solutions. In region I and III the coefficients A and F have to be equal, and in region II we have to drop the sine:

$$\psi(x) = \begin{cases} Fe^{\kappa x} & x < -a \\ D\cos(lx) & |x| < a \\ Fe^{-\kappa x} & x > a \end{cases} \quad . \tag{3.5.5}$$

The continuity condition for the function itself and its derivative then read

$$Fe^{-\kappa a} = D\cos(la) \qquad -\kappa Fe^{-\kappa a} = -Dl\sin(la) \ , \tag{3.5.6}$$

and if we divide the second by the first we get

$$\kappa = l\tan(la) \ . \tag{3.5.7}$$

This is a trascendental equation for the energy, which is the only unknown in the equation and appears both inside κ and l. The equation can be solved numerically. In two extreme cases we can find approximate analytical solutions:

1. Very deep well, *i.e.* $l_{\max}a = \sqrt{2MV_0}a/\hbar \gg 1$. In this case as we vary the energy E between zero and $-V_0$ the argument of the tangent decreases from a very large value ($l_{\max}a$) down to zero. Every time la gets close to $(2n+1)\pi/2$ the tangent becomes very large. In the region $E \sim -V_0$ κ/l is very large and so the equation will have many solutions, all of them near the points where $la \sim (2n+1)\pi/2$. For the energy this means

$$E + V_0 \sim \frac{(2n+1)^2\pi^2\hbar^2}{2M(2a)^2} \ , \qquad n = 0, 1, \ldots \tag{3.5.8}$$

   The right-hand side gives the eigenvalues of the energy for the infinite square well of size $2a$, cf. Eq. (3.2.9). We should indeed expect that if we consider a very deep well and look at the lowest eigenvalues of the energy, these should be well approximated by those of the infinite square well.

2. Very shallow well, $l_{\max}a = \sqrt{2MV_0}a/\hbar \ll 1$. In this case the argument of the tangent is always small. The equation then becomes approximately

$$\kappa = l^2 a \ \Rightarrow \ \hbar\sqrt{-2ME} = 2M(E + V_0)a \ . \tag{3.5.9}$$

[6]The second derivative of the solution is discontinuous, as Eq. (3.5.2) tells us, but if we integrate this once or twice, we get a continuous function.

The left-hand side of the equation grows as we move from $E = 0$ down to $-V_0$. The right-hand side, on the other hand decreases from $2MaV_0$ at $E = 0$ to zero at $E = -V_0$. It is then clear that there will always be one solution to the equation: no matter how shallow the well is, there is always one negative energy eigenvalue. The quadratic equation (3.5.9) admits two solutions. The one with $E > -V_0$ reads:

$$E = -V_0 + \frac{\hbar^2}{4Ma^2}\left(\sqrt{1 + \frac{8Ma^2V_0}{\hbar^2}} - 1\right) \quad . \tag{3.5.10}$$

Once we solve Eq. (3.5.7) and determine the negative energy eigenvalues, we still have two constants to determine (D and F) if we want to have also the corresponding eigenfunctions fully explicitly. The first of the two equations in (3.5.6) gives F in terms of D, and D we can determine by the normalization condition. The relevant integral is (after expressing F in terms of D)

$$2|D|^2\left[\int_0^a dx\cos^2(lx) + \cos^2(la)\int_a^\infty dx e^{-2\kappa(x-a)}\right] = 1 \quad , \tag{3.5.11}$$

and the solution for D reads:

$$|D|^2 = \frac{2\kappa l}{\kappa(\sin(2la) + 2la) + 2l\cos^2(la)} \quad . \tag{3.5.12}$$

With this we now have the eigenfunction fully explicitly in terms of the negative eigenvalues of the energy (which we can determine only numerically, unfortunately).

3.5.2 Positive eigenvalues

If we look at the positive eigenvalues the equation to be solved is again given piecewise

$$\begin{array}{lllll}
\text{Region I} & (x < -a) & -\frac{\hbar^2}{2M}\frac{d^2}{dx^2}\psi(x) = E\psi(x) & E > 0 \\
\text{Region II} & (|x| < a) & -\frac{\hbar^2}{2M}\frac{d^2}{dx^2}\psi(x) = (E+V_0)\psi(x) & (E+V_0) > 0 \quad . \\
\text{Region III} & (x > a) & -\frac{\hbar^2}{2M}\frac{d^2}{dx^2}\psi(x) = E\psi(x) & E > 0
\end{array} \tag{3.5.13}$$

In contrast to the case of the negative eigenvalues the equation has now the same form in all three regions, and it is only the constant that changes (not even its sign, as with the negative eigenvalues). The solutions has therefore the form

$$\begin{aligned}
\psi_I(x) &= Ae^{ikx} + Be^{-ikx} \\
\psi_{II}(x) &= C\sin(lx) + D\cos(lx) \\
\psi_{III}(x) &= Fe^{ikx} + Ge^{-ikx}
\end{aligned} \tag{3.5.14}$$

where $k = \sqrt{2ME}/\hbar$. In this case we cannot eliminate any of the terms in the general solution, because none of these explodes at infinity. We do have the problem, however, that these eigenfunctions will not be integrable (just like in the case of the free particle). This is a generic feature of all the eigenfunctions with eigenvalues larger than the value of the potential at infinity. Since one can add at will a constant to the potential without changing the physics of the problem, one usually takes the potential to go to zero at infinity. In which case the problem with the normalization occurs for all eigenfunctions corresponding to positive eigenvalues.

As in the case of the free particle, the eigenfunctions of the energy, although not normalizable, are nonetheless useful as a basis on which to expand the proper wave functions. What we still have to do before being able to do so is to solve the continuity conditions: we have four of them all in all, two at $x = -a$ and two at $x = a$. This means that we can express four of the six constants appearing in Eq. (3.5.14) in terms of the remaining two. The remaining two will be then fixed by the initial conditions and we have then the explicit solution.

Before doing this, however, we remark that using the solutions in the form (3.5.14) does still provide useful information. We reason as follows. Suppose we have as initial condition a wave packet with momenta concentrated around k, and with $|\Psi(x,0)|^2$ concentrated somewhere on the left-hand side of the real axis (if the distribution in momenta is very much peaked, the uncertainty relation implies that the distribution in space will be rather flat, but this does not matter – we can always take it to be practically zero around $x = 0$ by moving it far enough to the left). We would have to describe this as an integral in k, but for simplicity we look at one single value of k. We could then ask ourselves what is the probability that this particle will travel over the well, and at far times in the future be concentrated on the right-hand side of the well, or that it will be bounced back by the potential well, and be on the left-hand side of the potential well, travelling towards the left. This is a question which we can ask independently of the normalization of the function as a whole. What matters are the ratios:

$$R = \frac{|B|^2}{|A|^2} \ , \qquad T = \frac{|F|^2}{|A|^2} \ , \tag{3.5.15}$$

which are respectively called reflection and transmission coefficients. Notice that we do not need to have a term with G: if we do not have in the initial conditions a wave on the right-hand side of the axis travelling left, this will not be generated by the dynamics. The coefficients R and T can be calculated even if the solution cannot be normalized. In fact, if we drop G from Eq. (3.5.14), we are left with five constants and four conditions. All constants can be expressed in terms of A, and the ratio will be independent of A.

The four continuity conditions read:

$$\begin{aligned} Ae^{-ika} + Be^{ika} &= -C\sin(la) + D\cos(la) \\ ik(Ae^{-ika} - Be^{ika}) &= l[C\cos(la) + D\sin(la)] \\ C\sin(la) + D\cos(la) &= Fe^{ika} \\ l[C\cos(la) - D\sin(la)] &= ikFe^{ika} \quad . \end{aligned} \tag{3.5.16}$$

The solution allows us to express B and F in terms of A:

$$\begin{aligned} B &= i\frac{\sin(2la)}{2kl}(l^2 - k^2)F \\ F &= \frac{2klAe^{-2ika}}{2kl\cos(2la) - i(k^2 + l^2)\sin(2la)} \quad . \end{aligned} \tag{3.5.17}$$

The transmission coefficient is then given by:

$$T = \left[1 + \frac{V_0}{4E(E+V_0)}\sin^2\left(\frac{2a}{\hbar}\sqrt{2M(E+V_0)}\right)\right]^{-1} \quad . \tag{3.5.18}$$

Notice that the transmission coefficient becomes one if the sine is zero, *i.e.* if its argument is a multiple of π:

$$\frac{2a}{\hbar}\sqrt{2M(E+V_0)} = n\pi \quad \Rightarrow \quad E = -V_0 + \frac{n^2\pi^2\hbar^2}{2M(2a)^2} \quad . \tag{3.5.19}$$

Remarkably, the values of the energy for which the well becomes transparent to an incoming wave packet coincide with the eigenvalues of the infinite square well. Note, however, that talking about a transmission coefficient makes sense only if $E > 0$, so that Eq. (3.5.19) is valid only if n is large enough.

Chapter 4

The formalism of quantum mechanics

Until now we have solved the Schrödinger equation for a few simple one-dimensional potentials. In these cases we have seen a number of interesting mathematical properties emerge, but have not yet tried to have a systematic understanding of these. The scope of this chapter is to analyze and understand the formal mathematical structure of quantum mechanics. As we will see, the possible solutions of the Schrödinger equation live in a vector space, albeit an infinite dimensional one. This is a consequence of the linearity property of the Schrödinger equation: a linear combination of different solutions is still a solution. Moreover when we interpret the modulus square of the wave function as a probability distribution we must require that its integral is finite – the latter integral has all the properties of the norm of a vector, and can be seen as a scalar product of a vector with itself. The space of all the wave functions is a vector space in which a scalar (or inner) product is defined. Such a space is called an inner product vector space, or a Hilbert space[1]. Analyzing in some more details this mathematical structure is essential before we embark in the discussion of more complicated physical systems in three dimensions, like the hydrogen atom.

4.1 Vector spaces

A linear vector space is a set $\mathbb{V}$ of objects $\mathbf{v}$, $\mathbf{w}$, ... where the operation of sum of two such objects $\mathbf{v} + \mathbf{w}$ and of multiplication by a scalar $a\mathbf{v}$ are defined and yield elements of the same vector space. These operations have the following properties:

- Scalar multiplication is distributive both in the vectors as well as in the

[1]The latter has the property of completeness, namely that every Cauchy sequence of vectors converges to a vector in the same space.

scalars:

$$a(\mathbf{v}+\mathbf{w}) = a\mathbf{v} + a\mathbf{w} \quad \text{and} \quad (a+b)\mathbf{v} = a\mathbf{v} + b\mathbf{v} \ . \tag{4.1.1}$$

- Scalar multiplication is associative

$$a(b\mathbf{v}) = ab\mathbf{v} \ . \tag{4.1.2}$$

- Addition is associative and commutative

$$\mathbf{v} + (\mathbf{w} + \mathbf{z}) = (\mathbf{v} + \mathbf{w}) + \mathbf{z} \quad \text{and} \quad \mathbf{v} + \mathbf{w} = \mathbf{w} + \mathbf{v} \ . \tag{4.1.3}$$

- There exists a null vector $\mathbf{0}$ such that

$$\mathbf{v} + \mathbf{0} = \mathbf{v} \quad \forall \mathbf{v} \in \mathbb{V} \ . \tag{4.1.4}$$

- For every vector $\mathbf{v}$ there exists an inverse under addition $-\mathbf{v}$ such that

$$\mathbf{v} + (-\mathbf{v}) = \mathbf{0} \ . \tag{4.1.5}$$

In quantum mechanics one considers linear combinations with complex numbers. In this case one says that the vector space is defined over the field of complex numbers.

Linear dependence. A set of n vectors $\{\mathbf{v}_i\}$ is said to be linearly independent if the relation

$$\sum_{i=1}^{n} a_i \mathbf{v}_i = \mathbf{0} \tag{4.1.6}$$

can be satisfied only with $a_i = 0$, $\forall i = 1, \ldots, n$.

Dimension of a vector space. A vector space has dimension n if the maximum number of linearly independent vectors is n.

It is then easy to prove that any element of an n-dimensional vector space can be written as a linear combination of n linearly independent vectors. A set of n linearly independent vectors $\{\mathbf{v}_i\}$ is called a basis. Once a basis is fixed any vector $\mathbf{v}$ can also be identified by its coordinates on this basis, *i.e.* by the set of n scalars $\{v_i\}$ which specify the unique linear combination of the basis vectors which gives $\mathbf{v}$:

$$\mathbf{v} = \sum_{i=1}^{n} v_i \mathbf{v}_i \ . \tag{4.1.7}$$

Sometimes vectors are represented by putting all the coordinates in a column:

$$\mathbf{v} = \begin{pmatrix} v_1 \\ v_2 \\ \vdots \\ v_n \end{pmatrix} \ .$$

4.2 Inner product spaces

A scalar or inner product is a familiar concept when we speak about vectors in a three-dimensional space. In that case the scalar product is given by the product of the lengths of the vectors times the cosine of the angle between them. This understanding, however, proceeds in the wrong direction, because we can define lengths and angles only starting from a scalar product – the problem is that we have a visual, intuitive understanding of lengths and angles in three-dimensional space and are led to believe that we can define the scalar product in terms of these. The right way to proceed is to define a scalar product in abstract terms, by listing its essential properties.

A scalar product in a vector space is an operation which associates a complex number to every pair of vectors:

$$(\mathbf{v}, \mathbf{w}) \in \mathbb{C} \tag{4.2.1}$$

and has the following properties

- $(\mathbf{v}, \mathbf{w}) = (\mathbf{w}, \mathbf{v})^*$ skew–symmetry;
- $(\mathbf{v}, \mathbf{v}) \geq 0,\ 0 \Leftrightarrow \mathbf{v} = \mathbf{0}$ positive semidefiniteness;
- $(\mathbf{v}, a\mathbf{w} + b\mathbf{z}) = a(\mathbf{v}, \mathbf{w}) + b(\mathbf{v}, \mathbf{z})$ linearity in the right-hand vector.

Linearity in the right-hand vector and skew-symmetry imply that the scalar product is antilinear in the left-hand vector:

$$(a\mathbf{v} + b\mathbf{w}, \mathbf{z}) = a^*(\mathbf{v}, \mathbf{z}) + b^*(\mathbf{w}, \mathbf{z}) \ . \tag{4.2.2}$$

A few important definitions:
1. Two vectors are said to be *orthogonal* if their scalar product vanishes.
2. $|\mathbf{v}| = \sqrt{(\mathbf{v}, \mathbf{v})}$ is the *norm* of the vector $\mathbf{v}$. A vector is *normalized* if its norm is one.
3. A basis is *orthonormal* if the vectors which belong to it are mutually orthogonal and are all normalized:

$$(\mathbf{e}_i, \mathbf{e}_j) = \delta_{ij} \ . \tag{4.2.3}$$

Working with an orthonormal basis is very convenient, because the coordinates of any vector on this basis are obtained by taking the scalar product with the corresponding basis vector

$$\mathbf{v} = \sum_{i=1}^{n} v_i \mathbf{e}_i \ , \quad v_i = (\mathbf{e}_i, \mathbf{v}) \tag{4.2.4}$$

According to the theorem of Gram-Schmidt, it is always possible to construct an orthonormal basis. In fact they have formulated an explicit procedure for constructing such a basis starting from a basis of non orthogonal vectors.

4.3 Quantum mechanics and Hilbert spaces

In quantum mechanics we represent states of physical systems through functions of the relevant spatial coordinates (until now we have considered only single particles in one dimension, but it is clear that in the physically more interesting cases, we will have more particles in three-dimensional space and correspondingly more variables). Since superpositions of different states are still admissible states of the physical system, we must establish the principle that linear combinations of wave functions are still admissible wave functions. The principle of superposition translates into the fact that all the possible wave functions behave like vectors. Actually, before we can conclude that they really form a vector space, we have to remember that the essential property of the wave functions, which allows us to interpret their modulus squared as a probability distribution, is that their modulus squared is an integrable function. It is easy to show that linear combinations of functions whose modulus squared is integrable also have an integrable modulus squared: be f and g two functions with an integrable modulus squared, and $h = af + bg$, then

$$\int dx|h(x)|^2 = |a|^2 \int dx|f(x)|^2 + |b|^2 \int dx|g(x)|^2 + 2\int dx \mathrm{Re}(a^* b f^*(x) g(x)) \ . \tag{4.3.1}$$

The last integral is finite as follows from the Schwarz inequality

$$\left| \int dx f^*(x) g(x) \right| \leq \sqrt{\int dx|f(x)|^2 \int dx|g(x)|^2} \ , \tag{4.3.2}$$

and therefore so is the integral of $|h(x)|^2$. This shows that all the possible wave functions indeed form a vector space. The integral of the modulus square is naturally interpreted as the norm of the vector represented by the wave function, and the integral

$$\int dx f^*(x) g(x)$$

as the scalar product in this vector space. Again because of Schwarz inequality (4.3.2), this scalar product is always finite. The admissible wave functions of a physical system have the structure of an inner product vector space, albeit of an infinite dimensional one – in short this is called a **Hilbert space**.

Very often the manipulations or the operations one performs on wave functions (like expanding it on a basis of functions) can be made on the basis of their vector properties alone, and not because they are functions or have any special form. When doing these manipulations it is convenient to view the wave functions like vectors – the notation should reflect this.

The notation adopted until now for vectors and vector spaces is the usual one when considering finite dimensional vector spaces. In quantum mechanics,

where one deals with infinite dimensional Hilbert spaces, it is common and more convenient to adopt the notation invented by Dirac, where vectors are represented as follows:

$$\psi(x) \to |\psi\rangle \in \mathcal{H}$$

where $\mathcal{H}$ indicates the Hilbert space. In this notation scalar products are conveniently represented as

$$\langle\phi|\psi\rangle = \int dx \phi^*(x)\psi(x) \ . \tag{4.3.3}$$

4.3.1 Operators

In quantum mechanics observables are represented by linear, hermitian operators on the Hilbert space. We first introduce a few general notions about operators on vector spaces and then concentrate on the special features of operators representing observables. Operators in a Hilbert space are maps of the space onto itself:

$$\mathcal{O} : \mathcal{H} \to \mathcal{H} \ .$$

Their action on vectors is represented by

$$\mathcal{O}|\psi\rangle = |\mathcal{O}\psi\rangle \ .$$

They are linear if, for every $a, b \in \mathbb{C}$ and $|\phi\rangle, |\psi\rangle \in \mathcal{H}$

$$\mathcal{O}(a|\phi\rangle + b|\psi\rangle) = a\mathcal{O}|\phi\rangle + b\mathcal{O}|\psi\rangle \ . \tag{4.3.4}$$

In an inner product vector space we can define the adjoint of an operator in the following way:

$$\langle\phi|\mathcal{O}\psi\rangle = \langle\mathcal{O}^\dagger\phi|\psi\rangle \ . \tag{4.3.5}$$

An operator is called hermitian if it coincides with its adjoint:

$$\mathcal{O}^\dagger = \mathcal{O} \ ,$$

and antihermitian if it is equal to minus its adjoint

$$\mathcal{O}^\dagger = -\mathcal{O} \ .$$

A generic operator which has neither of the two properties can always be decomposed into its hermitian and antihermitian components:

$$\mathcal{O} = \frac{1}{2}(\mathcal{O} + \mathcal{O}^\dagger) + \frac{1}{2}(\mathcal{O} - \mathcal{O}^\dagger) \equiv \mathcal{O}_h + \mathcal{O}_{ah} \ .$$

Finally an operator is defined to be unitary if its adjoint is equal to its inverse:

$$\mathcal{O}^\dagger\mathcal{O} = \mathcal{O}\mathcal{O}^\dagger = \mathbb{1} \ .$$

Unitary operators are important because they do not change the norm of the vectors on which they act:

$$\langle \mathcal{O}\psi|\mathcal{O}\psi\rangle = \langle \psi|\mathcal{O}^\dagger\mathcal{O}\psi\rangle = \langle\psi|\psi\rangle \ . \tag{4.3.6}$$

If the vector space is finite dimensional, we can choose a basis $\{|i\rangle\}$ on it and represent every vector through its coordinates. We can then ask ourselves how the action of an operator on a generic vector changes its coordinates. Every linear operator can be represented by a matrix which can be obtained by representing the transformed basis vectors in the same basis:

$$\mathcal{O}|i\rangle = \sum_j \mathcal{O}_{ji}|j\rangle \ . \tag{4.3.7}$$

As usual, it is convenient to work with an orthonormal basis, in which case the matrix element $\mathcal{O}_{ji}$ can be obtained by projecting the transformed basis vector $\mathcal{O}|i\rangle$ onto another basis vector $|j\rangle$:

$$\mathcal{O}_{ji} = \langle j|\mathcal{O}|i\rangle \ . \tag{4.3.8}$$

The coordinates of the transformed vector $\mathcal{O}|\psi\rangle$ are obtained by multiplying the column vector c_i given by the coordinates $|\psi\rangle = \sum_i c_i|i\rangle$ with the matrix $\mathcal{O}_{ij}$, as follows from the linearity property of the operator:

$$\mathcal{O}|\psi\rangle = \mathcal{O}\sum_i c_i|i\rangle = \sum_i c_i\mathcal{O}|i\rangle = \sum_{ij} c_i\mathcal{O}_{ji}|j\rangle \ . \tag{4.3.9}$$

The coordinates of the transformed vector are:

$$c'_i = \sum_j \mathcal{O}_{ij}c_j \ . \tag{4.3.10}$$

4.4 Observables as hermitian operators

We have seen that in quantum mechanics observables are represented by linear operators on the Hilbert space, and that the expectation value of the measurement of that observable in the state described by the wave function $\psi(x)$ is given by the integral[2]

$$\langle Q\rangle = \int dx\psi^* Q\psi = \langle\psi|Q|\psi\rangle \ , \tag{4.4.1}$$

[2]In preceding chapters we distinguished the observable from the operator by putting a hat on the operator. Whenever it is evident from the context that we speak of operators we drop the hat in order to simplify the notation.

where the latter representation is given in the Dirac notation we just introduced. The result of a measurement must be a real number and so must be its expectation value. This means that

$$\langle\psi|Q|\psi\rangle = \langle\psi|Q|\psi\rangle^* = \langle Q\psi|\psi\rangle = \langle\psi|Q^\dagger|\psi\rangle \tag{4.4.2}$$

must hold for any state $|\psi\rangle$. This implies that $Q = Q^\dagger$, *i.e.* observables are represented by hermitian operators.

We have seen that it is possible to have states in which a measurement of an observable gives always the same result q. In particular, if we perform a measurement and then immediately after a second one of the same observable, we expect that the second result will be identical to the first by physical continuity. Such determinate states are physically important and easy to generate (by doing a measurement) and we now ask ourselves how we can formulate their property mathematically. In such a state the expectation value must be equal to the fixed result of the measurement and the standard deviation must be equal to zero:

$$\langle\psi|Q|\psi\rangle = q \qquad \sigma_Q^2 = \langle\psi|(Q-q)^2|\psi\rangle = \langle(Q-q)\psi|(Q-q)\psi\rangle = 0 \ ,$$

where the second equality sign follows because Q is hermitian and the value q is of course real. The requirement that the standard deviation be zero is equivalent to the requirement that the vector $|(Q-q)\psi\rangle$ has zero norm, and from the properties of the scalar product this means that the vector $|(Q-q)\psi\rangle$ must be zero:

$$Q|\psi\rangle = q|\psi\rangle \ , \tag{4.4.3}$$

i.e. that $|\psi\rangle$ is an eigenstate of the operator Q corresponding to the eigenvalue q.

The set of eigenvalues of an operator is called its spectrum and we now discuss some important properties of the spectra of hermitian operators. We distinguish the case of a discrete and of a continuous spectrum.

4.4.1 Discrete spectra of hermitian operators

If the spectrum of a hermitian operator is discrete then the following properties hold:

- **The eigenvalues of hermitian operators are real.**
  Suppose that $|\psi\rangle$ is the eigenvector associated to the eigenvalue q which we assume to be complex. Then

  $$\langle Q\psi|\psi\rangle = \langle\psi|Q\psi\rangle \quad \Rightarrow \quad q^*\langle\psi|\psi\rangle = q\langle\psi|\psi\rangle \tag{4.4.4}$$

  which implies $(q^* - q)\langle\psi|\psi\rangle = 0$. Since we do not discuss the trivial eigenvector $|0\rangle$, the relation implies that $q^* = q$, *i.e.* that q is real.

- **Eigenvectors related to different eigenvalues are orthogonal.**
  Be $|\phi\rangle$ and $|\psi\rangle$ two eigenvectors with eigenvalues q_1 and q_2 respectively. We then have
  $$q_2\langle\phi|\psi\rangle = \langle\phi|Q\psi\rangle = \langle Q\phi|\psi\rangle = q_1\langle\phi|\psi\rangle \ . \tag{4.4.5}$$
  Since we have assumed that $q_2 \neq q_1$ it follows that $\langle\phi|\psi\rangle = 0$. If we want to conclude that all eigenvectors of a hermitian operator are orthogonal, we must also discuss the case of degenerate eigenvectors. In this case we cannot prove that the eigenvectors are orthogonal, but since linear combinations of degenerate eigenvectors are still eigenvectors belonging to the same eigenvalues, we can apply the Gram-Schmidt orthogonalization procedure and choose a basis of orthogonal eigenvectors in this linear subspace.

- **All the eigenvectors of a hermitian operator representing an observable form a basis in the Hilbert space.**
  In finite dimensional vector spaces it can be proven that the eigenvectors of a hermitian operator span the space. For infinite dimensional vector spaces there is no proof that this is the case. However Dirac argued that it must be taken as an axiom of quantum mechanics that the spectrum of any hermitian operator which represents an observable must span the Hilbert space. The argument is quite important and we now discuss it in detail.

We have already stated that after we make a measurement and obtain a certain result, a second measurement of the same quantity immediately after the first will give the same result. This happens even if before the first measurement its outcome is not certain. The measurement then forces the system to change its state and to collapse into an eigenstate of the operator representing the observable. If we interpret the measurement in this way we have to draw a few important conclusions:

1. The possible outcomes of a measurement of an observable are all possible eigenvalues of the operator representing that observable.

2. Viceversa, any eigenvalue of an operator is a possible outcome of a measurement of the observable represented by that operator.

3. A measurement makes a system collapse into an eigenstate of that operator; however, it should not change the system so much as to make it jump into an eigenstate which is not contained in its original state. *I.e.* if the system is in a state $|\psi\rangle$ which is given by a superposition of eigenstates $|\psi_i\rangle$ of the observable Q:
   $$|\psi\rangle = \sum_i c_i|\psi_i\rangle$$
   the possible outcomes of a measurement of Q in this state are all the eigenvalues corresponding to the eigenstates contained in $|\psi\rangle$.

Since the latter statement applies to any state $|\psi\rangle$ it means that it must be possible to represent any state as a linear superposition of the eigenstates of any observable. Even if we cannot prove that this is the case, it is necessary to assume that it is so in order to have a consistent formulation of quantum mechanics.

We stress that the latter statement is a physical one, not a mathematical one. Should one find a hermitian operator whose eigenstates do not span the Hilbert space, this does not contradict our statement and does not imply that we have to give up our axiom. We would only have to conclude that that operator cannot represent an observable.

4.4.2 Continuous spectra of hermitian operators

Ideally one would like to extend the situation we just described for discrete spectra to continuous ones. The problem is that eigenfunctions corresponding to continuously varying eigenvalues are not normalizable, and so they do not belong to the Hilbert space. It is nonetheless convenient to use the eigenfunctions as a basis in the Hilbert space, although this may sound very weird. The best way to illustrate how this is done is to discuss a few examples.

Eigenvalues and eigenfunctions of momentum

We have seen that momentum is represented by the following operator:

$$\hat{p} = \frac{\hbar}{i}\frac{d}{dx} \quad .$$

Its eigenfunctions are obtained by solving the differential equation:

$$\frac{\hbar}{i}\frac{d}{dx}\psi_p(x) = p\psi_p(x) \quad , \tag{4.4.6}$$

which has as solution

$$\psi_p(x) = Ae^{ipx/\hbar} \quad . \tag{4.4.7}$$

The latter function is not square integrable for any complex value of p and so does not belong to the Hilbert space. Yet, if we require that p be real, as it should be, we can indeed use the exponential functions $\psi_p(x)$ as a basis, in the sense that any function which is square-integrable can be Fourier transformed and so can be written as

$$\psi(x) = \int_{-\infty}^{\infty} dp\; c(p)\psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} dp\; c(p)e^{ipx/\hbar} \quad , \tag{4.4.8}$$

where we have chosen as normalization $A = 1/\sqrt{2\pi\hbar}$, and where $c(p)$ is the Fourier transformation of $\psi(x)$. The "basis" functions $\psi_p(x)$ also satisfy a generalized orthonormality property because:

$$\int_{-\infty}^{\infty} dx\; \psi_p^*(x)\psi_{p'}(x) = |A|^2\int_{-\infty}^{\infty} dx\; e^{i(p-p')x/\hbar} = \delta(p-p') \quad , \tag{4.4.9}$$

so that the "coefficients" $c(p)$ are obtained by a projection onto a basis function $\psi_p(x)$:

$$c(p) = \int_{-\infty}^{\infty} dx\ \psi_p^*(x)\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dx e^{-ipx/\hbar}\psi(x) \tag{4.4.10}$$

which is nothing but the Fourier transform. Despite the fact that the functions $\psi_p(x)$ do not belong to the Hilbert space, it is nonetheless convenient to represent them also as vectors $|p\rangle$. The extended orthonormality condition then reads

$$\langle p|p'\rangle = \delta(p - p') \ , \tag{4.4.11}$$

and the projection onto a basis function (*i.e.* the Fourier transform):

$$\langle p|\psi\rangle = c(p) \ . \tag{4.4.12}$$

Eigenvalues and eigenfunctions of position

The position operator is multiplication by the position variable, $\hat{x} = x$ and the eigenfunction equation reads:

$$x\psi_y(x) = y\psi_y(x) \ , \tag{4.4.13}$$

where y on the left-hand side has to be interpreted as the eigenvalue and so as a fixed value, in contrast to x on the right-hand side and in the argument of the function, which is a continuous variable. Equation (4.4.13) does not admit solutions unless the function $\psi_y(x)$ is zero for any value of $x \neq y$. In other words the solution is

$$\psi_y(x) = A\delta(x - y) \ , \tag{4.4.14}$$

for any constant A. Choosing $A = 1$ again gives for the eigenfunctions of $\hat{x}$ a generalized orthonormality condition:

$$\int_{-\infty}^{\infty} dx\ \psi_{y'}^*(x)\psi_y(x) = \int_{-\infty}^{\infty} dx\ \delta(x - y')\delta(x - y) = \delta(y - y') \ . \tag{4.4.15}$$

The eigenfunctions of $\hat{x}$ are not normalizable (in fact they are not even functions but distributions), but any function can again be written as a superposition of them. This is in fact trivial:

$$\psi(x) = \int_{-\infty}^{\infty} dy\ c(y)\psi_y(x) = \int_{-\infty}^{\infty} dy\ c(y)\delta(x - y) = c(x) \ , \tag{4.4.16}$$

as the coefficients of the expansion are given by the function itself.

These two examples show that dealing with eigenvalues and eigenfunctions of hermitian operators in the continuum part of the spectrum brings us outside of the Hilbert space. It is nevertheless convenient to consider these eigenfunctions and extend the same properties of reality of the eigenvalues, orthogonality and completeness of the eigenfunctions also to this case and treat the two cases (discrete or continuous spectra) in exactly the same manner.

4.5 Generalized statistical intepretation

We started by defining the wave function, a function of the position variable x with the property of being square integrable, as describing completely the state of a particle. In particular its modulus squared, multiplied by the interval dx gives the probability of finding the particle in a small interval dx around the point x:

$$\text{Probability of finding the particle in } (x, x+dx) = |\Psi(x,t)|^2 dx \ . \tag{4.5.1}$$

Position, however, is only one of many possible observables and now that we have described the formal structure of quantum mechanics, there seems to be no reason to privilege it with respect to other observables. The aim of quantum mechanics is to determine the state of the system meant as a vector $|\psi(t)\rangle$ in Hilbert space as a function of time. Once we know this state we can answer all the questions about the probability of a measurement of any observable. To obtain this probability we must distinguish again the case of a discrete spectrum from that of a continuous spectrum.

1. **Discrete spectrum**
   If we know the eigenvectors $|\psi_n\rangle$ and the corresponding eigenvalues q_n, we can project any state $|\psi\rangle$ on these:

   $$|\psi\rangle = \sum_n c_n |\psi_n\rangle \quad \text{with} \quad c_n = \langle\psi_n|\psi\rangle \ . \tag{4.5.2}$$

   The probability of obtaining q_n in a measurement of the observable Q is given by

   $$|c_n|^2 \ . \tag{4.5.3}$$

2. **Continuous spectrum**
   Be $|\psi_q\rangle$ the eigenvectors corresponding to the continuously varying eigenvalues q. Although $|\psi_q\rangle$ do not live in the Hilbert space we can write any state $|\psi\rangle$ as

   $$|\psi\rangle = \int dq c(q) |\psi_q\rangle \quad \text{with} \quad c(q) = \langle\psi_q|\psi\rangle \tag{4.5.4}$$

   and the probability of obtaining a value between q and $q+dq$ in a measurement of the observable Q is given by

   $$|c(q)|^2 dq \ . \tag{4.5.5}$$

   The wave function is nothing but the projection of the abstract state $|\psi\rangle$ onto the eigenfunctions of x: $\psi(x) = \langle x|\psi\rangle$. The same information is contained in the projection onto the eigenfunctions of p: $\psi(q) = \langle q|\psi\rangle$. The latter is the Fourier transform of $\psi(x)$ and indeed knowing either of the two implies knowing also the other as follows from the theory of Fourier transforms.

4.6 The uncertainty principle

At the beginning we have discussed without proof the uncertainty principle of Heisenberg, stating that one cannot know simultaneously momentum and position of a particle with any precision – the product of the two uncertainties satisfies an inequality. We are now in a position to prove the inequality, but will do it without referring to momentum and position in particular. We will prove it for two generic observables A and B. The standard deviations of the two are defined as

$$\begin{aligned} \sigma_A^2 &= \langle(\hat{A}-\langle A\rangle)\psi|(\hat{A}-\langle A\rangle)\psi\rangle \equiv \langle f|f\rangle \\ \sigma_B^2 &= \langle(\hat{B}-\langle B\rangle)\psi|(\hat{B}-\langle B\rangle)\psi\rangle \equiv \langle g|g\rangle \ . \end{aligned} \tag{4.6.1}$$

The product of the two standard deviations, being the product of two norms squared satisfies the Schwarz inequality:

$$\sigma_A^2\sigma_B^2 = \langle f|f\rangle\langle g|g\rangle \geq |\langle f|g\rangle|^2 \ . \tag{4.6.2}$$

The product $\langle f|g\rangle$ is a complex number, and its modulus squared is larger than the square of its imaginary part:

$$\sigma_A^2\sigma_B^2 \geq |\langle f|g\rangle|^2 \geq \left(\frac{1}{2i}[\langle f|g\rangle - \langle g|f\rangle]\right)^2 \ . \tag{4.6.3}$$

The imaginary part can be explicitly given as follows

$$\begin{aligned} \langle f|g\rangle &= \langle\psi|(\hat{A}-\langle A\rangle)(\hat{B}-\langle B\rangle)|\psi\rangle = \langle AB\rangle - \langle A\rangle\langle B\rangle \\ \langle g|f\rangle &= \langle BA\rangle - \langle A\rangle\langle B\rangle \\ \Rightarrow \quad & \frac{1}{2i}[\langle f|g\rangle - \langle g|f\rangle] = \frac{1}{2i}\langle[\hat{A},\hat{B}]\rangle \ . \end{aligned} \tag{4.6.4}$$

The inequality for the product of the two standard deviations then reads

$$\sigma_A^2\sigma_B^2 \geq \left(\frac{1}{2i}\langle[\hat{A},\hat{B}]\rangle\right)^2 \ . \tag{4.6.5}$$

For the case of momentum and position we have $[\hat{x},\hat{p}] = i\hbar$ and therefore

$$\sigma_x^2\sigma_p^2 \geq \left(\frac{\hbar}{2}\right)^2 \ . \tag{4.6.6}$$

If two operators do not commute it is impossible to construct a basis of simultaneous eigenstates of the two operators. If this were possible, then the commutator would always vanish on any basis vector, and this would mean that it would be zero.

4.6.1 Minimum uncertainty wave packets

The proof of the uncertainty principle is based on the use of two inequalities:

$$\langle f|f\rangle\langle g|g\rangle \geq |\langle f|g\rangle|^2 \quad \text{and} \quad |z|^2 \geq (\mathrm{Im}\, z)^2 \ , \tag{4.6.7}$$

the latter being valid for any complex number z. We now want to see what happens if we require that both inequalities become equalities, such as to minimize the product of the two uncertainties, and have a state with minimal quantum character, so to say. The first inequality becomes an equality if

$$|g\rangle = c|f\rangle \ , \tag{4.6.8}$$

while the second one becomes an equality if the scalar product $\langle g|f\rangle$ is purely imaginary. The latter condition is fulfilled if c is purely imaginary:

$$|g\rangle = ia|f\rangle \qquad a \in \mathbb{R} \ . \tag{4.6.9}$$

Let us now see what these conditions mean in the case of the position–momentum uncertainty principle:

$$\begin{aligned} |g\rangle &= (\hat{p} - \langle p\rangle)|\psi\rangle \ , \quad |f\rangle = (\hat{x} - \langle x\rangle)|\psi\rangle \\ |g\rangle &= ia|f\rangle \quad \Rightarrow \quad \left(\frac{\hbar}{i}\frac{d}{dx} - \langle p\rangle\right)|\psi\rangle = ia(\hat{x} - \langle x\rangle)|\psi\rangle \ . \end{aligned} \tag{4.6.10}$$

The latter differential equation has as solution

$$|\psi\rangle = Ae^{-a(x-\langle x\rangle)^2/(2\hbar)}e^{i\langle p\rangle x/\hbar} \ . \tag{4.6.11}$$

The minimum uncertainty wave function is a plane wave multiplied by a gaussian distribution in x around the expectation value $\langle x\rangle$. The width of the gaussian distribution is determined by the parameter a, the smaller the latter, the wider the gaussian. Independently of that, however the product of the two standard deviations is always minimal, equal to $\hbar/2$.

4.6.2 Energy-time uncertainty

We now consider the uncertainty principle for the energy and another unspecified observable which we assume not to commute with the Hamiltonian. As we will see at the end of the discussion, no matter what observable we choose we will find that the product of the uncertainty in the energy and a time interval has to satisfy an inequality. This is what is usually referred to as energy-time uncertainty.

We assume that $[\hat{H}, \hat{Q}] \neq 0$ and therefore that

$$\sigma_E^2\sigma_Q^2 \geq \left(\frac{1}{2i}\langle[\hat{H}, \hat{Q}]\rangle\right)^2 \ . \tag{4.6.12}$$

An observable whose operator does not commute with the Hamiltonian cannot be constant in time. We have seen that the eigenfunctions of the Hamiltonian are stationary states – these, because of the nonzero commutator between $\hat{H}$ and $\hat{Q}$, cannot be eigenstates of $\hat{Q}$. The eigenstates of $\hat{Q}$ must then have a nontrivial time dependence. Let us look, *e.g.* at the time derivative of the expected value of Q:

$$\frac{d}{dt}\langle Q\rangle = \frac{d}{dt}\langle\psi|\hat{Q}|\psi\rangle = \langle\frac{\partial}{\partial t}\psi|\hat{Q}|\psi\rangle + \langle\psi|\frac{\partial}{\partial t}\hat{Q}|\psi\rangle + \langle\psi|\hat{Q}|\frac{\partial}{\partial t}\psi\rangle \ . \tag{4.6.13}$$

The time derivative of the state ψ is given by the action of the Hamiltonian on that state. We then have

$$\frac{d}{dt}\langle Q\rangle = \frac{i}{\hbar}\langle\hat{H}\psi|\hat{Q}|\psi\rangle - \frac{i}{\hbar}\langle\psi|\hat{Q}|\hat{H}\psi\rangle + \langle\frac{\partial\hat{Q}}{\partial t}\rangle \ . \tag{4.6.14}$$

If the operator $\hat{Q}$ does not explicitly depend on time we have

$$\frac{d}{dt}\langle Q\rangle = \frac{i}{\hbar}\langle\psi|[\hat{H},\hat{Q}]|\psi\rangle = \frac{i}{\hbar}\langle[\hat{H},\hat{Q}]\rangle \ . \tag{4.6.15}$$

The time derivative of the expectation value of an operator is equal to ($i/\hbar$ times) the expectation value of the commutator of the same operator with the Hamiltonian. Since the latter is what enters the inequality (4.6.12) we can rewrite this as

$$\sigma_E^2\sigma_Q^2 \geq \left(\frac{\hbar}{2}\frac{d}{dt}\langle Q\rangle\right)^2 \ . \tag{4.6.16}$$

The ratio $\Delta t \equiv \sigma_Q/(d\langle Q\rangle/dt)$ has the dimension of a time and represents the time needed by a state to change the expectation value of Q by one standard deviation. Roughly speaking this is the time during which the system does not change significantly its state. In terms of this time interval the uncertainty relation (4.6.12) reads

$$\Delta E\Delta t \geq \frac{\hbar}{2} \ . \tag{4.6.17}$$

The energy-time uncertainty relation can be described as follows: if a system is in a state which evolves in time, such that, *e.g.* an observable changes its value with time, then the energy of this state cannot be measured with any precision. The shorter the time needed for this state to change significantly, the larger is the minimum uncertainty with which one can determine the energy of this state. The energy-time uncertainty relation is particularly relevant to unstable particles. The latter particles only live for a finite amount of time (some of them a very short one) and the measurement of their mass is a measurement of their energy when they are at rest. As it follows from the uncertainty relation it is impossible to measure the mass of these particles with a precision higher than the inverse of their lifetime (multiplied by $\hbar/2$). In this respect it is instructive to glance through the PDG [4] and check explictly that this is the case for some of the many particles which are listed there.

Chapter 5

Angular momentum

Before analyzing some interesting physical systems in three spatial dimensions we now discuss in some detail a new observable which emerges as we move from one to three dimensions: angular momentum. Classically it is defined as

$$\mathbf{L} = \mathbf{x} \times \mathbf{p} \ , \tag{5.0.1}$$

and the corresponding quantum operator reads

$$\hat{\mathbf{L}} = \hat{\mathbf{x}} \times \hat{\mathbf{p}} = \frac{\hbar}{i} \mathbf{x} \times \vec{\nabla} \ , \tag{5.0.2}$$

with individual components given by

$$\hat{L}_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right), \ \ \hat{L}_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right), \ \ \hat{L}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right).$$

It is usually assumed that the different spatial coordinates commute and that so do also the components of momentum. The commutation relations among the angular momentum components are then calculable and are given by[1]

$$[L_x, L_y] = i\hbar L_z \ , \text{ and cyclic permutations.} \tag{5.0.3}$$

All three commutation relations can also be written compactly with the help of the totally antisymmetric tensor of rank three ϵ_{ijk}, $\epsilon_{123} = 1$:

$$[L_i, L_j] = i\hbar\epsilon_{ijk} L_k \ , \tag{5.0.4}$$

where we have adopted Einstein's summation convention. As we have learned in the previous chapter, these commutation relations imply that there exists an uncertainty relation among the three different components of angular momentum, which reads

$$\sigma_{L_x}\sigma_{L_y} \geq \frac{\hbar}{2}\left|\langle L_z \rangle\right| \ , \text{ and cyclic permutations.} \tag{5.0.5}$$

[1] To simplify the notation we again drop the hat to indicate an operator.

This means that one cannot build eigenfunctions of more than one component of angular momentum at a time. If we consider the angular momentum squared, however, $\mathbf{L}^2 = L_x^2 + L_y^2 + L_z^2$ we find out that this observable commutes with all three components:

$$\begin{aligned}[\mathbf{L}^2, L_z] &= [L_x^2, L_z] + [L_y^2, L_z] = \\ &= L_x[L_x, L_z] + [L_x, L_z]L_x + L_y[L_y, L_z] + [L_y, L_z]L_y = \\ &= -i\hbar\left(L_xL_y + L_yL_x - L_yL_x - L_xL_y\right) = 0 \ . \end{aligned} \tag{5.0.6}$$

We can find simultaneous eigenfunctions of $\mathbf{L}^2$ and one of the components, *e.g.* L_z, and will do this next.

5.1 Eigenfunctions of $\mathbf{L}^2$ and L_z.

Simultaneous eigenfunctions of two operators are identified by two eigenvalues. We indicate the eigenvalues of $\mathbf{L}^2$ by λ and those of L_z by μ and the eigenfunctions with $|\lambda\ \mu\rangle$. As in the case of the harmonic oscillator, Sec. 3.3, we can determine all the possible eigenvalues rather easily with the help of raising and lowering operators

$$L_\pm \equiv L_x \pm iL_y \ . \tag{5.1.1}$$

These operators obviously commute with $\mathbf{L}^2$ but not with L_z – the commutator with the latter is proportional to themselves

$$[L_z, L_\pm] = [L_z, L_x] \pm i[L_z, L_y] = \hbar\left(iL_y \pm L_x\right) = \pm\hbar L_\pm \ . \tag{5.1.2}$$

With the help of these commutation relations we can show that the state $L_\pm|\lambda\ \mu\rangle$ is still an eigenstate of $\mathbf{L}^2$ with the same eigenvalue (obviously), and of L_z although with eigenvalue $\mu \pm \hbar$:

$$\begin{aligned}\mathbf{L}^2L_\pm|\lambda\ \mu\rangle &= L_\pm\mathbf{L}^2|\lambda\ \mu\rangle = \lambda L_\pm|\lambda\ \mu\rangle \ , \\ L_zL_\pm|\lambda\ \mu\rangle &= L_\pm L_z|\lambda\ \mu\rangle \pm \hbar L_\pm|\lambda\ \mu\rangle = (\mu \pm \hbar)L_\pm|\lambda\ \mu\rangle \end{aligned} \tag{5.1.3}$$

Acting repeatedly with $L_\pm$ on an eigenstate we can therefore change at will, by units of $\hbar$, the eigenvalue of L_z. At some point, however, we reach a value which is too low $\mu - n\hbar < -\lambda$ or too high, $\mu + m\hbar > \lambda$. These values are not admissible because

$$\lambda = \langle\lambda\ \mu|\mathbf{L}^2|\lambda\ \mu\rangle = \langle\lambda\ \mu|L_x^2|\lambda\ \mu\rangle + \langle\lambda\ \mu|L_y^2|\lambda\ \mu\rangle + \mu^2 \ , \tag{5.1.4}$$

which shows that $|\lambda| \geq |\mu|$, because $L_{x,y}$ are hermitian operators and the expectation value of their square in any state is therefore positive. We conclude that for any λ there must be a maximal eigenvalue of μ, indicated by μ_{max}, such that

$$L_+|\lambda\ \mu_{max}\rangle = 0 \ . \tag{5.1.5}$$

We now observe that the angular momentum squared can be expressed as follows:

$$\mathbf{L}^2 = L_\pm L_\mp + L_z^2 \mp \hbar L_z \ . \tag{5.1.6}$$

This relation is obtained by writing

$$L_\pm L_\mp = L_x^2 + L_y^2 \mp i[L_x, L_y] = \mathbf{L}^2 - L_z^2 \pm hL_z \ , \tag{5.1.7}$$

and bringing $\mathbf{L}^2$ on the left-hand side of the equation. We now use Eq. (5.1.6) on $|\lambda\ \mu_{max}\rangle$ and write

$$\begin{aligned} \lambda|\lambda\ \mu_{max}\rangle &= \left(L_-L_+ + L_z^2 + \hbar L_z\right)|\lambda\ \mu_{max}\rangle \\ &= \left(0 + \mu_{max}^2 + \hbar\mu_{max}\right)|\lambda\ \mu_{max}\rangle \\ \\ \Rightarrow \qquad \lambda &= \mu_{max}(\mu_{max} + \hbar) \ . \end{aligned} \tag{5.1.8}$$

Writing $\mu_{max} = \hbar\ell$ in terms of the dimensionless number ℓ, we have

$$\lambda = \hbar^2\ell(\ell+1) \ . \tag{5.1.9}$$

Analogously we can show that

$$\lambda = \mu_{min}(\mu_{min} - \hbar) \quad \Rightarrow \quad \mu_{min} = -\hbar\ell \tag{5.1.10}$$

where the other possible solution, $\mu_{min} = \hbar(\ell+1)$ has been excluded because $\mu_{max} > \mu_{min}$. In addition to the two extreme values, all other possible eigenvalues of L_z are of the form $\hbar(n-\ell)$ or $\hbar(\ell-m)$, with $n, m \in \mathbb{N}$. In particular there must be a maximal integer n_{max} for which $\hbar\ell = \hbar(n_{max} - \ell)$. This implies that the admissible values of ℓ are such that $2\ell \in \mathbb{N}$. We have now identified all possible eigenvalues of $\mathbf{L}^2$ and L_z, which can be expressed in terms of two half-integers, ℓ and m, with $m = n-\ell$, $\forall n \in \mathbb{N}$ such that $|m| \leq \ell$,. The simultaneous eigenstates of $\mathbf{L}^2$ and L_z are then written as $|\ell\ m\rangle$ and

$$\mathbf{L}^2|\ell\ m\rangle = \hbar^2\ell(\ell+1)|\ell\ m\rangle \ , \quad L_z|\ell\ m\rangle = \hbar m|\ell\ m\rangle \ . \tag{5.1.11}$$

5.1.1 Explicit form of the eigenfunctions

We now derive the explicit form of the eigenfunctions of angular momentum. To this aim it is convenient to start by rewriting the angular momentum operators in spherical coordinates:

$$\begin{aligned} L_\pm &= \pm\hbar e^{\pm i\varphi}\left(\frac{\partial}{\partial\theta} \pm i\cot\theta\frac{\partial}{\partial\varphi}\right) \\ L_z &= \frac{\hbar}{i}\frac{\partial}{\partial\varphi} \\ \mathbf{L}^2 &= -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] \ . \end{aligned} \tag{5.1.12}$$

Since the angular momentum operators do not involve any derivative with respect to r, any function of the form:

$$\psi_{\ell m}(r,\theta,\varphi) = R(r) Y_\ell^m(\theta,\varphi) \ , \tag{5.1.13}$$

is an eigenfunction of angular momentum provided that the angular dependent part satisfies the eigenvalue equations:

$$\begin{aligned} \mathbf{L}^2 Y_\ell^m(\theta,\varphi) &= \hbar^2 \ell(\ell+1) Y_\ell^m(\theta,\varphi) \ , \\ L_z Y_\ell^m(\theta,\varphi) &= \hbar m Y_\ell^m(\theta,\varphi) \ . \end{aligned} \tag{5.1.14}$$

The last of the two equations is easy to solve:

$$Y_\ell^m(\theta,\varphi) = f_\ell^m(\theta) e^{im\varphi} \tag{5.1.15}$$

and makes the first one into a one-dimensional differential equation for f_ℓ^m:

$$\left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) - \frac{m^2}{\sin^2\theta} \right] f_\ell^m(\theta) = -\ell(\ell+1) f_\ell^m(\theta) \ . \tag{5.1.16}$$

Instead of solving this differential equation, we now discuss an alternative route for the explicit derivation of f_ℓ^m, which is simpler. We exploit the fact that $L_+ f_\ell^\ell = 0$, which amounts to the following equation:

$$\left(\frac{\partial}{\partial\theta} - \ell \cot\theta \right) f_\ell^\ell = 0 \ , \tag{5.1.17}$$

whose solution is $f_\ell^\ell = \sin^\ell\theta$, as can be immediately checked. Given the eigenfunction with the highest allowed value of m, all the others can be obtained by repeated action of the L_- operator:

$$f_\ell^{\ell-1} \propto \left(\frac{\partial}{\partial\theta} + \ell \cot\theta \right) \sin^\ell\theta \ , \tag{5.1.18}$$

and in general

$$Y_\ell^m(\theta,\varphi) \propto L_-^{\ell-m} Y_\ell^\ell(\theta,\varphi) \ , \tag{5.1.19}$$

which provides an explicit form for the eigenfunctions. We have written only a proportionality factor, because L_- does not leave the norm of the state on which it acts unchanged, and one has to renormalize the function after every action of the L_- operator. Without discussing these issues we now give the explicit form of the eigenfunctions of angular momentum

$$Y_\ell^m(\theta,\varphi) = \epsilon \sqrt{\frac{(2\ell+1)}{4\pi} \frac{(\ell-|m|)!}{(\ell+|m|)!}} e^{im\varphi} P_\ell^m(\cos\theta) \ , \tag{5.1.20}$$

where $\epsilon = (-1)^m$ for $m > 0$ and $\epsilon = 1$ otherwise. The functions P_ℓ^m are the so-called associated Legendre functions, and are so defined:

$$P_\ell^m(x) = (1-x^2)^{|m|/2} \left(\frac{d}{dx}\right)^{|m|} P_\ell(x) \ , \tag{5.1.21}$$

where $P_\ell(x)$ are the Legendre polynomial defined as

$$P_\ell(x) = \frac{1}{2^\ell \ell!} \left(\frac{d}{dx}\right)^\ell (x^2-1)^\ell \ . \tag{5.1.22}$$

The eigenfunctions Y_ℓ^m as given in Eq. (5.1.20) are an orthonormal set of functions

$$\int_{-1}^{1} d\cos\theta \int_0^{2\pi} d\varphi \, [Y_\ell^m]^* \, Y_j^n = \delta_{\ell j}\delta_{mn} \ . \tag{5.1.23}$$

5.2 Spin

In nature angular momentum is not only associated to an orbital motion of a particle, but is also an intrinsic property of particles, even if they are at rest. There are known particles with spin 0 (like pions, kaons etc.), spin 1/2 (like electrons, muons, protons, etc.), spin 1 (like photons, Z and W bosons, ρ mesons etc.), spin 3/2 (like the Delta and other baryonic resonances), spin 2 (like the graviton or hadronic resonances). We now discuss the quantum treatment of a particle of spin 1/2 ignoring the x-dependent part of its wave function.

As far as its spin is concerned, there are two possible states for such a particle:

$$|1/2\ 1/2\rangle \ \text{ or } \ |1/2\ {-1}/2\rangle \ . \tag{5.2.1}$$

If we use these as basis vectors we can express any other vector as a column with two entries and operators as 2×2 matrices. The two basis vectors, in particular have the form:

$$|1/2\ 1/2\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad |1/2\ {-1}/2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{5.2.2}$$

The operators $\mathbf{S}^2$ and S_z are diagonal on this basis:

$$\mathbf{S}^2|1/2\ \pm 1/2\rangle = \hbar^2(3/4)|1/2\ \pm 1/2\rangle, \qquad S_z|1/2\ \pm 1/2\rangle = \hbar(\pm 1/2)|1/2\ \pm 1/2\rangle \tag{5.2.3}$$

and can therefore be represented by the following diagonal matrices

$$\mathbf{S}^2 = \frac{3\hbar^2}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \qquad S_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{5.2.4}$$

There are two more operators to consider, $S_{x,y}$ or $S_\pm$, related by

$$S_x = (S_+ + S_-)/2 \ , \quad S_y = (S_+ - S_-)/2i \ . \tag{5.2.5}$$

The action of $S_\pm$ on the basis vectors is known:

$$\begin{aligned} S_+|1/2\ 1/2\rangle &= 0\ , & S_+|1/2\ {-1/2}\rangle &= \hbar|1/2\ 1/2\rangle\ , \\ S_-|1/2\ 1/2\rangle &= \hbar|1/2\ {-1/2}\rangle\ , & S_-|1/2\ {-1/2}\rangle &= 0\ , \end{aligned}$$

$$\Rightarrow \qquad S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \qquad S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}\ , \tag{5.2.6}$$

and this gives us the matrix representation of the operators $S_{x,y}$:

$$S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}. \tag{5.2.7}$$

In summary, if the total spin is 1/2 the four spin operators can be represented in terms of the unit matrix and three so-called Pauli matrices:

$$\mathbf{S}^2 = \hbar^2(3/4)\sigma_0\ , \quad S_x = \hbar/2\,\sigma_1\ , \quad S_y = \hbar/2\,\sigma_2\ , \quad S_z = \hbar/2\,\sigma_3\ , \tag{5.2.8}$$

where σ_0 is the unit matrix and

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{5.2.9}$$

In a spin one half system the Hilbert space is finite dimensional (has dimension two) and very simple to deal with. On the other hand it allows one to see how quantum mechanics works, with all its complexities. For example if the particle is in a state $|1/2\ 1/2\rangle$ we can ask ourselves what results can come out of a measurement of the x component of spin. In order to answer this question we have to determine the eigenvalues and eigenvectors of S_x. The possible eigenvalues we know already, and are the same as those of S_z, $\pm\hbar/2$. If we want to determine the eigenvectors of S_x in the basis of the S_z eigenvectors we can work directly with the matrices (5.2.8,5.2.9). It is easy to find out that the eigenvectors are

$$|1/2\ m_x{=}1/2\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}\ , \quad |1/2\ m_x{=}{-1/2}\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}\ . \tag{5.2.10}$$

We then have to expand the state $|1/2\ 1/2\rangle$ in the basis of the eigenvectors of S_x and the modulus squared of the coefficients of this expansion gives us the probability to obtain either of the eigenvalues as result of the measurement:

$$|1/2\ 1/2\rangle = \frac{1}{\sqrt{2}}|1/2\ m_x{=}1/2\rangle + \frac{1}{\sqrt{2}}|1/2\ m_x{=}{-1/2}\rangle\ . \tag{5.2.11}$$

The probabilities to get either $+\hbar/2$ or $-\hbar/2$ in a measurement of S_x are therefore equal, and both 50%. A measurement of S_x would then make the particle change its state and collapse on either $|1/2\ m_x{=}1/2\rangle$ or $|1/2\ m_x{=}{-1/2}\rangle$. If we now make

a measurement of S_z we are not anymore sure to get $\hbar/2$, because the system is now in a superposition of the two states $|1/2\,\pm 1/2\rangle$. From Eq. (5.2.10) we read off that the probability to get either of the two possible results is again 50%.

Similar questions can be asked about S_y. All one needs to know in that case is again the representation of its eigenvectors in the basis of the eigenvectors of S_z:

$$|1/2\; m_y{=}1/2\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix}\;, \quad |1/2\; m_y{=}{-1}/2\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \end{pmatrix}\;. \tag{5.2.12}$$

5.2.1 Electron in a magnetic field

The treatment of spin presented so far has not made reference to any dynamics related to the spin. We now discuss the time evolution of the spin states if the Hamiltonian depends on spin, and consider as an example a spin coupled to a magnetic field:

$$\hat{H} = -\vec{\mu}\cdot\mathbf{B}\;, \quad \text{where} \quad \vec{\mu} = \gamma\mathbf{S}\;, \tag{5.2.13}$$

is the magnetic moment associated with the spin $\mathbf{S}$. In the case of electrons, *e.g.* $\gamma = g_e e/(2m_e)$ where e and m_e are charge and mass of the electron, respectively, and g_e its gyromagnetic ratio, equal to 2 up to a one per mille correction (the so-called electron anomalous magnetic moment, which can be calculated in quantum field theory and is measured nowadays with incredible accuracy [5]). Let us now consider a constant magnetic field pointing in the z direction:

$$\mathbf{B} = B_0\mathbf{e}_z \quad \Rightarrow \quad \hat{H} = -\gamma B_0 S_z = -\gamma B_0\hbar/2\;\sigma_3\;. \tag{5.2.14}$$

Where the latter representation is given in the basis of the S_z eigenvectors: in this case the Hamiltonian (like any other operator) can be expressed as a 2×2 matrix. The solution of the Schrödinger equation then reads

$$|\psi(t)\rangle = ae^{i\gamma B_0 t/2}|1/2\;1/2\rangle + be^{-i\gamma B_0 t/2}|1/2\;{-1}/2\rangle\;\;, \tag{5.2.15}$$

where a and b specify the initial conditions:

$$|\psi(0)\rangle = a|1/2\;1/2\rangle + b|1/2\;{-1}/2\rangle = \begin{pmatrix} a \\ b \end{pmatrix}. \tag{5.2.16}$$

Since $|\psi(0)\rangle$ must be normalized to one and we are free to choose its phase, we take both a and b real and equal to

$$a = \cos(\alpha/2)\;, \quad \beta = \sin(\alpha/2)\;, \tag{5.2.17}$$

which gives

$$|\psi(t)\rangle = \begin{pmatrix} \cos(\alpha/2)e^{i\gamma B_0 t/2} \\ \sin(\alpha/2)e^{-i\gamma B_0 t/2} \end{pmatrix}\;. \tag{5.2.18}$$

We can now evaluate the expectation values of all three spin components in such a t dependent state, and see how they evolve in time:

$$\begin{aligned}\langle S_x\rangle &= \langle\psi(t)|S_x|\psi(t)\rangle = \frac{\hbar}{2}\sin\alpha\cos(\gamma B_0 t)\ ,\\ \langle S_y\rangle &= \langle\psi(t)|S_y|\psi(t)\rangle = -\frac{\hbar}{2}\sin\alpha\sin(\gamma B_0 t)\ ,\\ \langle S_z\rangle &= \langle\psi(t)|S_z|\psi(t)\rangle = \frac{\hbar}{2}\cos\alpha\ .\end{aligned} \tag{5.2.19}$$

Although a measurement of any of these spin components will always give either $\hbar/2$ or $-\hbar/2$, the probabilities of these results evolve in time (those of the x and y components only), and so do the expectation values. The expectation value of the vector $\mathbf{S}$ behaves like a vector at a given angle α with respect to the magnetic field which precesses about that axis. The precession frequency $\omega = \gamma B_0$ is called the Larmor frequency and is the same frequency with which an angular momentum in a magnetic field would precess. This result is in accordance with Ehrenfest's theorem, which says that the expectation values behave like the corresponding classical quantities.

5.3 Addition of angular momenta

If we build a system out of two spins 1/2 what kind of states can we make out of these? What possible outcomes of measurements of the total spin or of a single component thereof could we get? These questions we can answer explicitly because we can build the state of the system out of products of the states of the single spins, and the operator of the total spin is given by the sum of the operators of the two spins. Since we have two states for each spin, two spins together have four states:

$$|\uparrow\uparrow\rangle \equiv |{}^1\!/_2\ {}^1\!/_2\rangle_1 |{}^1\!/_2\ {}^1\!/_2\rangle_2\,,\ \ |\uparrow\downarrow\rangle,\ \ |\downarrow\uparrow\rangle,\ \ |\downarrow\downarrow\rangle, \tag{5.3.1}$$

where the last three states are defined in analogy to the first one, *i.e.* the first (second) arrow refers to the third component of the first (second) spin. The action of the operator $S_z \equiv S_z^{(1)} + S_z^{(2)}$ on these states is easy to calculate:

$$\begin{aligned}S_z|\uparrow\uparrow\rangle &= S_z^{(1)}|{}^1\!/_2\ {}^1\!/_2\rangle_1|{}^1\!/_2\ {}^1\!/_2\rangle_2 + |{}^1\!/_2\ {}^1\!/_2\rangle_1 S_z^{(2)}|{}^1\!/_2\ {}^1\!/_2\rangle_2\\ &= \hbar({}^1\!/_2 + {}^1\!/_2)|{}^1\!/_2\ {}^1\!/_2\rangle_1|{}^1\!/_2\ {}^1\!/_2\rangle_2 = \hbar|\uparrow\uparrow\rangle\end{aligned} \tag{5.3.2}$$

and similarly for the others

$$S_z|\uparrow\downarrow\rangle = 0\,,\ \ S_z|\downarrow\uparrow\rangle = 0\,,\ \ S_z|\downarrow\downarrow\rangle = -\hbar|\downarrow\downarrow\rangle\,. \tag{5.3.3}$$

If we would ask an observer to measure the spin of such a system without telling him/her that this is made out of two spin one half particles, he/she would still

get results in accordance with the general properties of spin. In other words we have to be able to reexpress these product states as states of the form $|\ell m\rangle$. Since the maximal value of m which we have obtained is 1, cf. (5.3.2), we expect to have the three states $|1\,1\rangle$, $|1\,0\rangle$ and $|1\,-1\rangle$. We have one more state with $m=0$, however. In order to understand this, we first identify the three $\ell=1$ states by starting from $|\uparrow\uparrow\rangle = |11\rangle$ and acting on this with $S_- = S_-^{(1)} + S_-^{(2)}$:

$$\begin{aligned} S_-|\uparrow\uparrow\rangle &= S_-^{(1)}|1/2\ 1/2\rangle_1|1/2\ 1/2\rangle_2 + |1/2\ 1/2\rangle_1 S_-^{(2)}|1/2\ 1/2\rangle_2 \\ &= |1/2\ {}^{-1}/_2\rangle_1|1/2\ 1/2\rangle_2 + |1/2\ 1/2\rangle_1|1/2\ {}^{-1}/_2\rangle_2 = |\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle. \end{aligned} \tag{5.3.4}$$

Since $S_-|11\rangle = c|10\rangle$ where c is a normalization factor, we conclude that

$$|10\rangle = \frac{1}{\sqrt{2}}(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle) \ . \tag{5.3.5}$$

Acting once more with S_- on this state we get:

$$S_-\frac{1}{\sqrt{2}}(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle) = \sqrt{2}|\downarrow\downarrow\rangle \ \ \Rightarrow \ \ |1\ -1\rangle = |\downarrow\downarrow\rangle, \tag{5.3.6}$$

as it should be (note that again we have adjusted the normalization factor).

The linearly independent state we are left with is $1/\sqrt{2}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$. Having $m=0$ and being the only state left, we suspect that this is the $|00\rangle$ state. Let us act on it with S_+ and S_- and see if we end up getting something else:

$$\begin{aligned} S_+(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) &= (|\uparrow\uparrow\rangle - |\uparrow\uparrow\rangle) = 0 \ , \\ S_-(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) &= (|\downarrow\downarrow\rangle - |\downarrow\downarrow\rangle) = 0 \ . \end{aligned} \tag{5.3.7}$$

This proves that zero is both maximal as well as the minimal m for this states, and therefore that $\ell = 0$: $(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2} = |00\rangle$.

As a further check we can calculate $\mathbf{S}^2$ on the four states. We first write the total spin squared as follows:

$$\begin{aligned} \mathbf{S}^2 &= (\mathbf{S}^{(1)})^2 + (\mathbf{S}^{(2)})^2 + 2\mathbf{S}^{(1)}\cdot\mathbf{S}^{(2)} \ , \\ \mathbf{S}^{(1)}\cdot\mathbf{S}^{(2)} &= S_x^{(1)}S_x^{(2)} + S_y^{(1)}S_y^{(2)} + S_z^{(1)}S_z^{(2)} \\ &= \frac{1}{2}(S_+^{(1)}S_-^{(2)} + S_-^{(1)}S_+^{(2)}) + S_z^{(1)}S_z^{(2)} \ , \end{aligned} \tag{5.3.8}$$

and then apply them on the states we constructed:

$$\begin{aligned} \mathbf{S}^2|\uparrow\uparrow\rangle &= \left[(\mathbf{S}^{(1)})^2 + (\mathbf{S}^{(2)})^2 + 2\mathbf{S}^{(1)}\cdot\mathbf{S}^{(2)}\right]|\uparrow\uparrow\rangle \\ &= \left[\hbar^2(3/4+3/4) + 0 + 0 + 2\hbar^2 1/4\right]|\uparrow\uparrow\rangle = \hbar^2 2|\uparrow\uparrow\rangle, \end{aligned} \tag{5.3.9}$$

where the last three terms correspond to the three terms in the expansion of $\mathbf{S}^{(1)}\cdot\mathbf{S}^{(2)}$ as in Eq. (5.3.8). This confirms that $|\uparrow\uparrow\rangle = |11\rangle$, because $\mathbf{S}^2|11\rangle =$

$\hbar^2 1(1+1)|11\rangle = \hbar^2 2|11\rangle$. The same check can be made on all the other $\ell = 1$ states. Let us now check what happens with $|00\rangle$:

$$\begin{aligned} \mathbf{S}^2(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) &= \hbar^2 \left[(3/4+3/4) - 1 - 2\cdot 1/4\right](|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \\ &= 0(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)\,, \end{aligned} \tag{5.3.10}$$

which confirms that $|00\rangle = (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$.

The one we have just worked out is a special case of a general rule, whose derivation we will not provide. Combining two angular momenta ℓ_1 and ℓ_2 one gets all possible states with $\ell = |\ell_1 - \ell_2|, \ldots, \ell_1 + \ell_2$. As a minimal check on this rule, we can count the number of states in both cases. A state of angular momentum ℓ has $2\ell + 1$ states. So the product of two angular momenta ℓ_1 and ℓ_2 has a total of $(2\ell_1 + 1)(2\ell_2 + 1) = 4\ell_1\ell_2 + 2(\ell_1 + \ell_2) + 1$ states. In the second case we have to sum $2\ell + 1$ from $\ell = |\ell_1 - \ell_2|$ up to $\ell_1 + \ell_2$[2]

$$\sum_{n=\ell_1-\ell_2}^{\ell_1+\ell_2} (2n+1) = 4\ell_1\ell_2 + 2\ell_1 + 2\ell_2 + 1\,, \tag{5.3.11}$$

as it should be.

[2]We assume without loss of generality that $\ell_1 > \ell_2$.

Chapter 6

Symmetries in quantum mechanics

Symmetries play an important role in physics. In quantum physics, where the mathematics is from the start more complicated and where only a handful of problems admit analytical solutions, it is very important to have an understanding of the symmetry properties of a system. As in classical physics, and according to Noether's theorem, to every continuous symmetry in a system corresponds a conserved quantity, and identifying them is very important even (or maybe especially) if one is not able to solve a problem analytically. In this chapter we explore these concepts with a few simple examples, translations and rotations, before getting to the hydrogen atom, where indeed rotational invariance is of fundamental importance.

6.1 Translations

Assume that $\psi(x)$ is the wave function of a particle whose dynamics is governed by the Hamiltonian $\hat{H}$ and imagine to translate the particle backwards by a. Its new wave function then becomes

$$\tilde{\psi}(x) = \psi(x+a) \ , \tag{6.1.1}$$

because after the translation the probability to find the particle at x is equal to the probability to find the particle before the translation at $x+a$. Can we obtain the wave function after the translation from the wave function before the translation by the action of an operator on it? Let us do a Taylor expansion of $\psi(x+a)$ around $a=0$:

$$\begin{aligned} \tilde{\psi}(x) &= \psi(x) + \psi^{'}(x)a + \frac{1}{2}\psi^{''}(x)a^2 + \ldots = \left(1 + a\frac{d}{dx} + \frac{1}{2}a^2\frac{d^2}{dx^2} + \ldots\right)\psi(x) \\ &= \left[1 + \frac{i}{\hbar}a\hat{p} + \frac{1}{2}\left(\frac{i}{\hbar}a\hat{p}\right)^2 + \ldots\right]\psi(x) = e^{\frac{ia}{\hbar}\hat{p}}\psi(x) \equiv \hat{T}(a)\psi(x) \ . \end{aligned} \tag{6.1.2}$$

The operator $\hat{T}(a)$ generates a translation of a system by $-a$. A properly defined transformation should be unitary, so as to leave invariant the norm of the wave function on which they act. It is easy to verify that this is the case (the inverse of a translation by a is a translation by $-a$ and this indeed corresponds to the transforming $\hat{T}$ into ist adjoint), and see that this is intimately related to the fact that in the exponential a hermitian operator multiplied by a purely imaginary constant appears. This is a general property of unitary transformations: when expanded infinitesimally close to the unit operator they are related to hermitian operators:

$$\begin{aligned} \hat{U}(\epsilon) &= \mathbb{1} + i\epsilon\hat{X} + O(\epsilon^2) \\ \mathbb{1} &= \hat{U}(\epsilon)^\dagger\hat{U}(\epsilon) = \left(\mathbb{1} - i\epsilon\hat{X}^\dagger + O(\epsilon^2)\right)\left(\mathbb{1} + i\epsilon\hat{X} + O(\epsilon^2)\right) \\ &= \mathbb{1} + i\epsilon(\hat{X} - \hat{X}^\dagger) + O(\epsilon^2) \quad \Rightarrow \quad \hat{X}^\dagger = \hat{X} \ . \end{aligned} \tag{6.1.3}$$

The hermitian operator $\hat{X}$ is called the generator of the transformation $\hat{U}$.

Shifting the wave function by a may change the status of the system substantially: for example if the Hamiltonian is a square well, shifting the wave function will significantly change the energy of that state. If the translation leaves the system invariant, however, the energy, *e.g.* will not change at all:

$$\langle\psi|\hat{H}|\psi\rangle = \langle\tilde{\psi}|\hat{H}|\tilde{\psi}\rangle = \langle\psi|\hat{T}^\dagger(a)\hat{H}\hat{T}(a)|\psi\rangle \ . \tag{6.1.4}$$

Since we do not want the invariance of the energy as an accidental result related to the particular state, but as a true symmetry of the system, which therefore holds for any state $\psi(x)$, this relation implies that

$$\hat{H} = \hat{T}^\dagger(a)\hat{H}\hat{T}(a) \ . \tag{6.1.5}$$

If we now consider infinitesimal transformations, this relation translates into

$$\hat{H} = \left(1 - \frac{i\epsilon}{\hbar}\hat{p} + \ldots\right)\hat{H}\left(1 + \frac{i\epsilon}{\hbar}\hat{p} + \ldots\right) = \hat{H} + \frac{i\epsilon}{\hbar}[\hat{H}, \hat{p}] + O(\epsilon^2) \ , \tag{6.1.6}$$

which means that translations are a symmetry of a system if and only if momentum commutes with the Hamiltonian. In Chap. 3 we have encountered only one such system, the free particle, and indeed in that case the eigenstates of energy were also eigenstates of momentum.

The argument, however, is general and if the transformation $\hat{U}(a)$ leaves the Hamiltonian invariant for any a, then if we consider infinitesimal transformations $a = \epsilon$ we have to conclude that the Hamiltonian commutes with the hermitian operator $\hat{X}$. For any continuous transformation we have a hermitian operator, and therefore a possible observable, and the latter is a constant of motion if the transformation is a symmetry:

$$\frac{\partial}{\partial t}\langle X\rangle = \frac{i}{\hbar}\langle[\hat{H}, \hat{X}]\rangle = 0 \ . \tag{6.1.7}$$

6.2 Rotations in two dimensions

In two dimensions we can consider a new kind of transformations of the coordinates, namely rotations. As for translations we can view this as a transformation of the system of coordinates or as a transformation of the physical system. If we rotate the system backward by an angle ϕ, then the wave function after the rotation will be

$$\tilde{\psi}(x,y) = \psi(x',y') = \psi(x\cos\phi - y\sin\phi, x\sin\phi + y\cos\phi) \ . \tag{6.2.1}$$

Again we want to write this as the action of an operator on the wave function $\psi(x,y)$, and to make things simple we do it directly for an infinitesimal rotation $\phi = \epsilon$:

$$\begin{aligned} \psi(x',y') &= \psi(x-\epsilon y, y+\epsilon x) = \psi(x,y) + \epsilon\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\psi(x,y) + O(\epsilon^2) \\ &= \left[\mathbb{1} + \frac{i\epsilon}{\hbar}\hat{L}_z\right]\psi(x,y) + +O(\epsilon^2) \ . \end{aligned} \tag{6.2.2}$$

So the generator of rotations in the xy plane is the z component of angular momentum.

A two-dimensional Hamiltonian is invariant under rotations if it commutes with $\hat{L}_z$. Let us verify this explicitly by considering an invariant Hamiltonian, for example one of the type

$$\hat{H} = \frac{\hbar^2}{2M}\left(\hat{p}_x^2 + \hat{p}_y^2\right) + V(r) \ , \tag{6.2.3}$$

with $r = \sqrt{x^2+y^2}$. From the commutation relations $[p_x, L_z] = -i\hbar p_y$ and $[p_y, L_z] = i\hbar p_x$ it is easy to show that

$$[\hat{p}_x^2 + \hat{p}_y^2, L_z] = 0 \ . \tag{6.2.4}$$

For the potential we have:

$$\begin{aligned} \frac{i}{\hbar}[L_z, V(r)] &= \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)V(r) = \left(x\frac{\partial r}{\partial y} - y\frac{\partial r}{\partial x}\right)\frac{\partial}{\partial r}V(r) \\ &= \left(x\frac{y}{r} - y\frac{x}{r}\right)\frac{\partial}{\partial r}V(r) = 0 \ . \end{aligned} \tag{6.2.5}$$

So, we conclude that if the potential is of the form $V(r)$ then $[\hat{H}, \hat{L}_z] = 0$.

These properties become obvious if we work in polar coordinates

$$x = r\cos\varphi \ , \quad y = r\sin\varphi \ , \tag{6.2.6}$$

in which case the third component of angular momentum has a particularly simple representation:

$$\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\varphi} \quad . \tag{6.2.7}$$

Indeed with these coordinates a rotation is nothing but a shift of the angular coordinate φ and the generator of such a shift is just the derivative with respect to this coordinate (just like momentum for translations). The invariant Hamiltonian can be written as follows in these coordinates

$$\begin{aligned} \hat{H} &= -\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\varphi^2}\right) + V(r) \\ &= -\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} - \frac{1}{r^2}\frac{1}{\hbar^2}\hat{L}_z^2\right) + V(r) \quad , \end{aligned} \tag{6.2.8}$$

which immediately shows that it commutes with $\hat{L}_z$. So we can choose the eigenfunctions of the Hamiltonian to be simultaneously eigenfunctions of $\hat{L}_z$ too. Let us identify the latter. We look for functions which satisfy

$$\hat{L}_z\psi(r,\varphi) = \ell_z\psi(r,\varphi) \quad , \tag{6.2.9}$$

and so functions of the form

$$\psi_{\ell_z}(r,\varphi) = R(r)e^{i\ell_z\varphi/\hbar} \quad , \tag{6.2.10}$$

for any function $R(r)$. The latter is a single-valued function only if $\ell_z = \hbar m$ with $m \in \mathbb{N}$.

Let us now look for solutions of the Schrödinger equation of the form $\psi_{\ell_z}(r,\varphi)$:

$$\hat{H}R(r)e^{im\varphi} = ER(r)e^{im\varphi} \quad . \tag{6.2.11}$$

The Hamiltonian contains only one term with a derivative with respect to φ (or $\hat{L}_z$) and is otherwise independent thereof. If we let the Hamiltonian act on $R(r)e^{im\varphi}$, $\hat{L}_z^2$ becomes $(\hbar m)^2$ and everything is independent of φ apart from the overall phase factor which can however be removed, because it appears on both sides of the equation. The Schrödinger equation then becomes

$$\left[-\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} - \frac{m^2}{r^2}\right) + V(r)\right] R(r) = ER(r) \quad . \tag{6.2.12}$$

Exploiting the invariance properties of this Hamiltonian, we have simplified the Schrödinger equation by reducing a two-dimensional problem to a differential equation in one single variable.

6.3 Rotations in three dimensions

What is the operator that represents rotations in three dimensions? It is rather natural to generalize what we have learned about rotations in the xy plan to three-dimensional space. First of all, a generic rotation in three-dimensional space can be written as three successive rotations in the xy, then in the xz and finally in the yz plane (or in any other different order – notice, however, that the individual rotations would be different in general, because rotations in different planes do not commute). Such a rotation would then be represented by

$$T(a,b,c) = e^{iaL_x/\hbar} e^{ibL_y/\hbar} e^{icL_z/\hbar} \ . \tag{6.3.1}$$

One is tempted to write the three rotations together in the argument of a single exponential, but this is nontrivial, because the three operators do not commute. The argument of the single exponential then involves also the commutators of the individual arguments. But since the three angular momentum components do form a closed algebra, each commutator can be expressed in terms of the same three operators again. We therefore have:

$$T(a,b,c) = e^{i(a'L_x + b'L_y + c'L_z)/\hbar} \ , \tag{6.3.2}$$

where the relation among the angles a, b and c and the corresponding primed ones can be derived from the Baker-Campbell-Hausdorff formula. The latter representation for the rotation operator suggests a better one. Indeed we can rewrite Eq. (6.3.2) as follows:

$$T(\mathbf{n},\varphi) = e^{i\varphi \mathbf{n}\cdot\mathbf{L}/\hbar} \ , \tag{6.3.3}$$

where $\varphi = \sqrt{a'^2 + b'^2 + c'^2}$ and $\mathbf{n} = (a', b', c')/\varphi$. This formula is now easy to understand: indeed any three-dimensional rotation can be identified by an axis around which the rotation is performed ($\mathbf{n}$) and an angle of rotation (φ). If L_z is the generator of rotations around the z-axis, the generator of rotations around the $\mathbf{n}$ axis is the projection of angular momentum on the same axis: $\mathbf{n}\cdot\mathbf{L}$.

A system is invariant under rotations if all three components of angular momentum commute with the Hamiltonian:

$$[\hat{H}, \mathbf{L}] = 0 \ . \tag{6.3.4}$$

A Hamiltonian of the form

$$\hat{H} = -\frac{\hbar^2}{2M}\triangle + V(r) \ , \tag{6.3.5}$$

is obviously invariant under rotations. Can we check that it indeed commutes with all three components of $\mathbf{L}$? This can be easily done by using the representation of angular momentum in cartesian coordinates. It is however even more

direct to rewrite the Laplace operator in spherical coordinates

$$\begin{aligned} \triangle &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] \\ &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{\hbar^2 r^2}\mathbf{L}^2 \ , \end{aligned} \tag{6.3.6}$$

and notice that the part which involves the derivative in the angles is nothing but the angular momentum squared, cf. Eq. (5.1.12). A Hamiltonian of the form (6.3.5) therefore commutes with all three components of angular momentum and of course also with angular momentum squared.

If we have to deal with a rotationally invariant Hamiltonian, and want to look for its eigenfunctions, we can select those which are at the same time also eigenfunctions of angular momentum (of the square and of one of its components). We have therefore to solve the following three equations simultaneously:

$$\begin{aligned} \hat{H}\psi_{\ell m}(r,\theta,\varphi) &= E\psi_{\ell m}(r,\theta,\varphi) \\ \mathbf{L}^2\psi_{\ell m}(r,\theta,\varphi) &= \hbar^2\ell(\ell+1)\psi_{\ell m}(r,\theta,\varphi) \\ L_z\psi_{\ell m}(r,\theta,\varphi) &= \hbar m\psi_{\ell m}(r,\theta,\varphi) \ . \end{aligned} \tag{6.3.7}$$

The latter two are differential equations in the θ and φ variables, and their solution is independent of the the variable r – the eigenfunctions $\psi_{\ell m}$ must be of the form

$$\psi_{\ell m}(r,\theta,\varphi) = R(r)Y_\ell^m(\theta,\varphi) \ , \tag{6.3.8}$$

and for these the Schrödinger equation reads

$$\left\{-\frac{\hbar^2}{2M}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\ell(\ell+1)}{r^2}\right] + V(r)\right\} R(r)Y_\ell^m(\theta,\varphi) = ER(r)Y_\ell^m(\theta,\varphi) \ , \tag{6.3.9}$$

and so becomes an equation for the radial part of the wave function only, which we rewrite as

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2Mr^2}{\hbar^2}\left[V(r) - E\right]R = \ell(\ell+1)R \ . \tag{6.3.10}$$

As in two dimensions, by exploting the rotation invariance of the Hamiltonian, we have succeeded in transforming the eigenvalue problem for a three-dimensional Hamiltonian into a differential equation for a function of a single variable. In fact if we rewrite the unknown function R as $u(r)/r$ we get the following equation for u:

$$-\frac{\hbar^2}{2M}\frac{d^2u}{dr^2} + \left[V(r) + \frac{\hbar^2}{2M}\frac{\ell(\ell+1)}{r^2}\right]u = Eu \ , \tag{6.3.11}$$

which is nothing but a one-dimensional Schrödinger equation with an "effective potential" $V_{\text{eff}}(r)$ instead of the original one:

$$V_{\text{eff}}(r) = V(r) + \frac{\hbar^2}{2M}\frac{\ell(\ell+1)}{r^2} \ . \tag{6.3.12}$$

The extra term in the effective potential is due to angular momentum and is called the centrifugal barrier: the higher the value of ℓ, the stronger the potential term which acts like a repulsion from the origin will be. Correspondingly, the further away from the origin it will tend to stay. This phenomenon is the classical analogue of the centrifugal force: if a system is in a state with a large angular momentum, it must be rotating around the origin – in this case it will feel a force pulling it away from the origin.

We have now simplified the problem as much as possible as long as we keep the potential $V(r)$ unspecified. In order to discuss the solution of the radial equation we must give the potential explicitly. At this stage we still have one point to discuss, and this concerns the normalization of the radial function. The normalization condition for the wave function $\psi_{\ell m}$ reads

$$1 = \int d^3x |\psi_{\ell m}|^2 = \int_0^\infty dr r^2 |R|^2 \int_{-1}^1 d\cos\theta \int_0^{2\pi} d\varphi |Y_\ell^m|^2 \ . \tag{6.3.13}$$

Any choice of the individual normalizations of the radial and the angular-dependent part are fine, provided that the product of the two integrals is one. We have, however, already normalized the Y_ℓ^m functions so that the angular integral of their modulus squared is one (5.1.23). Consequently, the normalization condition for $u = rR$ reads

$$\int_0^\infty dr |u(r)|^2 = 1 \ . \tag{6.3.14}$$

6.4 Two examples of rotation-invariant Hamiltonians

To make the discussion more concrete let us consider two examples of rotation-invariant Hamiltonians, before considering the Hydrogen atom. The first example is that of an infinitely deep, spherical potential well:

$$V(r) = \begin{cases} 0 & r < a \\ \infty & r \geq a \end{cases} \ . \tag{6.4.15}$$

The solution of the Schrödinger equation will describe the motion of a particle confined inside a sphere of radius a. As discussed above we can write the Eigenfunctions of the Hamiltonian as follows:

$$\psi_{n\ell m}(r,\theta,\varphi) = \frac{u_{n\ell}(r)}{r} Y_\ell^m(\theta,\varphi) \ , \tag{6.4.16}$$

where the function $u_{n\ell}(r)$ has to satisfy the equation:

$$\frac{d^2 u_{n\ell}(r)}{dr^2} = -\left(\frac{\ell(\ell+1)}{r^2} - \kappa^2\right) u_{n\ell}(r) \ , \tag{6.4.17}$$

with $\kappa = \sqrt{2ME}/\hbar$. If we look for solutions with $\ell = 0$, then Eq. (6.4.17) becomes identical to the Schrödinger equation for the one-dimensional infinitely deep potential well. Not quite, because the boundary conditions for the one-dimensional case are $\psi(0) = \psi(a) = 0$, whereas in this case we apparently only have $u_{n0}(a) = 0$. But if we look at the definition of the full, three-dimensional wave function, Eq. (6.4.16), we realize that if $u_{n0}(0)$ does not vanish, $\psi_{n00}(r, \theta, \varphi)$ diverges at $r = 0$ like $u(0)/r$, and it cannot represent a solution of the Schrödinger equation. So, the radial function $u_{n0}(r)$ must indeed satisfy the exact same equation as the eigenfunction for the one-dimensional infinitely deep potential well, for which we already know the solution:

$$u_{n0}(r) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) , \qquad E_{n0} = \frac{n^2\pi^2\hbar^2}{2Ma^2} . \tag{6.4.18}$$

The case $\ell \neq 0$ is more involved and will not be discussed here, but what we can immediately see is that the Eigenvalues $E_{n\ell}$ cannot depend on m, which means that they will have a $2\ell + 1$ degeneracy.

The second example we consider is the three-dimensional harmonic oscillator, whose potential is given by:

$$V(r) = \frac{1}{2}M\omega^2 r^2 , \qquad r^2 = x^2 + y^2 + z^2 . \tag{6.4.19}$$

Writing the solution as in Eq. (6.4.16), the radial function must satisfy the equation:

$$\left[-\frac{\hbar^2}{2M}\frac{d^2}{dr^2} + \frac{1}{2}M\omega^2 r^2 + \frac{\hbar^2\ell(\ell+1)}{2Mr^2}\right] u_{n\ell}(r) = E_{n\ell} u_{n\ell}(r) . \tag{6.4.20}$$

Also in this case we concentrate on the case $\ell = 0$, for which the equation reduces to the one for the one-dimensional harmonic oscillator. But also in this case we have to impose as boundary condition $u_{n0}(0) = 0$, which is satisfied only for the solutions with n odd. We conclude that Eigenfunctions and Eigenvalues for $\ell = 0$ have the form

$$u_{n0}(r) = \frac{\alpha}{\sqrt{2^n n!}} H_n(\xi) e^{-\xi^2/2} \qquad E_{n0} = \hbar\omega(n + 1/2) , \qquad \text{for } n \text{ odd} , \tag{6.4.21}$$

with $\alpha = (M\omega/\pi\hbar)^{1/4}$ and $\xi = r\sqrt{M\omega/\hbar}$. This implies that the ground-state energy is $E_{10} = 3/2\hbar\omega$. The case $\ell \neq 0$ is more complex and will not be discussed here. But we cannot hide from the reader that in this case there is a much simpler way to get to a complete analytic solution which does not rely on rotational symmetry. The key observation is that the Hamiltonian of the three-dimensional harmonic oscillator can be written as the sum of three one-dimensional harmonic oscillators:

$$V(r) = \frac{1}{2}M\omega^2 x^2 + \frac{1}{2}M\omega^2 y^2 + \frac{1}{2}M\omega^2 z^2 , \tag{6.4.22}$$

which implies that the Eigenfunctions can be expressed as product of the three one-dimensional Eigenfunctions:

$$\psi_N(x,y,z) = \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z) \ , \tag{6.4.23}$$

and the Eigenvalues as sum of the three one-dimensional Eigenvalues

$$E_N = \hbar\omega\left(n_x + \frac{1}{2} + n_y + \frac{1}{2} + n_z + \frac{1}{2}\right) = \hbar\omega\left(N + \frac{3}{2}\right) \ , \tag{6.4.24}$$

which confirms that the ground-state energy is equal to $E_0 = 3/2\hbar\omega$. This formula, however, provides also all higher eigenvalues and their degeneracy level, and in an easier way than by exploiting rotational invariance. A useful exercise is to recast Eq. (6.4.23) in the form (6.4.16) and to explain the degeneracy level in terms of angular momentum states.

Chapter 7

The Hydrogen atom

The Hydrogen atom is the simplest atom in nature. It consists of a nucleus made of a single proton and an electron. To describe such a system we need a wave function of two position variables, each of which is three-dimensional. The (time-independent) wave function has the form

$$\psi^H = \psi(\mathbf{x}_p, \mathbf{x}_e) \ , \tag{7.0.1}$$

where $\mathbf{x}_{p(e)}$ is the position in space of the proton (electron). If we take the modulus squared of this wave function and multiply it by the infinitesimal volume elements:

$$|\psi(\mathbf{x}_p, \mathbf{x}_e)|^2 d^3x_p d^3x_e \tag{7.0.2}$$

we obtain the probability of finding simultaneously the proton in the infinitesimal volume d^3x_p around the point $\mathbf{x}_p$ and the electron in the infinitesimal volume d^3x_e around the point $\mathbf{x}_e$. Integrating the modulus squared over a finite volume in either of the two variables, one gets the probability to find either of the two particles inside that volume, while the other is at a given point in space. In particular the integral

$$\int d^3x_p |\psi(\mathbf{x}_p, \mathbf{x}_e)|^2 d^3x_e \tag{7.0.3}$$

gives the probability of finding the electron within an infinitesimal interval d^3x_e centered at $\mathbf{x}_e$ independently of where the proton is.

7.1 Separation of the center of mass from the relative motion

Before we start to solve the Schrödinger equation, we first remark that the Coulomb potential, which describes the force among the proton and the electron, depends only on the distance among the two particles:

$$V_C(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} \ . \tag{7.1.1}$$

As usual, for an isolated physical system there is no force depending on the position of its center of mass – the latter must therefore move with constant velocity.

We must be able to see this even in the quantum formulation of the problem, and translate it into a property of the Schrödinger equation. The center of mass coordinate is:

$$\mathbf{R} = \frac{m_e \mathbf{x}_e + m_p \mathbf{x}_p}{m_e + m_p} \ , \tag{7.1.2}$$

and the relative position

$$\mathbf{r} = \mathbf{x}_e - \mathbf{x}_p \ . \tag{7.1.3}$$

The Hamiltonian of the Hydrogen atom reads

$$-\frac{\hbar^2}{2m_p}\triangle_p - \frac{\hbar^2}{2m_e}\triangle_e + V_C(r) \ , \tag{7.1.4}$$

and can be rewritten in terms of the Laplacians of the variables $\mathbf{R}$ and $\mathbf{r}$ as follows

$$-\frac{\hbar^2}{2M}\triangle_{\mathbf{R}} - \frac{\hbar^2}{2\mu}\triangle_{\mathbf{r}} + V_C(r) \ , \tag{7.1.5}$$

where $M = m_e + m_p$ and $\mu = m_e m_p/M$ is the so-called reduced mass which, when one of the two masses is much larger than the other, is almost equal to the mass of the light particle. In this case $m_p \sim 2000\ m_e$, and therefore $\mu = m_e/(1 + m_e/m_p) \sim m_e/(1.0005) \sim m_e$.

The total wave function can therefore be written as a product of two functions, one which depends on the center-of-mass position only, and one which describes the relative motion:

$$\psi_H = \psi_{CM}(\mathbf{R})\psi(\mathbf{r}) \ . \tag{7.1.6}$$

The Hamiltonian is invariant under translations of the variable $\mathbf{R}$ and therefore its eigenfunctions can be chosen to be simultaneous eigenfunctions of the momentum of the total momentum $\mathbf{P} = \mathbf{p}_e + \mathbf{p}_p$. In other words ψ_{CM} is the wave function of a free particle and the expectation value of its momentum is conserved.

7.2 Schrödinger equation for the relative motion – radial equation

The wave function $\psi(\mathbf{r})$ contains the interesting dynamics of the system. This is a solution of the following equation

$$-\frac{\hbar^2}{2\mu}\triangle_{\mathbf{r}}\psi(\mathbf{r}) + V_C(r)\psi(\mathbf{r}) = E\psi(\mathbf{r}) \ . \tag{7.2.1}$$

Since this Schrödinger equation is invariant under rotation, we can immediately apply the conclusions of the previous chapter and write the solution as a product of a radial function times the eigenfunctions of angular momentum:

$$\psi_{E\ell m}(\mathbf{r}) = \frac{u_E(r)}{r} Y_\ell^m(\theta,\varphi) \ . \tag{7.2.2}$$

The radial equation then reads[1]

$$\frac{d^2u}{dr^2} + \left[\frac{2m_e e^2}{4\pi\epsilon_0\hbar^2}\frac{1}{r} - \frac{\ell(\ell+1)}{r^2}\right] u = \kappa^2 u \ , \tag{7.2.3}$$

where $\kappa = \sqrt{-2m_e E}/\hbar$ is defined for the case of negative energies, *i.e.* energies corresponding to bound states, which are the only ones relevant for atoms. We now simplify the notation by dividing the equation by κ^2 and introducing the variable $\rho = \kappa r$:

$$\frac{d^2u}{d\rho^2} = \left(1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right) u \ , \tag{7.2.4}$$

where

$$\rho_0 = \frac{2m_e e^2}{4\pi\epsilon_0\hbar^2\kappa} \ . \tag{7.2.5}$$

In the limits of $\rho \to \infty$ and $\rho \to 0$, the equation takes the following forms, respectively:

$$\frac{d^2u}{d\rho^2} = u \ , \qquad \frac{d^2u}{d\rho^2} = \frac{\ell(\ell+1)}{\rho^2} u \ , \tag{7.2.6}$$

whose solutions are

$$\begin{aligned} \rho \to \infty \qquad &\Rightarrow \quad u \sim e^{-\rho} \ , \\ \rho \to 0 \qquad &\Rightarrow \quad u \sim \rho^{\ell+1} \ . \end{aligned} \tag{7.2.7}$$

We factorize these two functions out of u, thereby explicitly showing the dominant behaviour at the two extrema of the r region:

$$u \equiv e^{-\rho}\rho^{\ell+1} v(\rho) \ , \tag{7.2.8}$$

and translate Eq. (7.2.4) into an equation for v. The latter reads

$$\rho v''(\rho) + 2(\ell + 1 - \rho)v'(\rho) + (\rho_0 - 2(\ell+1))v(\rho) = 0 \ . \tag{7.2.9}$$

We now express $v(\rho)$ as a power series:

$$v(\rho) = \sum_{i=0}^{\infty} c_i \rho^i \ , \tag{7.2.10}$$

[1]To simplify the notation we drop the subscript E on u in what follows and approximate the reduced mass by the one of the electron.

and rewrite (7.2.9) as an equation for the power series:

$$\sum_{i=0}^{\infty}\Big[i(i+1)c_{i+1}+2(\ell+1)(i+1)c_{i+1}-2ic_i+(\rho_0-2(\ell+1))c_i\Big]\rho^i=0 \ . \quad (7.2.11)$$

The power series vanishes only if all the coefficients vanish, and this means that we obtain a recursive equation for the coefficients c_i:

$$c_{i+1}=\frac{2(i+\ell+1)-\rho_0}{(2(\ell+1)+i)(i+1)}c_i \ . \quad (7.2.12)$$

We seem to have obtained what we wanted—an explicit solution of the radial equation—but we first should check that the power series has an acceptable behaviour at infinity[2]. The behaviour at infinity is dictated by the behaviour of the coefficients c_i for large i. This we can read off from (7.2.12) by neglecting any constant term compared to i. We then get:

$$c_{i+1}=\frac{2}{(i+1)}c_i \quad \Rightarrow \quad c_i=\frac{2^i}{i!}c_0 \ , \quad (7.2.13)$$

which means that at large ρ the function v goes like:

$$v(\rho)\stackrel{\rho\to\infty}{\longrightarrow} c_0\sum_{i=1}^{\infty}\frac{2^i}{i!}\rho^i=c_0e^{2\rho} \ , \quad (7.2.14)$$

and so destroys the correct behaviour at infinity that we had built into the definition (7.2.8) of the function u. Unfortunately, the solution we have found is no solution at all! The only way out is if the recursion relation (7.2.12) terminates for a certain value of i, which we call $i_{\max}$. Namely if

$$2n\equiv 2(i_{\max}+\ell+1)=\rho_0 \ . \quad (7.2.15)$$

This condition means that we can make sense of the solution we have found in the form of a power series only if ρ_0 is twice an integer. This determines completely the eigenfunctions of the Hamiltonian for the Hydrogen atom.

7.3 The spectrum of the Hydrogen atom

Since ρ_0 depends on the energy, Eq. (7.2.15) is a quantization condition for the energy of the Hydrogen atom. Indeed it can be written as

$$E_n=-\frac{m_ee^4}{32\pi^2\hbar^2\epsilon_0^2}\frac{1}{n^2}=-\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{1}{n^2}=-\frac{m_ec^2}{2}\frac{\alpha^2}{n^2} \ , \quad (7.3.1)$$

[2]Obviously, at $\rho=0$ the power series converges to c_0, so there is no danger there.

where $\alpha = e^2/(4\pi\epsilon_0\hbar c) \simeq 1/137$ is the fine structure constant.

The ground state of the Hydrogen atom is obtained by setting $n = 1$. The eigenvalue of the energy is in this case

$$E_1 = -\frac{m_e c^2}{2}\alpha^2 = -13.6 \text{ eV} \quad . \tag{7.3.2}$$

With $n = 1$, Eq. (7.2.15) implies that $i_{\max} = \ell = 0$. In the transition from the excited to the ground state the atom emits light, one single photon in each transition. Conservation of energy and the de Broglie relation between energy of the photon and frequency of the electromagnetic wave implies that

$$\Delta E = E_{n_i} - E_{n_f} = h\nu \quad , \tag{7.3.3}$$

where $n_{i,f}$ are the principal quantum number of the initial and final state of the atom. The wavelength of the emitted photons reads

$$\lambda = \frac{c}{\nu} = \frac{hc}{\Delta E} = -\frac{hc}{E_1}\left(\frac{n_i^2 n_f^2}{n_i^2 - n_f^2}\right) \quad . \tag{7.3.4}$$

The constant $R = -E_1/(hc) = 1.09737316 \cdot 10^7 \text{ m}^{-1}$ is called the Rydberg constant and has the dimension of the inverse of a length. A number of possible transitions are shown in Fig. 7.1. Transitions in the Lyman series are in the ultraviolet, those in the Balmer series in the visible and those in the Paschen in the infrared.

Once the energy eigenvalues are fixed, the wave function is completely determined. To show this explicitly, we first of all rewrite κ, which has dimensions of the inverse of a length as

$$\kappa = \frac{1}{an} \quad \text{where} \quad a \equiv \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 0.529 \cdot 10^{-10} m \quad , \tag{7.3.5}$$

is the so-called Bohr radius. Indeed the latter length scale is a good measure of the size of an atom, as we can see by writing the wave function, *e.g.* of the ground state, as

$$\psi_{100}(\mathbf{r}) = \frac{1}{r}\frac{c_0 r}{a}e^{-r/a}Y_0^0(\theta,\varphi) = \frac{c_0}{a}e^{-r/a} = \frac{1}{\sqrt{\pi a^3}}e^{-r/a} \quad , \tag{7.3.6}$$

where we have fixed the constant c_0 by the normalization condition. In the ground state the wave function has no angular dependence, and the only dependence on the radius is in the exponential. The probability to find the electron within a distance d from the proton is given by

$$P(d) = \frac{1}{\pi a^3}\int_0^d dr r^2 e^{-2r/a}\int_{-1}^1 d\cos\theta \int_0^{2\pi} d\varphi = 1 - (1 + 2x + 2x^2)e^{-2x} \tag{7.3.7}$$

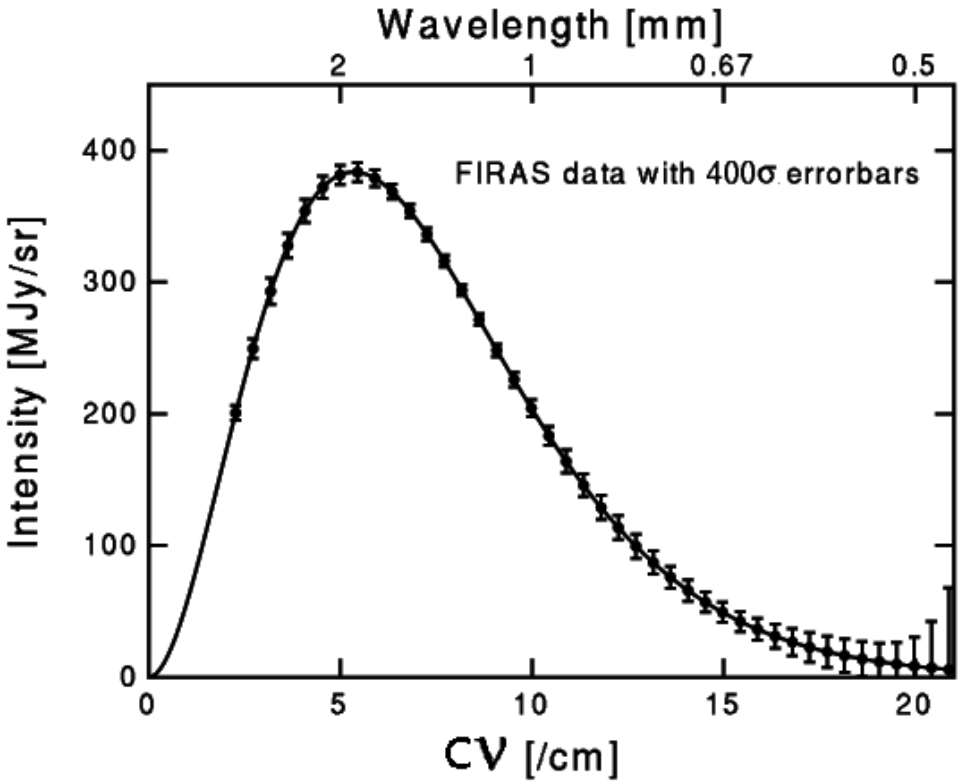

Figure 7.1: The spectrum of the Hydrogen atom and a few of the transitions among the lower levels, grouped into "series" labeled by the names of the spectroscopists who first discovered them.

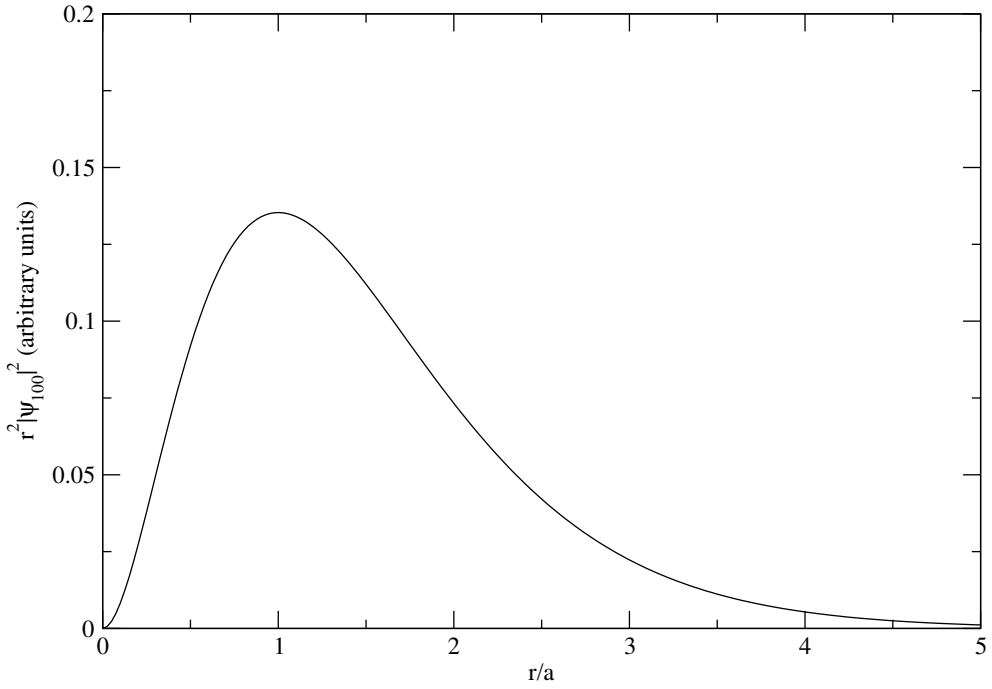

Figure 7.2: Probability distribution to find the electron at a distance r from the nucleus in the ground state of Hydrogen.

where $x = d/a$. Numerically, $P(a) = 0.32$, $P(2a) = 0.76$ and $P(3a) = 0.94$: the wave function of the electron is almost all contained within a sphere of radius of a few Bohr radii. We can read Eq. (7.3.7) also in the following way: we sum up the contributions of all the spherical layers of radius r up to a radius of d. The contribution of each layer is given by the integrand and is equal to $r^2|R_{n\ell}(r)|^2$. The plot of the latter for $n = 1$, $\ell = 0$ is shown in Fig. 7.2. The maximum of the probability is at $r = a$, as can be easily shown analytically: it is enough to take the derivative with respect to r of the integrand in (7.3.7) and see that this vanishes at $r = a$.

Another measure of the radius of an atom is given by the expectation value of the radius. This is equal to:

$$\langle r \rangle_{n\ell} = \int d^3x \; r \; |\psi_{n\ell m}|^2 = \int_0^\infty dr r^3 |R_{n\ell}(r)|^2 \quad , \tag{7.3.8}$$

where we have dropped the angular integral as follows from the normalization condition (5.1.23) of the Y_ℓ^m functions. The general form of the radial part of the eigenfunctions $\psi_{n\ell m}$ is fully known analytically and is given by

$$R_{n\ell} = \left(\frac{2}{na}\right)^{3/2} \sqrt{\frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}} e^{-r/na} \left(\frac{2r}{na}\right)^\ell L_{n-\ell-1}^{2\ell+1}(2r/na) \quad , \tag{7.3.9}$$

where L^p_{q-p} are the associated Laguerre polynomials defined as

$$L^p_{q-p}(x) \equiv (-1)^p \left(\frac{d}{dx}\right)^p L_q(x) \tag{7.3.10}$$

with L_q the Laguerre polynomials

$$L_q(x) \equiv e^x \left(\frac{d}{dx}\right)^q \left(e^{-x}x^q\right) \quad . \tag{7.3.11}$$

The calculation of the integral in Eq. (7.3.8) is quite nontrivial, but the result beautifully simple:

$$\langle r\rangle_{n\ell} = \frac{a}{2}\left[3n^2 - \ell(\ell+1)\right] \quad . \tag{7.3.12}$$

For example $\langle r\rangle_{10} = 3/2a$ is 1.5 times larger than the maximum of the distribution – evidently the "size" of the atom depends on how one defines it. For higher n's the maximum of the distribution is no longer a good way to define the size of the atom, because the functions $R_{n\ell}$ have zeros and correspondingly many maxima and minima. The expectation value of r is in this case a much better way to measure the size of the atom. Eq. (7.3.12) shows that the size grows very fast with n.

7.4 Fine and hyperfine effects in the spectrum of the Hydrogen atom

The spectrum of the Hydrogen atom as given in Eq. (7.3.1) has been verified experimentally to great accuracy. As soon as one goes below the level of the permille precision in the measurement of the wavelengths of the emitted photons, however, one starts to see small discrepancies from the predicted spectrum. The origin of these discrepancies is well understood as we are now going to discuss briefly here.

7.4.1 Relativistic kinetic energy

In the derivation of the Schrödinger equation it is assumed that the particles move at a speed much smaller than the speed of light. The corresponding kinetic energy is then the classical one, $T_{\rm cl} = \mathbf{p}^2/2m_e$. No matter how small the speed of the particle, this expression is only an approximation to the full relativistic theory, in which the kinetic energy is given by

$$T_{\rm rel} = \sqrt{(m_e c^2)^2 + (\mathbf{p}^2c^2)} - m_e c^2 \quad . \tag{7.4.1}$$

To see how good an approximation the classical expression for the kinetic energy is, one should expand $T_{\rm rel}$ in inverse powers of c and compare the size of the next-to-leading term to the leading one:

$$T_{\rm rel} = \frac{\mathbf{p}^2}{2m_e} - \frac{(\mathbf{p}^2)^2}{8m_e^3c^2} + \dots \tag{7.4.2}$$

In quantum mechanics the second term should be interpreted as an operator (substituting $\mathbf{p}$ with the corresponding operator $\hat{\mathbf{p}}$) and added as a correction to the Hamiltonian, which will be written as

$$\hat{H} = \hat{H}_0 + \hat{H}_1 \quad \text{where} \quad \hat{H}_1 = -\frac{(\hat{\mathbf{p}}^2)^2}{8m_e^3c^2} \ , \tag{7.4.3}$$

and $\hat{H}_0$ is the Hamiltonian appearing in Eq. (7.2.1). Having a new Hamiltonian, the problem to find the corresponding eigenfunctions and eigenvalues is a completely new one. If, however, one can show that one part of the Hamiltonian is "large" compared to another one, the eigenvalue problem can be solved perturbatively, and the eigenvalues be given as a power series in matrix elements of the "small" Hamiltonian. Details of perturbation theory will be discussed in QTIII. For the present discussion it is enough to say that the shift in the eigenvalues to first order in the "small" Hamiltonian is given by the expectation value of the perturbation in the unperturbed states:

$$\Delta E_n = \langle n\ell m|\hat{H}_1|n\ell m\rangle \ . \tag{7.4.4}$$

The ratio $\Delta E_n/E_n$ can be estimated to be of the order of $\sim (Z\alpha)^2 = Z^2 0.5\cdot 10^{-4}$. The analytic calculation gives

$$\langle n\ell m|\hat{H}_1|n\ell m\rangle = E_n\frac{(Z\alpha)^2}{n}\left[\frac{1}{\ell+1/2} - \frac{3}{4n}\right] \ . \tag{7.4.5}$$

Notice that the perturbation $\hat{H}_1$ lifts the degeneracy in the angular momentum by introducing a dependence of the eigenvalues on ℓ.

7.4.2 Spin-orbit coupling

Another small perturbation of the main Hamiltonian is due to the so-called spin-orbit coupling. Its origin can be explained as follows: if one sits on the electron one will see the nucleus rotating around it, and therefore generating a magnetic field. The latter will be proportional to the angular momentum of the state in which the atom is. The spin of the electron will then couple to this magnetic field through a scalar product, as usual. A careful derivation of this effect yields

$$\hat{H}_2 = -\frac{1}{2m_e^2c^2}\mathbf{S}\cdot\mathbf{L}\frac{e}{r}\frac{d\phi(r)}{dr} \ , \tag{7.4.6}$$

where $\phi(r)$ is the electrostatic potential due to the nuclear charge, and the factor of two in the denominator is a subtle relativistic effect first explained by Thomas (and goes under the name of Thomas precession). Again the effect of this interaction to the energy levels is given to first order by its expectation value in the eigenstates of the main, unperturbed Hamiltonian $\hat{H}_0$. The order of magnitude of this effect is again $E_n(Z\alpha)^2$. The combination of the two shifts can be written in a nice compact form – the effect of the latter perturbation is simply to change $\ell \to j$ in Eq. (7.4.5), where j fixes the eigenvalue of the total angular momentum $\mathbf{J} \equiv \mathbf{L} + \mathbf{S}$:

$$\Delta E = E_n \frac{(Z\alpha)^2}{n} \left[\frac{1}{j+1/2} - \frac{3}{4n} \right] \quad . \tag{7.4.7}$$

Since we are discussing one-electron states we have $j = \ell \pm 1/2$. Two states with the same n and ℓ differing by one unit end up having the same energy if the spin of the electron points in two different directions such that j is the same. For example the state $n = 2$, $\ell = 0$ has $s = 1/2$ and also $j = 1/2$, whereas the state with $n = 2$ and $\ell = 1$ generates two different states with $j = 3/2, 1/2$. These states are conveniently identified with the spectroscopic notation given by: ${}^{2s+1}L_j$, where L represents a letter which identifies a value of ℓ: S for $\ell = 0$, P for $\ell = 1$, D for $\ell = 2$, F for $\ell = 3$ and so on following the alphabetical order. With this notation we can say that even after taking into account the relativistic effects giving the fine structure of the spectrum, the states ${}^2S_{1/2}$ and ${}^2P_{1/2}$, *e.g*, are degenerate.

A very precise experiment carried out by Lamb and Retherford in 1947 detected a very small difference in the latter two energy levels. The effect goes under the name of Lamb shift, and can be understood in the framework of quantum electrodynamics. The effect is of order $m_e c^2 (Z\alpha)^4 \alpha \log \alpha$ and is almost another three orders of magnitude smaller than the fine splitting effects discussed above. At this level of precision there are yet other effects which also come into play, like the coupling of the spin of the electron to the spin of the nucleus, which however we will not discuss any further. These effects, of the relative order of 10^{-6} are called hyperfine splitting effects and have also been seen experimentally and well understood theoretically.

Chapter 8

Identical particles and the Helium atom

8.1 Identical particles, Pauli exclusion principle

Before considering multielectron atoms, we need to ask ourselves how to treat identical particles in quantum mechanics. In classical mechanics, even if two particles have exactly identical physical properties, as soon as I have different initial conditions between the two, the solution to the equations of motion will allow me to distinguish them. In quantum mechanics I cannot know where exactly each particle is at any given time. All I can ask myself is what is the probability to detect one particle with certain physical properties at a certain point (or small region) in space, at a certain point in time. If no measurement allows me to distinguish between the two particles the probability has to be the same whether I detect particle n. 1 or particle n. 2. If I define the coordinates of the two identical particles $\vec{x}_i$ with $i = 1, 2$ the wave function describing the state of the two particles must satisfy:

$$|\Psi(\vec{x}_1, \vec{x}_2)|^2 = |\Psi(\vec{x}_2, \vec{x}_1)|^2 \, . \tag{8.1.1}$$

Which means that at the level of wave function the only possible change after switching the two particles' coordinates is a phase factor:

$$P\Psi(\vec{x}_1, \vec{x}_2) = \Psi(\vec{x}_2, \vec{x}_1) = \eta\Psi(\vec{x}_1, \vec{x}_2) \quad , \tag{8.1.2}$$

where P is the operator which exchanges the two particles and η a phase factor: $|\eta|^2 = 1$. The square of the P operator, on the other hand, is the identity, and therefore $\eta^2 = 1$, $\eta = \pm 1$. One could in principle imagine that the wave function of two identical particles treats them differently – is not an eigenstate of P – but that we simply have no way of distinguishing the two particles. It turns out, however, that we can correctly describe Nature only if we assume that this cannot happen, and that the wave function describing two identical

particles is either symmetric ($\eta = +1$) or antisymmetric ($\eta = -1$) under the exchange of the two particles. Moreover whether one has to take symmetric or antisymmetric wave functions is not a matter of choice or dependent on the situation: it depends only and strictly from the spin of the particle. Particles with an integer spin are described by symmetric wave functions (and are called *bosons*), whereas particles with half-integer spins admit only antisymmetric wave functions (and are called *fermions*). This is the content of the "spin-statistics theorem", which can be proven only in quantum field theory (in quantum mechanics it needs to be assumed as a principle) and was first established by Wolfgang Pauli. Historically, he first formulated the "exclusion principle" which goes under his name and which states that two electrons cannot be in the same state, and later generalized it to a theorem.

8.2 The Helium atom

Having established Pauli exclusion principle, we can now consider multielectron atoms, and in particular the simplest of them, the Helium atom. Its Hamiltonian reads

$$\mathcal{H}_{\rm He} = -\frac{\hbar^2}{2m_e}\left(\triangle_1 + \triangle_2\right) - \frac{2e^2}{4\pi\epsilon_0}\frac{1}{r_1} - \frac{2e^2}{4\pi\epsilon_0}\frac{1}{r_2} + \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}} \quad , \tag{8.2.3}$$

where $\mathbf{r}_{1,2}$ are the position vectors of the two electrons (the center of the coordinate system being on the nucleus) and $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$, and as usual $r_i = |\mathbf{r}_i|$. If we ignore the repulsive interaction among the two electrons, we get an Hamiltonian which we can solve exactly: the Hamiltonian is the sum of two hydrogen-atom Hamiltonians, each with $Z = 2$. The eigenfunctions are given by products of eigenfunctions of the Hydrogen atom (with $Z = 2$), namely:

$$\psi^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \psi^{Z=2}_{n_1\ell_1 m_1}(\mathbf{r}_1)\psi^{Z=2}_{n_2\ell_2 m_2}(\mathbf{r}_2) \quad . \tag{8.2.4}$$

This would be the solution if the two electrons were distinguishable, but since they aren't, we need to build an antisymmetric wave function out of this. This is easy to do, in particular because the eigenfunctions of the Hamiltonian of the hydrogen atom are orthogonal to each other:

$$\psi^{(0)}_{-}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}\left[\psi^{Z=2}_{n_1\ell_1 m_1}(\mathbf{r}_1)\psi^{Z=2}_{n_2\ell_2 m_2}(\mathbf{r}_2) - \psi^{Z=2}_{n_1\ell_1 m_1}(\mathbf{r}_2)\psi^{Z=2}_{n_2\ell_2 m_2}(\mathbf{r}_1)\right] \quad . \tag{8.2.5}$$

This is not the whole story, however, because we are forgetting the spin degrees of freedom for the electron, but they are integral part of the wave function and also play a role in the exclusion principle: two electrons cannot be in the same state including their spin state! So the complete set of all possible solutions for

the Helium atom (still in the approximation in which we ignore the repulsive interaction among the two electrons) looks as follows

$$\Psi^{(0)}_{\rm He}(\vec{x}_1, s_1; \vec{x}_2, s_2) = \psi^{(0)}_{\pm}(\mathbf{r}_1, \mathbf{r}_2)\chi_{\mp}(s_1, s_2) \tag{8.2.6}$$

where $\psi^{(0)}_{+}$ is the symmetric combination of products of hydrogen wavefunctions (like in Eq. (8.2.5), but with a + sign in between), and $\chi_{\mp}(s_1, s_2)$ are the anti- and symmetric combinations of spin wavefunctions (s_i is the spin projection on the z axis of the i-th electron). A quick look at Sec. 5.3 allows us to conclude that the symmetric spin wave functions of two electrons are those of total spin 1, and the antisymmetric one is that of total spin 0:

$$\begin{aligned}
\chi_{+} &= \left\{ |\uparrow\uparrow\rangle, \frac{1}{\sqrt{2}}\left[|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right], |\downarrow\downarrow\rangle \right\} = \{|11\rangle, |10\rangle, |1\,-1\rangle\} \\
\chi_{-} &= \frac{1}{\sqrt{2}}\left[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right] \qquad\qquad\qquad\qquad = |00\rangle
\end{aligned} \tag{8.2.7}$$

Based on this discussion we can conclude that the ground state of the simplified Hamiltonian reads

$$\Psi^{(0)}_{\rm He,1}(\vec{x}_1, s_1; \vec{x}_2, s_2) = \psi^{(0)}_{0}(\mathbf{r}_1, \mathbf{r}_2)|00\rangle \tag{8.2.8}$$

where

$$\psi^{(0)}_{0}(\mathbf{r}_1, \mathbf{r}_2) = \psi^{Z=2}_{100}(\mathbf{r}_1)\psi^{Z=2}_{100}(\mathbf{r}_2) = \frac{8}{\pi a_0^3} e^{-2(r_1+r_2)/a_0} \quad . \tag{8.2.9}$$

In the following discussion we will ignore the spin part of the wavefunction which plays no role. The energy eigenvalue (of the simplified Hamiltonian) in the ground state is given by $E^{(0)}_0 = 2 \cdot Z^2 E_1 = -8 \cdot 13.6$ eV $= -109$ eV, which is quite a bit lower than the measured ionization energy (the energy needed to take both electrons to infinity) of Helium, which is -79 eV. Ignoring the positive contribution of the repulsive term is certainly a bad approximation. We can, however, immediately improve our estimate by using the function (8.2.9) and evaluate the expectation value of the full Hamiltonian (8.2.3) in this state:

$$\langle\psi^{(0)}_0|\mathcal{H}_{\rm He}|\psi^{(0)}_0\rangle = 8E_1 + \frac{e^2}{4\pi\epsilon_0}\left\langle\frac{1}{r_{12}}\right\rangle \quad . \tag{8.2.10}$$

The calculation of the latter expectation value is simple (cf. the paragraph at the end of this subsection) and yields

$$\left\langle\frac{1}{r_{12}}\right\rangle = \frac{5}{4a_0} \quad , \tag{8.2.11}$$

so that the expectation value of the energy is

$$\langle\psi^{(0)}_0|\mathcal{H}_{\rm He}|\psi^{(0)}_0\rangle = 8E_1 - \frac{5}{2}E_1 = \frac{11}{2}E_1 = -75 \text{ eV} \quad , \tag{8.2.12}$$

which is already quite a good approximation to the true energy.

As we will learn next semester, it is possible to improve our estimate of the ground state energy (by at the same time improving the approximation for the wave functions), by not fixing the paramater $Z = 2$ in the wave function (8.2.9), but rather leaving it free to float. Applying the so-called variational principle we will use a procedure to optimize the choice of this parameter Z and get as close as possible to the true ground state wavefunction and energy. Anticipating the outcome here: the optimal value is $\bar{Z} = 27/16 \simeq 1.69$ which indeed shows that each electron sees the charge of the nucleus somewhat screened. Putting this back into the expectation value of the energy (as a function of Z), we obtain

$$E(\bar{Z}) = \frac{1}{2}\left(\frac{3}{2}\right)^6 E_1 = -77.5 \text{ eV} \quad , \tag{8.2.13}$$

which is indeed very close to the correct energy – the overestimate is only by 2%!

Calculation of $\langle r_{12}^{-1}\rangle$

We want to calculate

$$\langle r_{12}^{-1}\rangle \equiv \left(\frac{Z^3}{\pi a_0^3}\right)^2 \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \frac{e^{-2Z(r_1+r_2)/a_0}}{r_{12}} \quad . \tag{8.2.14}$$

We start with the integral over $\mathbf{r}_2$ and choose to align the third component of the coordinate system to $\mathbf{r}_1$. We then have

$$\begin{aligned}
\int d^3\mathbf{r}_2 \frac{e^{-2Zr_2/a_0}}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}} &= 2\pi \int dr_2 r_2^2 e^{-2Zr_2/a_0} \\
&\quad \times \int_{-1}^{1} d\cos\theta_2 \frac{1}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}} = \\
&= 2\pi \int dr_2 r_2^2 e^{-2Zr_2/a_0} \frac{1}{r_1 r_2}\left(\sqrt{r_1^2+r_2^2+2r_1r_2} - \sqrt{r_1^2+r_2^2-2r_1r_2}\right) \\
&= 2\pi \int dr_2 r_2^2 e^{-2Zr_2/a_0} \frac{1}{r_1 r_2}\Big[(r_1+r_2) - |r_1-r_2|\Big] \\
&= 4\pi\left(\frac{1}{r_1}\int_0^{r_1} dr_2 r_2^2 e^{-2Zr_2/a_0} + \int_{r_1}^{\infty} dr_2 r_2 e^{-2Zr_2/a_0}\right) \\
&= \frac{\pi a_0^3}{Z^3 r_1}\left[1 - \left(1+\frac{Zr_1}{a_0}\right)e^{-2Zr_1/a_0}\right] \quad ,
\end{aligned} \tag{8.2.15}$$

where the next-to-last equality sign follows because $(r_1 + r_2) - |r_1 - r_2| = 2r_2$ $(2r_1)$ if $r_1 > r_2$ $(r_2 > r_1)$. We now have to evaluate the integral over $\mathbf{r}_1$. The integrand does not depend on any angle, so that the angular part of the integral

is trivial, and gives 4π. We only have to calculate the radial integral:

$$\begin{aligned}\langle r_{12}^{-1}\rangle &= \left(\frac{Z^3}{\pi a_0^3}\right) 4\pi \int_0^\infty dr_1 r_1 \left[1 - \left(1 + \frac{Zr_1}{a_0}\right) e^{-2Zr_1/a_0}\right] e^{-2Zr_1/a_0} \\ &= \left(\frac{Z^3}{\pi a_0^3}\right) 4\pi \, \frac{5a_0^2}{32Z^2} = \frac{5Z}{8a_0} \quad . \end{aligned} \tag{8.2.16}$$

8.3 Free electron gas

In order to illustrate the relevance of the Pauli exclusion principle in the physics of condensed matter we briefly discuss a simple model, the free electron gas, *i.e.* a gas of free fermions, confined in a rectangular box. This has been historically proposed by Sommerfeld as a model for metals. One can imagine that on the average, the Coulomb attraction due to the ions (which are sitting almost steady at the sites of a three-dimensional lattice) and the Coulomb repulsion due to the delocalized electrons compensate each other inside the metal – the delocalized electrons, on the other hand cannot escape from the metal.

We already know the energy eigenfunctions for such a Hamiltonian, defined by an infinite potential well in the three directions, with lengths ℓ_x, ℓ_y and ℓ_z. The wave function (imposing for convenience periodic boundary conditions, *i.e.* $\psi(x + \ell_x) = \psi(x)$ in each direction) has the form:

$$\psi(x, y, z) = \frac{1}{\sqrt{\ell_x \ell_y \ell_z}} e^{i\vec{k}\cdot\vec{x}} \tag{8.3.17}$$

where

$$\vec{k} = 2\pi \left(\frac{n_x}{\ell_x}, \frac{n_y}{\ell_y}, \frac{n_z}{\ell_z}\right) \quad , \tag{8.3.18}$$

with n_x, n_y and n_z three integers. The corresponding energy eigenvalues are:

$$E = \frac{\hbar^2 \vec{k}^2}{2m_e} \quad . \tag{8.3.19}$$

For a gas of bosons each of the many particles will be in a certain energy state, with an average kinetic energy proportional to the temperature. If we decrease the temperature to zero all the particles will decrease their energy, until all of them will be in the ground state. The total wave function will be symmetric under the exchange of any two particles, but apart from that there is no other constraint to be considered.

In case of fermions at zero temperature, the Pauli exclusion principle forbids all particles to be in the ground state. After we have put there two particles (we consider for definiteness spin 1/2 particles), one with spin up and the other with spin down with an antisymmetric spin wave function, the third one has to be in

a state with $|\vec{n}| = 1$. In this energy level we have room for twelve electrons, and then again we have to put the fifteenth electron in a higher energy state. If we have about 10^{23} particles, it does not make sense to continue the counting in this way, but it is more convenient to replace the sums by integrals. If we integrate in the space of momenta over a sphere of radius k_F and divide by the volume occupied by one state, $V_1 = (2\pi/\ell_x)(2\pi/\ell_y)(2\pi/\ell_z)$, and multiply by two (to take into account the two possible spin states), we get the total number of particles

$$N = \frac{\ell_x}{2\pi}\frac{\ell_y}{2\pi}\frac{\ell_z}{2\pi} \cdot 2 \cdot 4\pi \int_0^{k_F} dk k^2 = \frac{V}{8\pi^3}\frac{8\pi}{3}k_F^3 = \frac{V}{3\pi^2}k_F^3 \quad . \tag{8.3.20}$$

k_F, the maximal momentum of an occupied state, is called the Fermi momentum. This equation provides a direct link between the density (number of electrons divided by the volume) of electrons and the Fermi momentum:

$$\rho = \frac{k_F^3}{3\pi^2} \quad . \tag{8.3.21}$$

We can then calculate the average energy of this gas of free electrons by multiplying the integrand in (8.3.20) by the energy for a fixed momentum and dividing by the number of particles

$$\bar{E} \equiv \frac{E_{\rm tot}}{N} = \frac{1}{N} \cdot \frac{V}{\pi^2} \int_0^{k_F} dk k^2 \frac{\hbar^2 k^2}{2m_e} = \frac{3\hbar^2 k_F^2}{10 m_e} = \frac{3\hbar^2}{10 m_e}(3\pi^2\rho)^{2/3} \quad . \tag{8.3.22}$$

While for a free gas of bosons the average energy at zero temperature is constant and coinciding with the ground state energy of a single particle, for electrons the energy grows with the $2/3$ power of the density. In particular, for a constant particle number, the average energy is inversely proportional to the volume (the $2/3$ power thereof) – this means that a gas of free electrons exerts a pressure on the walls of the box in which it is confined. This pressure is easy to calculate:

$$P \equiv -\frac{dE_{\rm tot}}{dV} = \frac{2}{3}\frac{E_{\rm tot}}{V} = \frac{\hbar^2}{15\pi^2 m_e}(3\pi^2\rho)^{5/3} \quad . \tag{8.3.23}$$

Appendix A

The Einstein-Podolsky-Rosen paradox and Bell's inequalities

A.1 The Einstein-Podolsky-Rosen paradox in Bohm's formulation

At the end of our discussion of the basic aspects of quantum mechanics and after having seen how it works, we can now come back to the question of what it means and spend some time to decide whether it is a puzzling theory or not. We do this by discussing an apparent paradox discussed by Einstein, Podolsky and Rosen in 1935 [6], in the form it was formulated later by Bohm in 1952 [7]. I say "apparent" because if one takes the view that quantum mechanics correctly describes the reality, then there is no paradox at all, but if we take the *a priori* view of Einstein and collaborators of what the reality is, then quantum mechanics is indeed paradoxical: the conclusion of Einstein et al. was that there must be an underlying, more complete theory, and that quantum mechanics is "incomplete".

In the formulation of Bohm one considers the decay of a neutral pion into an electron-positron pair (the so-called Dalitz decay): $\pi^0 \to e^+e^-$. Since the pion has spin zero and angular momentum is conserved, if we look at the decay of a pion at rest we must find that the total angular momentum of the electron-positron state is also zero. Momentum conservation implies that they fly in opposite directions and that their orbital angular momentum is zero. Their spins must therefore be aligned in opposite directions. Not only that: they must be in a singlet state of the total spin. As shown in Sect. 5.3 this state is given by (the first arrow indicates the spin of the electron and the second the one of the positron):

$$|00\rangle = \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right) \quad . \tag{A.1.1}$$

Note that we have not written the x-dependent part of the wave function, which has to describe the fact that the two particles are moving away from each other

with a certain speed so that, if one waits long enough, will be found away from each other by any distance. If we now make a measurement of the z component of the spin of the electron with detector A and get $+\hbar/2$, the wave function of our system will collapse into

$$|\uparrow\downarrow\rangle \ . \tag{A.1.2}$$

This is what we have learned to be the description of nature provided by quantum mechanics. If we think about it, however, we do see that it is not something which is easy to swallow: before the measurement at the detector A were made, a detector B at a certain distance (as large as we want, if we wait long enough) from detector A, and ready to measure the z component of the positron spin would have had 50% probability to get $+1$[1] and 50% to get -1. Immediately after the measurement the probability suddenly become 0 and 100% respectively. This has been tested experimentally many times and is so beyond any doubts. The quantum mechanical interpretation of such an experiment is that the change of a state of a physical system happens instantaneously no matter how large the extension of the physical system is. Apparently this violates the principle that signals may travel at most with a speed of light (of course, in this case one would have to argue whether there is any "signal" travelling instantaneously). Einstein, Podolsky and Rosen found the standard interpretation of quantum mechanics unacceptable – in their view it would collide with the concept of "reality". The only way out, for them was that quantum mechanics is an incomplete theory and that there must be an underlying (to us yet unknown) theory which properly describes the "reality". In particular there must be a hidden variable which fixes the sign of the spin of each particle at the moment in which they are created. The formalism of quantum mechanics has been created on the basis of our ignorance of such a variable.

A.2 Bell's inequality

In 1964 Bell [8] showed that the question whether the standard quantum mechanical interpretation is correct or whether there are hidden variables can be answered experimentally. If one assumes the existence of hidden variables and consider a variant of the EPRB paradox, one can show that an inequality must hold. Such an inequality, on the other hand is violated in quantum mechanics. Let us see how.

What Bell proposed is to measure the component of the two spins with detectors A and B along two different directions, identified by the unite vectors $\mathbf{a}$ and $\mathbf{b}$. Repeating the measurement many times one can measure the average of the product of the two spins, which we indicate with $P(\mathbf{a}, \mathbf{b})$. In quantum mechanics this is the expected value of the product of the two measurements in the state

[1] From now on we speak about ± 1 as possible results of spin measurements instead of $\pm\hbar/2$.

(A.1.1) and is given by:

$$\langle(\mathbf{S}^{(1)}\cdot\mathbf{a})(\mathbf{S}^{(2)}\cdot\mathbf{b})\rangle = a^i b^j \langle S_i^{(1)} S_j^{(2)}\rangle \ . \tag{A.2.1}$$

It is easy to show that in the state (A.1.1) the expectation value of the product of any two components of the two spins is equal to $\langle S_i^{(1)} S_j^{(2)}\rangle = -\hbar^2/4\delta_{ij}$, and therefore:

$$\langle(\mathbf{S}^{(1)}\cdot\mathbf{a})(\mathbf{S}^{(2)}\cdot\mathbf{b})\rangle = -\frac{\hbar^2}{4}\mathbf{a}\cdot\mathbf{b} \ . \tag{A.2.2}$$

If we have a hidden variable λ, then the result of the measurement at A (B) is given by $A(\mathbf{a},\lambda)$ ($B(\mathbf{b},\lambda)$). As it is known experimentally the results can only be ± 1 and these are the only values that the two functions A and B can take. They must also satisfy the property that if $\mathbf{a}=\mathbf{b}$ then the results are perfectly anticorrelated:

$$A(\mathbf{a},\lambda) = -B(\mathbf{a},\lambda) \ . \tag{A.2.3}$$

In this theory we can also evaluate the average of the two measurements

$$P(\mathbf{a},\mathbf{b}) = \int d\lambda\rho(\lambda), A(\mathbf{a},\lambda)B(\mathbf{b},\lambda) = -\int d\lambda\rho(\lambda), A(\mathbf{a},\lambda)A(\mathbf{b},\lambda) \ , \tag{A.2.4}$$

where ρ is some probability distribution which satisfies the property $\int d\lambda\rho(\lambda) = 1$.

Bell then suggested to consider the projection of spin onto a third unit vector $\mathbf{c}$ and subtract the two averages

$$\begin{aligned} P(\mathbf{a},\mathbf{b}) - P(\mathbf{a},\mathbf{c}) &= -\int d\lambda\rho(\lambda)\left[A(\mathbf{a},\lambda)A(\mathbf{b},\lambda) - A(\mathbf{a},\lambda)A(\mathbf{c},\lambda)\right] \\ &= -\int d\lambda\rho(\lambda)\left[1 - A(\mathbf{b},\lambda)A(\mathbf{c},\lambda)\right]A(\mathbf{a},\lambda)A(\mathbf{b},\lambda) \ , \end{aligned} \tag{A.2.5}$$

where the last step follows from $A(\mathbf{b},\lambda)^2 = 1$. Since $-1 \le A(\mathbf{b},\lambda)A(\mathbf{c},\lambda) \le 1$ the part between square brackets in the integrand in (A.2.5) is positive. The same holds for the probability distribution $\rho(\lambda)$. If we take the modulus of both sides of Eq. (A.2.5) and use Schwarz inequality we end up with

$$|P(\mathbf{a},\mathbf{b}) - P(\mathbf{a},\mathbf{c})| \le \int d\lambda\rho(\lambda)\left[1 - A(\mathbf{b},\lambda)A(\mathbf{c},\lambda)\right] \ , \tag{A.2.6}$$

which can be rewritten as

$$|P(\mathbf{a},\mathbf{b}) - P(\mathbf{a},\mathbf{c})| \le 1 + P(\mathbf{b},\mathbf{c}) \ . \tag{A.2.7}$$

In deriving this inequality we have used nothing but the positivity property of the probability distribution and the fact that the outcome of the spin measurements can be only ± 1. This means that the inequality is absolutely general: if there exist a hidden variable which determines the outcome of the spin measurement then the

inequality must hold. The inequality, on the other hand, is violated in quantum mechanics as one can easily show by taking $\mathbf{a} \cdot \mathbf{b} = 0$ and $\mathbf{a} \cdot \mathbf{c} = \mathbf{b} \cdot \mathbf{c} = 0.707$, *i.e.* taking the vector $\mathbf{c}$ to be at 45° from both $\mathbf{a}$ and $\mathbf{b}$. Plugging in the numbers for this configuration for the quantum mechanics case we get:

$$|\mathbf{a} \cdot \mathbf{b} - \mathbf{a} \cdot \mathbf{c}| \leq 1 - \mathbf{b} \cdot \mathbf{c} \qquad i.e. \qquad 0.707 \leq 1 - 0.707 \ . \tag{A.2.8}$$

The conclusion is that any hidden variable theory is incompatible with quantum mechanics and that which of the two theory is realized in nature is a question which can be settled experimentally, because these averages can be measured. The first such measurement was made by Aspect, Grangier and Roger [9] in Orsay and gave a result in perfect agreement with quantum mechanics. From the result we have to conclude that the world we live in displays nonlocal phenomena like the one that Einstein, Podolsky and Rosen found absolutely paradoxical.

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