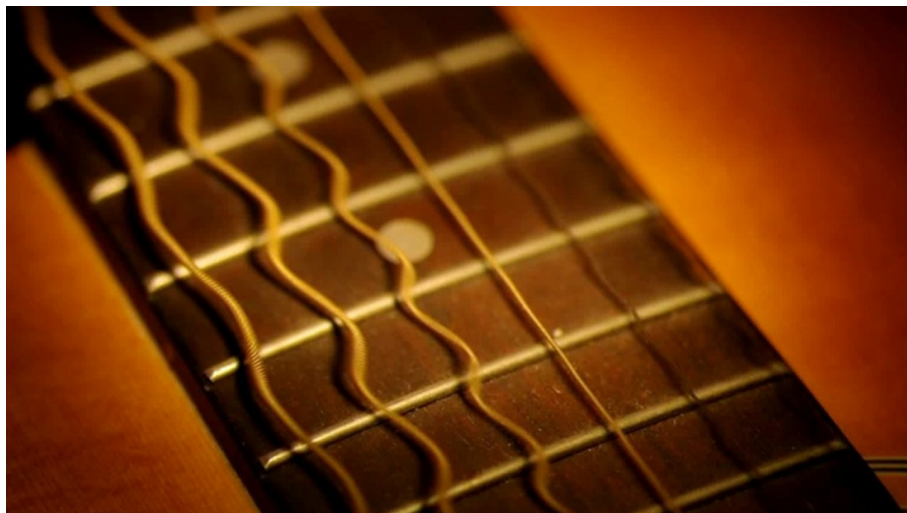# An Exploratory Introduction to Quantum Physics

Sølve Selstø
Oslo Metropolitan University

Preface

This book is meant to give you a bit of a feel for quantum physics, which is the mathematical description of the material micro world behaves. Since all matter is build up of micro particles, this is obviously rather important theory. Thus, it is only fair that we spend some time learning about it. I believe the best way to do so is by exploring it for ourselves – rather than just reading about it. That is what this book intends to do. Most of the book consists of exercises; it does not make any sense whatsoever to skip these and only read the text in between. The hope is that in doing the exercises, which make use of both numerical and analytical methods, you will learn that the quantum world is both weird and beautiful.

Quantum physics is not the easist subject to learn. In order to build understanding, we must resort to mathematics. This book strives to illuminate quantum phenomena using examples which are as simple and clear cut as possible – while not directly banal either. As a consequence, most exercises are confined to a one dimensional world. While this, of course, differ from the actual dimensionality of the world, it still allow us to introduce non-intuitive quantum phenomena without excessive technival complications.

You should know your basic concept from (classical) physics. In terms of mathematics, you should be familiar with basic calculus and linear algebra – both numerically and analytically. Topics like differentiation, Taylor expansions, integration, differential equations, linear transforms, matrix operations and eigen values should be rather familiar. When such quantities are to be determined, we will predominantly do so by numerical means. Thus, it is crucial that you have some experience in doing so. This, in turn, requires familiarity with relevant software or programming languages, be it MATLAB, Python, R, Octave, Julia, Java, C(++), Fortran or anything simliar.

Now, let's play!

Contents

Chapter 1

The Wave Function

The physical world we see around is seems to follow the well known laws of Newton. His second law may be written

$$m\frac{\mathrm{d}^2}{\mathrm{d}t^2}\mathbf{r}(t) = -\nabla V(\mathbf{r},t) \quad , \tag{1.1}$$

where m is the mass of a point object at position $\mathbf{r}$ and t is the time. In this case it is assumed that the force $\mathbf{F}$ is provided by some potential V which may be time dependent[1]. This potential could for instance be the gravitational attraction from a planet, in which case we would have

$$V = -k\frac{Mm}{r} \quad , \tag{1.2}$$

where k is a constant and M is the mass of the planet, who's centre we have chosen as the origin of our coordinate system.

Early in the 20th century it became clear that this Newtonian law of gravitaion, which had been inmensly sucessful until then, was not sufficiently accurate. There were observation wich just didn't fit with Eq. 1.2. And the more massive the gravitatilal object became, the more severe became the error in using Newton's law. The solution to the problem was provided by Albert Einstein with his *general theory of relativity*.

More or less at the same time, it also became clear that Newtonian mechanics just wouldn't do at the other end of the scale either. For various reasons, another description of microscopical objects such as molecules, atoms and particles was called for.

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[1]This is the last time we will use the **F**-word in this context; the term simply does not apply in quantum physics, instead we talk about *potentials* and *interactions*.

1.1　Quantum Physics: The Early Years

Once again, Albert Einstein had quite a lot to do with resolving these issues. But where the *theory of relativity*, both the *special* and *general* one, to a large extent is the prodouct of one single brilliant mind, this development is the beautiful product of several brilliant minds contributing constructively. The story leading up to the birth of *quantum physics* is an extremely interesting one. It's worth mentioning a few highlits.

At the time, it was well established how the Maxwell equations provided a very accurate description of how electromagnetic radiation, including visible light, works in terms of travelling waves. However, as it turned out, there where observed phenomena with light which just didn't fit with this wave description. Two people, Max Planck and our friend Albert, both succefully explained physical phenomena by assuming radiation to be made up of small energy lumps, or *quanta*. In Planck's case, he managed to understand how the radiation emitted from a so-called *black body* at thermal equilibrium is distributed. In doing so he imposed a simple but non-intuitive relation between the frequency of the radiation and the energy of each quantum,

$$E_{\text{quant}} = hf \quad , \tag{1.3}$$

where f is the frequency and $h \approx 6.63 \times 10^{-34}$ Js is the Planck constant. Clearly, it's not large. But it's certainly not zero either.

The same relation was also crucial in Eistein's explanation of the *photoelectric effect*, in which electrons are torn lose from a metal plate by shining light upon it.

These works of Plack and Einstein certainly did not dismiss the idea that light is a wave. They just proved that, complementary to this concept, we also need to consider light as quanta. For the sake of simplicity, let's call these quanta *particles* for now.

The next major conceptual breakthrough is an impressive one. At the time scientists was coming to realize that matter indeed consited of atoms somehow; it was eventually established that matter indeed consists of particles. But, just as light turned out to not just be waves, also the perseption of matter as particles also turned out to be an incomplete one. In his PhD dissertation, the French nobleman Louis de Broglie lounched the following thought[2]: *Since light turns out to behave both at particles and waves, maybe matter isn't just particles – maybe it behaves as waves as well.*

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[2]For the sake of clarity: This is not actually a quote

And he was right! This view quickly gained experimental and theoretical support[3]. This, in turn, called for a mathematical wave-description of matter. We needed someone to formulate a wave description for matter – just like Maxwell had done for light. We got two: Werner Heisenberg and Erwin Schrödinger. Both their theories are frequently applied to this date. Schrödinger's formulation is, however, the most common one. And it's his formulation we will use in the following.

In this context, it's worth mentioning that the Dane Niels Bohr used the ideas of Luis de Brogile in order to formulate a "wave-theory" for the atom. This model somehow managed to predict the right energies for the hydrogen atom, and it was an important stepping stone towards our understanding of the atom at the time. However, the "Bohr-atom" does not provide a very adequate picture of the atom, and the theory is long since abandoned.

Figure 1.1: Not your avarage crowd; 17 of the 29 attendees at the 5th Solvay conference in 1927 was or went on to become Nobel Prize laureates. Marie Curie, front row, number three from the left, even recieved two! All the people mentioned above are here – along with a few other brilliant minds.

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[3]Maybe the most important experiment in this regad was repeating the Young double slit experiment – with electrons rather than light.

1.2 How Different is Quantum Physics?

The formulation in which small particles are described in terms of waves is known as *quantum physics*. It's fair to ask in which way and to what extent this description differs from a Newtonian, classical picture – one with little "balls" bouncing around. The answer is that quantum phsyics is *very, very different* from classical physics – in several aspects, including phenomena which really couldn't have been foreseen with the strongest of imagination. In Newtonian mechanics, an object has a well-defined position and velocity/momentum at all times. A quantum object doesn't. A wave isn't localized to a single point in space. And when it travelles, it typically does so dispersively; it spreads out. The more confined the wave is spatially, the wider is its distrubution in velocity. If the position (x) is known, the momemtum (p) is completely indetermined – and *vise verca*. The Heisenberg uncertainty principle states this quite precicely:

$$\sigma_x \sigma_p \leq \frac{h}{4\pi} \quad , \tag{1.4}$$

where σ_x is the uncertainty in position and σ_p is the uncertainty in momentum. In other words: If we want to have information about both position and momentum of a small object, there is a fundamental limit to the accuracy. This is not a limit imposed by practical issues such as the quality of our measurment devices; this seems to be a limit inherent in Nature herself.

And it gets worse.

First, however, we need to say a few words about the *wave function*.

1.3 The wave function and the curse of dimensionality

Thie wave function is provided by a set of approprate initial conditions and Schrödinger's famous equation. We will get back to this one – for sure. For a system consistning of, say, N particles, the system is described by a complex function Ψ depending on the coordinates of all particles and (parametrically) on time,

$$\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N; t) \quad . \tag{1.5}$$

If we could have described the stystem clasically, according to classical Newtonian physics, it would be described by the set of positions and velocities for the same particles:

$$[\mathbf{r}_1(t), \mathbf{r}_2(t, ..., \mathbf{v}_1(t), \mathbf{v}_2(t), ...]. \tag{1.6}$$

If each the objects or particles that make up the system[4] resides in an d-dimensional world, where d typically is three, this constitutes **a single point** in a real space of dimension $2Nd$. If you want to simulate the evolution of such a classical system, you can do so by $2Nd$ time-dependent parameters.

For a quantum system, however, we need the wave function of Eq. 1.5 for a full descrition. This is certainly not a single point in the any Nd-dimensional space; for **each and every single point** in that space, the wave function has a certain value which we need to know. And the fact that we are talking about an Nd-dimensional space rather than a $2Nd$-dimensional one as in the classical case, doesn't help us either; the wave function is *complex*.

If we want to describe a function numerically, we typically need to limit the extension of the space to a finite interval and "chop it into pieces"; we need to discretize it. Suppose our system consists of N particles for which the numerical domain consists of s points. Then our numerical, approximate wave function will consist of s^N complex numbers. The corresponding classical state will consist of $2Nd$ real numbers. In other words: In the quantum case, the complexity grows **exponentially** with the number of particles, while it just increases linearly in the classical case.

This is the infamous *curse of dimensionality*. It's certainly a curse when you want to simulate quantum systems with several particles; this is really, realy hard. In terms of information processing, however, it may be an advantage: With very few simple particle, you can save and process enormous amounts of information. Quantum information theory and quantum computing is one of the fastest growing fields within modern science and technology[5].

For now, we will limit our wave function to a single particle, such as an electron. Moreover, for the sake of simplicity, we will take the world to be one-dimensional (as opposed to three dimensional):

$$\Psi = \Psi(x;t) \quad . \tag{1.7}$$

The wave function is required to be finite and differentiable on it's entire domain[6]. It contains all information there is to be obtained about the quantum system we are interested in. However, extracting and interpreting this information may require some work.

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[4]Here, we don't consider the particles' structure.

[5]In fact, the curse of dimensionality is what motivated the famous physicist and the 1965 Nobel laureate Richard Feynman to propose the quantum computer in the first place.

[6]This restriction is not limited to the one-dimensional one-particle case.

1.4   Interpretation of the Wave Function

As mentioned, a quantum particle, as any other wave, does not really have a well defined position nor momentum. However, a mearsurement of either position or momentum would in fact produce a definite answer. But wait, if we first measure position x and then momentum p and get definite answers, wouldn't that violate the uncertainty principle, Eq. 1.4? No, because when you perform a measurement, you alter the wave function. If you measure the position of a quantum particle and then its momentum, a second position mesurement would probably provide a result different from the first one. The uncertainty principle refers to *simultaneous* measurements only.

Instead of explaining this feature of the wave function further, we will simply continue to explain how phiscal quantities are calculated from the wave function. This really isn't fair; the issue, which tycially is referred to as "the collapse of the wave function", certainly deserve more attention. However, the fact that the wave function is affected by the action of a measurement is really not trivial. It has been the issue of much debate – both from the philosophical and the technical point of view. And it still is. Several papers and books have been written on the subject.

Instead of definite positions and momenta, the wave function only provide *probabilties* for each possible outcomes of a measurement. Suppose we set out to measure the position of the particle at time t. In that case, the quantity

$$|\Psi(x;t)|^2 \tag{1.8}$$

provides the probability density for measuring the particle's position to be x. Or, in other words, the probability of finding the particle between position a and b is[7]

$$P(x \in [a,b]) = \int_a^b |\Psi(x;t)|^2 \, dx \quad . \tag{1.9}$$

1.4.1   Excerise: Normalization

For a quantum system consistsing of a single particle in one dimension, we must insist that the following holds at all times for the wave function:

$$\int_{-\infty}^{\infty} |\Psi(x)|^2 \, dx = 1. \tag{1.10}$$

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[7]This interpretation, which was stated as a footnote in his publication, won the German physicist and mathematician Max Born the 1954 Nobel prize in Physics.

Why?

If we prepare lots of identical particles in the very same state and then measure the position of each and every one of them, we will not get the same result every time; we would rather have a *distribution* of results. With many enough measurements, this distribution is simply Eq. 1.8 (with the proper over-all scaling/normalization). This distribution will have both a *mean value*, or *expecation value*, and a *standard deviation*, or *width*. The former is provided by the integral

$$\langle x \rangle = \int_{-\infty}^{\infty} [\Psi(x)]^* \, x \Psi(x) \, dx = \int_{-\infty}^{\infty} x |\Psi(x)|^2 \, dx \quad , \tag{1.11}$$

where the asterix indicates complex conjugation and the time-dependence of the wave function Ψ is taken to be implicit. In other words, the average result of our series of mesurements on particles with the same Ψ, will be Eq. 1.11.

Again, it is hard to avoid asking questions like "but where *is* the particle actually prior to measurement" and "how come the wave function is unable to reveal this"? And, again, this question is way to deep to be properly addressed here; as is the case for the collapse of the wave function, discussions and publications in this regard are quite numerous. The most famous of these discussions is the one between Einstein and Bohr themselves. In any case, many physicists resort to answering the above questions by "it does not make sense to talk about a particle's position without actually measuring it" and "there is no more information obtainable beyond that contained in the wave function". In other words, the stochastical nature of the microworld seems to be a truly fundamental one.

Let's place these issues at the back of our minds, for now, and continue with our more technical approach to Ψ.

Of course, position is not the only physical quantity pertaining to the system. In fact, every physical quantity has a corresponding *operator* in quantum physics. The position operator is simply multiplication by x, while the *momentum operator* is spatial differentiation:

$$\hat{p} = -i\hbar \frac{d}{dx} \quad , \tag{1.12}$$

where $\hbar$ is the Planck constant divided by 2π.

Correspondingly, the momentum expectation value is

$$\langle p \rangle = \int_{-\infty}^{\infty} [\Psi(x)]^* \, \hat{p} \Psi(x) \, dx = \tag{1.13}$$

$$\int_{-\infty}^{\infty} [\Psi(x)]^* \left(-i\hbar \frac{d}{dx} \right) \Psi(x) \, dx = -i\hbar \int_{-\infty}^{\infty} [\Psi(x)]^* \, \Psi'(x) \, dx \quad .$$

The operator for a physical quantity which depends on position and momemtum, depends on the position and momentum operators in the same manner. Kinetic energy, for instance, may be written as $1/2\,mv^2 = p^2/2m$; its operator is

$$\hat{T} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} \quad . \tag{1.14}$$

In the following exrecise, and all the other ones following this one, we will set

$$\hbar = 1 \quad . \tag{1.15}$$

This may seem a bit overly pragmatic, but it is in fact admissible. It simply corresponds to choosing a convenient set of units. And it facilitates our numerical calculations. We must be aware, though, that the numbers that comes out certainly will not correspond to number given in "ordinary" units such as metres or seconds.

1.4.2   Exercise: Expectation values

For each of the unnormalized wave functions below:

1. Normalize them, that is, impose a factor such that Eq. 1.10 is fulfilled.

2. Plot the absolute square of the wave function (plot real and imaginary contribution separately if complex).

3. From the plot: Estimate the most likely outcome of a position measurement.

4. Determine the position expectation value.

5. Determine the momentum expectation value.

We strongly suggest that you calcuate the integrals numerically, for instance using the trapezoidal rule:

$$\int_a^b f(x)\,dx = h\left(\frac{1}{2}f(x_0) + f(x_1) + \ldots + f(x_{n-1}) + \frac{1}{2}f(x_n)\right) + \mathcal{O}(h^2) \tag{1.16}$$

$$\text{where}\quad h = \frac{b-a}{n}\quad\text{and}\quad x_k = a + kh \quad .$$

In doing so, make sure that you use a numerical grid which is fine enough (large enough n) and exteds widely enough (the interval $[a,b]$ actually cover the wave function). In case some of your expectation values turn out complex, this may indicate that the latter requirement isn't met. And, while you are at it, you

could consider also doing the differentiation needed to obtain the momentum expecation value numerically as well – for instance by using the midpoint rule:

$$f'(x) = \frac{-f(a-h)+f(a+h)}{2h} + \mathscr{O}(h^2) \quad . \tag{1.17}$$

a) $\Psi(x) = \dfrac{1}{\sqrt{1+(x-3)^2}}$

b) $\Psi(x) = \dfrac{e^{-4ix}}{\sqrt{1+(x-3)^2}}$

c) $\Psi(x) = e^{-x^2}$

d) $\Psi(x) = xe^{-(x-2)^2/10+2ix}$

1.4.3 Exercise: Is the particle in *this* interval?

For each of the four wave functions in Exercise 1.4.2, what is the probability that a position measurement would find the particle between $x = 1$ and $x = 2$?

1.5 Some simplifying notation

After a while you may get tired of writing up integrals. In the following we will write expressions such as Eq. 1.11 and 1.13 somewhat more compactly. For two functions Ψ and Φ we define

$$\langle \Phi, \Psi \rangle = \int_{-\infty}^{\infty} [\Phi(x)]^* \, \Psi(x) \, dx \quad . \tag{1.18}$$

With this, the expectation value of some physical quantity A for a quantum system with wave function Ψ may be written

$$\langle A \rangle = \langle \Psi, \hat{A}\Psi \rangle \quad , \tag{1.19}$$

where $\hat{A}$ is the operator corresponding to the physical variable A, be it position, momentum, energy or something else. Correspondingly, the *width* or *standard deviation* of a physical variable is

$$\sigma_A \equiv \sqrt{\langle A^2 \rangle - \langle A \rangle^2} \quad . \tag{1.20}$$

Here, this notation simply serves as a lazy person's way of writing up integrals. However, it goes a lot deeper – specifially into linear algebra and functional analysis. Thing is, wave functions may be considered vectors, and the definition in Eq. 1.18 is in fact an *inner product*. A general inner product fulfills

$$\langle \beta, \alpha \rangle = \langle \alpha, \beta \rangle^* \qquad \text{(symmetry)} \qquad (1.21a)$$
$$\langle \alpha, c\beta \rangle = c\langle \alpha, \beta \rangle \qquad \text{(linearity)} \qquad (1.21b)$$
$$\langle \alpha, \beta + \gamma \rangle = \langle \alpha, \beta \rangle + \langle \alpha, \gamma \rangle \qquad \text{(linearity)} \qquad (1.21c)$$
$$\langle \alpha, \alpha \rangle > 0 \qquad \text{(positivity)} \qquad (1.21d)$$

where α, β and γ are general vectors and c is a complex number. The last equation above applies to all vectors in the space except the zero vector, which any vector space is required to have. (The inner product between the zero vector and itself is zero.)

1.5.1   Exercise: The inner product

Prove that the inner product between wave functions defined in Eq. 1.18 in fact fulfills the general requirements for an inner product Eqs. 1.21.

1.5.2   Execrise: Hermicity

In quantum physics we insist that all operators corresponding to physical variables are *Hermitian*. This means that any operator for a physical quantity A should fulfill

$$\langle \Psi, \hat{A}\Phi \rangle = \langle \hat{A}\Psi, \Phi \rangle \quad , \qquad (1.22)$$

for all admissible[8] wave functions Ψ.

a) For a wave function to be admisssible, we require that it is differentiable[9]. We also need to insist that the wave function vanish as $|x| \to \infty$. Why the latter?

b) Use integration by parts to show that $\hat{p}$ is in fact Hermitian.

c) Show that Hermicity ensures real expectation values.

   Why is this feature crucial for quantum physics to make sense?

---

[8]Admittedly, here we have taken for granted that if Ψ is admissible, so is $\hat{A}\Psi$; it remains admissible after being acted upon by the operator $\hat{A}$.

[9]How many times it's differentiable depends on the physics of the actual system.

1.5.3 Exercise: Standard deviations

For each of the four wave functions in Exercise 1.4.2, what is the standard deviation of the position? This quantity is defined in Eqs. 1.18, 1.19 and 1.20.

And what is the momentum standard devation? In answering the latter, this finite difference formula may come in handy:

$$f''(x) = \frac{f(x-h) - 2f(x) + f(x+h)}{h^2} + \mathcal{O}(h^2) \quad .$$

Check that the uncertainty principle, Eq. 1.4, isn't violated. Does any of the wave functions fulfill it with equailty?

1.5.4 Exercise: The hydrogen atom and atomic units

In order to get a feel for which kind of quantities we typically are dealing with for quantum systems, we will calculate expectation values for an electron attached to a proton, that is a hydrogen atom, when its energy is minimal. In this case, we may use the wave function

$$\Psi(r) = \frac{r}{\sqrt{\pi a_0^3}} e^{-r/a_0} \tag{1.23}$$

to calculate expectation values in the same way as for quantum particles in one dimension, that is, as in Eqs. 1.11 and 1.13. Here r is the distance between the electron and the proton. When dealing with atoms, it is convenient to introduce atomic units, which may be defined by choosing the electron's mass m_e, the elementary charge e and the so-called Bohr radius a_0 as units for the respective quantities – in addition to setting $\hbar = 1$ as in Eq. 1.15. In general units, the Bohr radius reads

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} \quad ; \tag{1.24}$$

since all other factors are one in the above expression, that means that also $4\pi\varepsilon_0 = 1$ in atomic units.

a) Calculate the expectation values $\langle r \rangle$ and $\langle p \rangle$ using SI units. Here, as in the one dimensional cases above, you can take the operator for r to be r itself, and the p-operator, corresponding to the momentum component in the radial direction, to be $-i\hbar\partial/\partial r$.

b) Repeat the calculations from a) using atomic units[10].

The energy operator is the sum of the operator for kinetic energy, Eq. 1.14, and the potential energy. The potential energy corresponding to the attraction from the proton is

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} \quad , \tag{1.25}$$

so the full energy operator may be written[11]

$$\hat{H} = -\frac{\hbar^2}{2m_e}\frac{d^2}{dr^2} - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} \quad . \tag{1.26}$$

The reason why we call it "$\hat{H}$" rather than "$\hat{E}$" will be explained in the next chapter.

c) Calculate the expectation value for the energy of the system – both using SI units and atomic units.

---

[10]Atomic units are usually abbreviated "a.u." – irrespective of which quantity we are dealing with. In other words, we usually don't denote if we are talking about atomic length units or atomic time units, for instance.

[11]Here we rather pragmatically jump from one dimension to a fully three-dimensional example. This is not in general as straight forward as this example would indicate. The reason we can simplify it in this case, is that the wave function only depends on the distance from the origin; it is independent of direcion.

Chapter 2

The Schrödinger Equation

This chapter is concerned with the Schrödinger equation, which is a partial differential equation in time and space. In this chapter we will solve it for certain cases. In a compact manner, the Schrödinger equation, in its time-dependent version, may be written

$$i\hbar\frac{\partial}{\partial t}\Psi = \hat{H}\Psi \quad , \tag{2.1}$$

where the *Hamiltonian* $\hat{H}$ is the energy operator. It has inherited its name from the irish matematician Willian Rowan Hamilton, who made significant contributions to the theoretical foundation of classical mechanics in the nineteenth century. For a single particle which is not subject to any external interactions such as electric fields, the Hamiltonian is simly the sum of kinetic and potential energy,

$$\hat{H} = \hat{T} + \hat{V} = \frac{\hat{\mathbf{p}}^2}{2m} + V(\mathbf{r}) \quad , \tag{2.2}$$

where $\hat{V}$ is simply a function of position. Here momentum and position, $\mathbf{p}$ and $\mathbf{r}$, are written as vectors, that is, we are not necessarily restricted to one spatial dimension. In this case, the position operator is still just multiplication with the position itself, $\hat{\mathbf{r}} = \mathbf{r}$, while the momentum operator is proportioinal to a gradient operator,

$$\hat{\mathbf{p}} = -i\hbar\nabla \quad . \tag{2.3}$$

In case there are, say, N particles – which interact with each other and, possibly, with some external electromagnetic field – the Hamiltonian is more complex:

$$H = \sum_{i}^{N}\left[\frac{(\mathbf{p} - q_i\mathbf{A}(\mathbf{r}_i,t))^2}{2m_i} + V(\mathbf{r}_i)\right] + \sum_{i>j}^{N} W(\mathbf{r}_i,\mathbf{r}_j) \quad . \tag{2.4}$$

Here, q_i is the electric charge and m_i is the mass of particle number i. **A** is
the so-called *vector potential*, which provides the electric and magnetic field as
$\mathbf{E} = -\mathrm{d}/\mathrm{d}t\mathbf{A}$ and $\mathbf{B} = \nabla \times \mathbf{A}$, respectively[1]. In atomic and molecular physics,
the interaction W, which in this case is a two-particle interaction[2], is typically
the Coulomb repulsion between electrons:

$$W(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{4\pi\varepsilon_0} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \quad , \tag{2.5}$$

and the potential $V(\mathbf{r}_i)$ is the Coulomb attraction from the nuclei, whose positions
are frequently assumed to be fixed. The constants e and ε_0 are the elementary
charge and the permittivity of free space, respectively. Probably, the notation is
shifted in Exercise 1.5.4.

In the remainder of this chapter we will exclusively be occupied with one single
particle in one dimension – without interactions with any external electromag-
netic field. Our Hamiltonian will then be

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x) \quad . \tag{2.6}$$

To simplify things further we will, as in Exercise 1.5.4, take the particle's mass
as our mass unit in addition to setting $\hbar = 1$. With this we may write the kinetic
energy operator as

$$\hat{T} = -\frac{1}{2} \frac{\mathrm{d}^2}{\mathrm{d}x^2} \quad . \tag{2.7}$$

2.1 Discretization

We will start out by choosing a certain domain for our wave function Ψ to "live"
in. Assuming that the wave function virtually vanish for $x < a$ and $x > b$, vi may
disregard the parts of space beyond these points. Moreover, as you probably did
in Exercise 1.4.2, we will *discretize* the resulting interval and represent our wave
function by a set of points

$$\Psi(x) \rightarrow \mathbf{\Psi} = \begin{pmatrix} \Psi(x_0) \\ \Psi(x_1) \\ \vdots \\ \Psi(x_n) \end{pmatrix} \quad \text{where} \quad x_i = a + ih \quad \text{and} \quad h = \frac{b-a}{n} \quad . \tag{2.8}$$

---

[1] Actually, even Eq. 2.4 is a simplification; the vector potential **A** is really a much more involved
operator which takes into account how photons appear and dissappears. For strong fields, such as
laser pulses, it does, however, make sense to disregard this.

[2] In nuclear physics, Hamiltonians with even three-particle interaction are also considered.

Please do not confuse the numerical parameter h above with the Planck constant.

This is, of course, a tremendous reduction in complexity. The wave function can in principle be *any* complex function which is finite, differentiable and normalizable on $\mathbb{R}$, while in Eq. 2.8 it is reduced to a simple vector in $\mathbb{C}^{n+1}$.

When imposing discretization like this, it is absolutely crucial that we check for convergence; our results may certainly not depend significantly on our choices for the numerical parameters a, b and n. As we expand our interval, $[a,b]$, and reduce our step size h (increase n), the discretized representation of Ψ should become a reasonable approximation to the true wave function.

2.1.1 Exercise: Normalizing the discretized wave function

When the wave function is represented as a vector with elements $\Psi(x_0), \Psi(x_1), ...,$ we insist that

$$h \sum_{i=0}^{n} |\Psi(x_i)|^2 = h\,\Psi^{\dagger}\Psi = 1 \quad , \tag{2.9}$$

where $\dagger$ indicates Hermitian adjoint, that is, transpose and complex conjugation. Why do we insist on this?

Hint: Apply Riemann integration or the trapezoidal rule, Eq. 1.16, to Eq. 1.10.

2.2 Kinetic Energy – Numerically

Now, with a proper numerical discretization of Ψ we may apply numerical differentiation methods to it. The most straight forward approach would be that of *finite difference schemes*. We may, for instance, apply the three point rule we saw in Exercise 1.5.3 or the five point rule for the double derivative,

$$f''(x) = \frac{f(x-h) - 2f(x) + f(x+h)}{h^2} + \mathcal{O}(h^2) \quad \text{and} \tag{2.10a}$$

$$f''(x) = \frac{-f(x-2h) + 16f(x-h) - 30f(x) + 16f(x+h) - f(x+2h)}{12h^2} + \mathcal{O}(h^4) \quad , \tag{2.10b}$$

respectively.

2.2.1 Exercise: The kinetic energy operator as a matrix

With Ψ given on vector form as in Eq. 2.8, we may write the action of $\hat{T}$ on Ψ as a matrix multiplication. For the above choices, Eqs. 2.10, what will the

corresponding matrices be? Assume that $\Psi(x) = 0$ for $x \notin [a,b]$.

There are, of course, several other methods to estimate differentiation of various orders numerically. A particularly convenient one is provided by the Fourier transform, which is defined as

$$\Phi(k) = \mathscr{F}\{\Psi(x)\}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-ikx} \Psi(x) \, dx \quad . \tag{2.11}$$

This shifts our position-dependent wave function into a function wich depends on the wave number k instead. We may transform this one back into the original x-dependent function again by the inverse Fourier transform, $\mathscr{F}^{-1}$:

$$\Psi(x) = \mathscr{F}^{-1}\{\Phi(k)\}(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{+ikx} \Phi(k) \, dk \quad . \tag{2.12}$$

Within the "k-space", differentiations are trivial[3]:

$$\frac{d^n}{dx^n} \int_{-\infty}^{\infty} e^{-ikx} \Phi(k) \, dk = \int_{-\infty}^{\infty} \left(\frac{d^n}{dx^n} e^{-ikx} \right) \Phi(k) \, dk = (-ik)^n \int_{-\infty}^{\infty} e^{-ikx} \Phi(k) \, dk \quad . \tag{2.13}$$

That means that differentiation may be performed by first Fourier-transforming Ψ into "k-space", then perform the actual differentiation as above and, finally, transform it back into the x-representation. Thus, the action of the kinetic energy operator, for instance, may be calculated as

$$\hat{T}\Psi = \mathscr{F}^{-1}\left\{ \frac{\hbar^2}{2m} k^2 \mathscr{F}\{\Psi\} \right\} \quad . \tag{2.14}$$

In terms of implementation, this is really good news because discrete numerical Fourier transforms may be done extremely quickly. In technical terms, a *Fast Fourier Transform*, FFT, would take $\mathscr{O}(n \log n)$ operators[4].

In discrete "k-space", the discrete x vector, $(x_0, x_1, ..., x_n)$ is replaced by a k vector. The maximum magnitude of k is inversely proportional to the numerical step size h; $k_{\max} = \pi/h$. The k-vector corresponding to the Fourier transformed wave function extends from $-k_{\max}$ to (almost) $k_{\max}$ in n steps of length $\Delta k = 2\pi/L$, where

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[3] Actually, quantum physics may also be formulated in "k-space" or *momentum space* rather than position space. In this case, the $\hat{x}$ and $\hat{p}$ operators change roles, so to speak, and the momentum wave function, $\Phi(k)$, gives the momentum distribution in the same manner as $\Psi(x)$ gives the position distribution. The momentum variable and k are related by $p = k\hbar$.

[4] It's fair to mention that due to their sparse band-diagonal nature, also finite difference schemes such as the ones in Eqs. 2.10 and Exercise 2.2.1 may be rather efficient.

$L = b - a$ is the size of the domain. Note, however, that FFT implementations typically distort this k-vector in a somewhat non-intuitive manner; when n is even, it typically starts from zero and reaches $(n/2 - 1) \cdot \Delta k$ and then continues from $-n/2 \cdot \Delta k$ to $-1 \cdot \Delta k$. Check the documentation of your FFT implementation of choice in order to work this out.

2.2.2   Exercise: Expectation values as matrix multiplications

a) For the wave functions in Exercise 1.4.2: Calculate the expectation value of the kinetic energy, Eq. 2.7, in the same manner as you did it in Exercise 1.4.2. Do this both using a finite difference formula, Eqs. 2.10 and some FFT-implementation in your prefered framework for numerics.

b) Now, do the same, however via matrix multiplication. Let your wave function be represented as in Eq. 2.8 and $\hat{T}$ be a square matrix. With this, and proper normalization, the expectation value may now be estimated as

$$\langle T \rangle \approx h\, \mathbf{\Psi}^{\dagger}\, T\, \mathbf{\Psi} \quad , \tag{2.15}$$

where $\mathbf{\Psi}$ is a complex row vector and T is a quadratic matrix.

For each of the four wave functions, chose an adequate domain, $[a, b]$, and implement both the representations of Exercise 2.2.1 and the correspondnig FFT matrix[5] – with an increasing number of grid points, n.

Does these estimates reproduce your findings in a)?

Are these numerical representations of the kinetic energy operator actually Hermitian – is $T = T^{\dagger}$?

2.3   Dynamics Without Explicit Time-Dependence

When the Hamiltonian $\hat{H}$ does not contain any explicit time-depencence, the solution of the Schrödinger equation, Eq. 2.1 may be formally written as

$$\Psi(t) = \exp\left[-i\hat{H}(t - t_0)/\hbar\right] \Psi(t_0) \quad , \tag{2.16}$$

[5]*Hint*: Just transform the identity matrix.

where $\Psi(t_0)$ is the wave function at some initial time t_0 and the spatial dependence of Ψ is implicit. The exponential of an operator is defined via series expansion:

$$e^{\hat{A}} \equiv \sum_{n=0}^{\infty} \frac{1}{n!}\hat{A}^n \quad , \tag{2.17}$$

where $\hat{A}^0 = \hat{I}$ is the identity operator.

When actually calculating matrix exponentials, however, we rarely resort to (truncated) Taylor series – at least not if the matrix to be exponentiated is dagonalizable. And ours is; theory from linear algebra ensures this for any Hermitian operator. Thus, there will always exist matrices P and D such that

$$H = PDP^{\dagger} \tag{2.18}$$

where D is diagonal with the eigen values of the matrix A along the diagonal, $D = \text{diag}(\lambda_1, \lambda_2, ...)$ and P is unitary.

With this we may write

$$e^{-i/\hbar H \Delta t} = P \, \text{diag}(e^{-i/\hbar \varepsilon_1 \Delta t}, e^{-i/\hbar \varepsilon_2 \Delta t}, ...)P^{\dagger} \quad , \tag{2.19}$$

where $\varepsilon_1, \varepsilon_2, ...$ are the eigen values of the Hamltionian matrix H. For obtaining these eigenvalues and the corresponding eigenvectors, the columns of P, you will certainly find adequate implementations. However, you are also likely to find implementations which can perform the exponentiation in Eq. 2.16 directly. We suggest that you do that for now, if you do have that option.

2.3.1   Exercise: Formal solution

Prove that Eq. 2.16 in fact is a solution of Eq. 2.1 with the proper initial condition.

2.3.2   Exercise: Exponentiation

Prove that Eq. 2.17 and Eq. 2.18 in fact leads to Eq. 2.19.

In the following we will play around with travelling wave packets. For that we need a proper initial wave function. In this context, Gaussian wave packets are ideal. A general Gaussian has the form

$$f(x) \sim \exp\left[-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2\right] \quad , \tag{2.20}$$
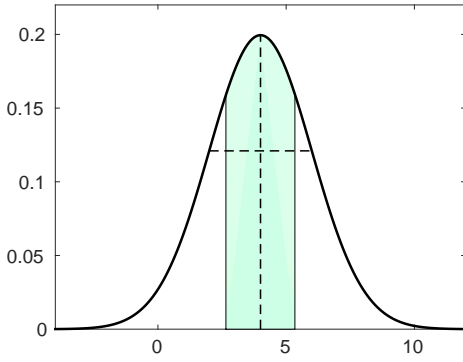
Figure 2.1: This is the shape of a normlized Gaussian curve, as defined in Eq. 2.20. Here the mean value $\mu = 4$, and the standard deviation $\sigma = 2$. These are illustrated by vertical and horizontal dashed lines, respectively. The coloured area has the area 1/2, while the entire area under the graph is one.

where μ is the mean position and σ is the width, see Fig. 2.3.2.

When the postion distribution $|\Psi(x)|^2$ has this shape, μ will be the mean position and σ is the width of the position distribution. Gaussians are convenient for various reasons. One of these is the rather simple form. And although their tale never actually vanish completely, they are, for all practical purposes, indeed confined in space[6] – and momentum. Moreover, the time evolution of a Gaussian wave function travelling freely may be written analytically. Suppose your state at time $t = 0$ is

$$\Psi(x, t = 0) = \sqrt{\frac{\sqrt{2}\sigma_p}{\sqrt{\pi}(1 - 2i\sigma_p^2\tau)}} \exp\left[-\frac{\sigma_p^2(x - x_0)^2/\hbar^2}{1 - 2i\sigma_p^2\tau/(\hbar m)} + ip_0x/\hbar\right],$$
(2.21)

then the absolute square of our wave function at time t is

$$|\Psi(x; t)|^2 = |N|^2 \exp\left[-\frac{2}{\hbar^2}\frac{\sigma_p^2(x - x_0 - p_0t/m)^2}{1 + 4\sigma_p^4(t - \tau)^2/(m\hbar)^2}\right]$$
(2.22)

with the time-dependent normalization factor

$$|N|^2 = \sqrt{\frac{2}{\pi}}\frac{\sigma_p/\hbar}{\sqrt{1 + 4\sigma_p^4(t - \tau)^2/(m\hbar)^2}}.$$

Although slightly more "messy", Eq. 2.22 is indeed of the same form as Eq. 2.20[7]. Here x_0 is the particle's mean position initially, τ is the time at which the wave packet is at its narrowest, p_0 is the mean momentum and σ_p is the width of the momentum distribution.

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[6]That is to say, their magnitude quicly falls below machine accuracy as x departs from μ.

[7]It becomes a bit "cleaner" with $m = 1$ and $\hbar = 1$.

2.3.3   Exercise: Wave propagation

In this exercise we are going to simulate a Gaussian wave packet which is not exposed to any potential V. With $V = 0$, the Hamtiltonian is simply the kinetic energy operator, $\hat{H} = \hat{T} = -1/2 \, d^2/dx^2$. This system serves well for checking the accuracy of our numerical approximations since the exact solution is known analytically (Eq. 2.22).

For starters, you can choose the following set of parameters:

x_0	σ_p	p_0	τ
-20	0.2	3	5

Also, let your domain be $[a,b] = [-L/2, L/2]$ where you set $L = 100$. Choose an initial number of grid points n, and let your intial time be $t = 0$. For the FFT implementation, it's and advantage to set $n = 2^m$ where m is a positive integer.

a) For each of our three approximations to the kinetic energy operator, simulate the evolution of the wave function according to Eq. 2.16 and compare the numerical estimate to the exact one, Eq. 2.22. Specifically, for a set of times $t_0 = 0$, t_1, t_2, ... where $t_{i+1} = t_i + \Delta t$, choose a reasonably small Δt and plot $|\Psi(x;t_i)|^2$ as you go along. Preferably, do this with all four versions of the wave function simultaniously as a movie. The transition from one time step to another is acheived by Eq. 2.16 and, if necessary, Eq. 2.19:

$$\Psi(t_{i+1}) = e^{-i\hat{H}\Delta t/\hbar} \, \Psi(t_i) \quad . \tag{2.23}$$

b) Play around with the numerical parameter n. For each of the three numerical estimates, how large n do you need for your estimate to, more or less, coincide with the analytical solution? Which implementation seems to be the most precise one? Is the wave function in fact at its narrowest when $t = \tau$?

c) What happens to the different approximations to the wave function when they hit the boundary at $x = \pm L/2$?

d) Repeat this exercise playing around with various choices for the Gauss parameters σ_p, p_0, x_0 and τ.

2.3.4 Exercise: Interference

Construct an initial wave packet of the form

$$\Psi(x, t = 0) = \frac{1}{\sqrt{2}} \left(\psi_1(x) + \psi_2(x) \right) \quad , \tag{2.24}$$

where each of the two functions ψ_1 and ψ_2 is of the form Eq. 2.21. The parameters should not be the same, make sure to choose values for the mean momentum and initial positions such that the two Gaussians travel towards eachother. Also, make sure that the two inital Gaussians have negligible overlap. In this case, the pre-factor $1/\sqrt{2}$ ensures normalization.

Now, as in Exercise 2.3.3, simulate the evolution according to the Schrödinger equation for the system (still without any potential). In this case, just use the FFT-version. What happenes? Maybe it would be interesting to also plott the real and imaginary parts of the wave function in this case, not just the absolute value squared.

Although somewhat simplified, the pattern you see is entirely analogous to what Thomas Young saw in his famous double slit experiment with light. Odd as it may seem, the phenomenon you just saw is real and measurable; the double slit has in fact been performed with particles instead of light, see Fig. 2.3.4. For the sake of clarity: This is not two particles interfering with each other; the quantum particle *interferes with itself*. Suppose that the spatial separation of the two "lobes" of the wave function originates for a double slit, this would mean that the single quantum particle passed through *both* slits, somehow.

2.3.5 Exercise: Expecation values and uncertainties

Choose a Gaussian wave packet, Eq. 2.22, with $\tau > 0$ and use the FFT-implementation from Exercise 2.3.3 to make a plot of the expectation values $\langle x \rangle$ and $\langle p \rangle$ as functions of time. The expecation values are defined by Eqs. 1.19 and 1.18

Also, calculate the uncertainty, or *standard deviation*, of the postion as a function of time. The uncertainty of a physical quantity is defined in Eq. 1.20.

Finally, confirm that the uncertanty in momentum remains constant and that the Heisenberg uncertainty principle, Eq. 1.4, is not violated.

At which time does equality in Eq. 1.4 apply?

A small reminder: We have set $\hbar = 1$, which means that $h = 2\pi$.

Figure 2.2: This figure shows how the famous double slit experment that Thomas Young performed with light back in 1801, can be done with *particles* as well. We see that as more and more particles are detected, an interference pattern emerges. This experiment, published in 1898, was conducted by Akaira Tonomura and coworkers at the Hitachy Advanced Research Laboratory. Electons are sendt through a double slit, one by one, and then detected as they hit an electron sensitive plate. The number of electrons counts are, from top to bottom, 11, 200, 6,000, 40,000 and 140,000. The first version of this experiment was performed by the italians Pier Giorgio Merli, Gian Franco Missiroli and Giulio Pozzi in 1974.
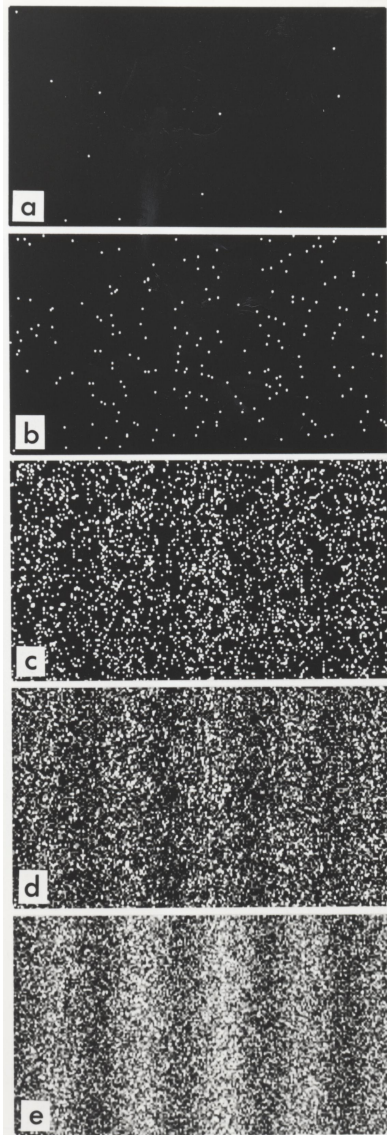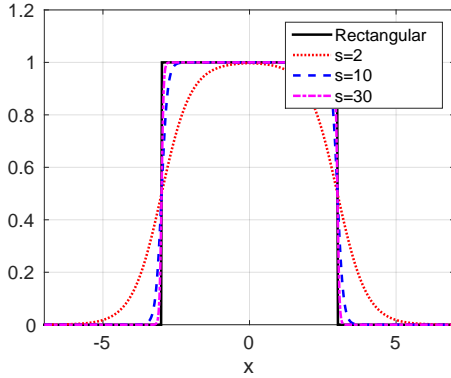
Figure 2.3: This figure shows the rectangular potential in Eq. 2.25 – along with the "smooth" version of Eq. 2.26 for three different values of *s*. Here $V_0 = 1$ and $w = 6$.

2.4 Scattering and Tunneling

We will now introduce a potential, V, in the Hamiltonian. For simplicity, we will let this potential be a rectangular one, centered at the middle of the grid:

$$V(x) = \begin{cases} V_0, & |x| \leq w/2 \\ 0, & |x| > w/2 \end{cases} \qquad (2.25)$$

The value V_0 can be positive, in wich case the potential is a barrier, or negative, in which case it may confine our quantum particle. For now we will address the former.

Actually, for numerical simulations we will, instead of the purely rectangular potential above, use a smoother version:

$$V_s(x) = \frac{V_0}{e^{s(|x|-w/2)} + 1} \qquad . \qquad (2.26)$$

This one is somewhat more convenient to work with numerically. The parameter s fixes the smoothess; in the limit $s \to \infty$, we reproduce the sharp corners of the potential in Eq. 2.25. The potentials are plotted in Fig. 2.4.

2.4.1 Execrise: Scattering on a barrier

In this exercise you do not get to choose the parameters yourself – at least not initially. In the implementation from Exercise 2.3.3, again with the initial state as in Eq. 2.22, you impose a potential of the above shape, Eq. 2.26. This is easy, you just augment your Hamiltonian with the potential V, which becomes a diagonal matrix in our representation, before you perform the exponentiation, Eq. 2.23. Again, we suggest you use the FFT representaion of kinetic energy.

Use the following parameters:

L	n	σ_p	p_0	x_0	τ	V_0	w	s
200	512	0.2	1	-20	0	3	2	5

As in Exercise 2.3.3, make an animation/simulation where your wave packet hits the barrier. You may want to indicate the position of the barrier in your simulation.

What happenes? After the wave packet has collided with the barrier, what is the final proabaility for the wave function to remain on the left side of the barrier ($x < 0$)? And what is the probability that it has passed into the right side of it ($x > 0$)? The former is called *reflection probability* and the latter is called *transmission probability*.

Play around with the parameters and repeat the whole scattering process. How is reflection and transmission probabilities affected by the height and the width of the barrier?

Do we still get reflection with a negative V_0 in the potential?

I suppose the answer to the last question is affermative? Would a classical partical do this?

2.4.2   Exercise: The dynamics of a classical particle

It could also be interesting to, along with the wave function, plot the position that a classical particle of unit mass would have along with the wave function. If we include this in the same simulation as in Exrecise 2.4.1, this will serve to illustrate some of the profound differences between classical physics and quantum physics.

Simulate numerically the trajectory of a classical particle with the initial conditions given by the mean position and velocity of the Gaussian wave packet; $x(t = 0) = x_0$ and the initial velocity would be $v(t = 0) = p_0/m$. The classical evolution is dictated by Newton's second law:

$$mx''(t) = -V'(x) \quad . \tag{2.27}$$

It may be useful to formulate it as a first order ordinary differential equation:

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} x \\ v \end{pmatrix} = \begin{pmatrix} v \\ -V'(x)/m \end{pmatrix} \quad , \tag{2.28}$$

and the differentiation of the potential could be done, for instance, by Eq. 1.17.

Now, suppose a ball is rolling uphill with an initial velocity of $v_0 = 4$ m/s. The top of the hill is $H = 1$ m above the ball's initial position. Why can we be absolutely certain that the ball will *not* make it to the other side of the hill?

-Because of energy conservation. It would take the ball with mass $m = 1$ kg an energy of $mgh \approx 10$ J to reach the top of the hill, while it only has $1/2 mv_0^2 = 8$ J to spend. Thus, for sure, the classical ball will roll down again on the same side; there is absolutely no way we would retrive the ball on the other side.

Let's look at the same process accoring to quantum physics:

2.4.3 Exercise: Tunneling

We start out in the same scenario as in Exercise 2.4.1 with the same parameters – except for one thing: This time, let $V_0 = 1$.

Again: Run the simulation and see what happens. And, again, calculate the reflection probability and transmission probability. What is the probability for this quantum physical "ball" to make it to the other side of the hill?

So, in spite of the quantum ball having a mean energy of about $p_0^2/(2m) = 0.5$ with our units, it still has a significant probability to be found on the other side of a "hill" it would take an energy of $V_0 = 1$ to climb. Itsn't that rather odd?

Well, you could argue that 0.5 is only the *mean* energy of the particle. Since the wave that is a quantum particle typically has a *distribution* in energy, rather than a specific one, it could contain some higher energy components which *could* make it over the barrier. If we think of the particle as a wave in water, parts of it could "splash" over.

This is, indeed, a bona fide argument. However, in the case coresponding to the parameters above, the probability of measuring an energy beyond 1 is actually just 1.6%. As seen in the exercise, the propabability of turning up on the other side of the barrier is considerably higher than this. So, the oddity remains.

Let's play around with this phenomenon, which is called *tunneling*, a bit more:

2.4.4 Exercise: Tunneling again

Now, we will replace the barrier with two narrow barriers, symmetrically placed on either side of $x = 0$. This can be achieved with this potential:

$$V(x) = V_s(x - d) + V_s(x + d) \quad , \tag{2.29}$$

where V_s refers Eq. 2.26. Here the displacement d must be significantly larger than the width w of the barriers.

Make your initial state a Gaussian wave packet well localized between the barriers – not too narrow, though. This time, let both the intial mean position x_0 and momentum p_0 be zero. For your barriers, you could use a width $w = 2$ and a hight $V_0 = 2$.

Then run your simulation again. What happens? Can we contain the wave functions between the barriers? Make a plot of the probability of finding the particle between the barriers as a function of time. You may need a large box and a rather long simulation for this one.

Try playing around with the width and the heights of your barriers.

We have seen two examples of situations in which a quantum physical object, such as an electron or an atom, penetrates regions in which it does not have sufficient energy to be and then come out on the other side.

This tunneling phenomenon has no analogue in classical physics[8]. In effect, this means that one can actually make electrons escape an atom or some metal piece although it does not have the sufficient energy for it (in the classical sense, that is). One very useful application of this phenomenon is the *scanning tunneling microscope* which actually allows you to *see* individual atoms, see Fig. 2.4. This technology expoits the fact that the tunneling propability is very sensitive to the width end the height of the barrier it tunnels through.

2.5   Stationary solutions

As we have already seen, quantum physics has several strange, non-intuitive features. Yet another one comes into play if we ask ourselves the following question: Are there solutions of the Schrödinger equation for which the proability density, $|\Psi(x;t)|^2$, does not change in time?[9] The answer is yes – if we have a confining potential.

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[8]A silly thought: Suppose sheep where quantum physcal object. In that case, just building fences wouldn't do; in fact the farmer would have to dig a sharp depression in the ground in order to confine the herd.

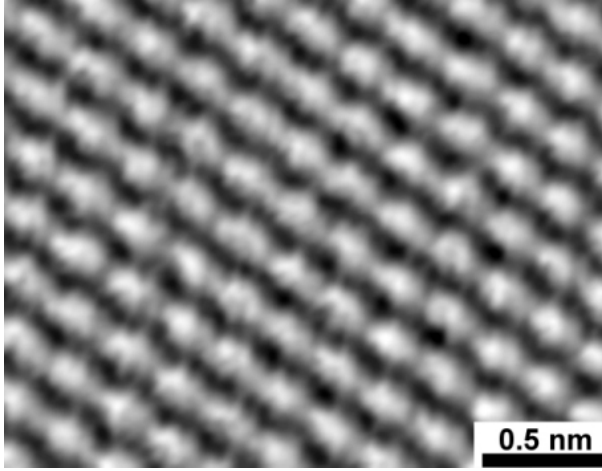[9]Such states would be remenicent of standig waves of a vibrating string.

Figure 2.4: This is a picture of a graphite surface obtained using a scanning tunneling microscope. The structure you can make out is made up by individual atoms; this is in fact a picture of atoms!

0.5 nm

2.5.1   Exercise: Enter the eigen value problem

Suppose that a wave function exposed to a time-independent Hamiltonian $\hat{H}$ is such that $|\Psi(x;t)|^2$ does not change in time.

a) Verify that this is acheived if the wave function is of this form:

$$\Psi(x,t) = e^{-i\,Et/\hbar}\psi(x) \tag{2.30}$$

for some real constant E.

b) Show that when we insert the wave function of Eq. 2.30 into the Schrödinger equation, Eq. 2.1, we arrive at the equation

$$\hat{H}\psi(x) = E\psi(x) \tag{2.31}$$

for the time-independent part $\psi(x)$.

c) Explain how the restriction that $|\Psi(x;t)|^2$ does not change in time in fact *leads to* Eq. 2.30.

Note: Be warned, this last exercise is hardly trivial. It may be done in the following way: First, note that since $|\Psi(x;t)|$ is time-independent, the wave function may be written on polar form as $\Psi(x;t) = \psi(x)e^{i\varphi(x;t)}$ where ψ and φ are both real and ψ is time-independent. Then, insert Ψ in this form into Eq. 2.1 with the Hamiltonian 2.2 and move purely x-dependent terms to one side of the equation in order to acheive a (partial) separation of variables. Finally, insist that φ remains real in time.

The next chapter is dedicated to Eq. 2.31. We recognize it as an *eigenvalue* equation; the Hamiltonian $\hat{H}$ is the operator corresponding to energy. And, the eigen value E on the right hand side is, in fact, energy.

The following is a fundamental postulate of quantum physics: A precise measurement of the energy of a quantum system will necessarily produce an eigenvalue of the energy operator $\hat{H}$ as a result. Later we will see that this imposes severe limitations as to which energies a quantum system can have when the system is confined.

The fact that we can only measure eigen values extends to *all* oservables in quantum physics, not just energy. The possible outcomes of measuring physical quantity A will necessarily be an eigen value a of the operator $\hat{A}$,

$$\hat{A}f_a(x) = af_a(x) \quad . \tag{2.32}$$

And after the measurement, the wave function is modified; it is now the eigen function corresponding to the eigen value that was measured; $\Psi(x) = f_a(x)$. This is the infamous *collapse of the wave function*, which we briefly discussed in Section 1.4.

So why do we insist on such an odd idea? The answer is simple: Because nature actually turns out to behave this way. Every time we have asked her about whether she really behaves like this, or in less poetic terms: whenever we have performed an experiment addressing this question, she has answered *yes*. In Fig. 2.4, for instance, we see this collapse manifested in the fact that electrons, which initially are descibed as waves extending in space, are detected as a tiny bright spot on a plate. Again, this quantum phenomenon has no analogue in classical physics.

Well, actually, let's try. Maybe we could think of a quantum system as an odd guitar – an imaginary *quantum guitar*. When you pick a string on an actual guitar, you set it vibrating. This vibration can be thought of as a buquet of standing waves – or *stationary solutions*. Each wave has a wavelength following the formula $\lambda_n = n \cdot \ell/2$ where n is an integer and ℓ is the length of the string. The higher the n, the more nodes has the standing wave and the shorter is its wavelength λ_n. Following to the relation $f\lambda = v$, where v is the velocity of the wave[10], there is a corresponding set of frequencies $f_n = 2v/(n\ell)$. So, when you picked the string, you didn't just produce a sound with the fundamental tone, the ground frequency $f_1 = 2v/\ell$, you also produced a set of *harmonics* of higher

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[10]This velocity, in turn, depends on length, thickness and tension of the string.

frequency. The admixture of these waves, each one with its own amplitude, is what gives the guitar its characteristic sound, its *timbre*.

Now, for a *quantum guitar* the oddity enters when we wish to *measure* the frequency of the sound. The vibrating string on a quantum guitar, like an ordinary guitar, would initially have a distribution between various possible frequencies – or energies, see Eq. 1.3. However, a quantum measurement would produce one, and only one, of the fequencies f_n. And after measuring it, the string will vibrate as a single standing wave – with frequency f_n. Gone is the boquet of harmonics.

And there is more. Both an actual guitar and the quantum guitar will have an amplitude associated with each possible frequency of stading waves or stationary solutions. For the quantum guitar, the probability of a frequency measurment is given by this amplitude. However, and we will see that this is a very important *however*, the amplitudes of the quantum guitar are *complex*, not real and non-negative as would be the case for a classical amplitude.

Admittedly, this analogy is somewhat far fetched. But hopefully, some of the parallels between a quantum system and this odd, imaginary guitar becomes more clear in the next chapter.

Chapter 3

The Time-Independent Schrödinger Equation

At the end of the last chapter, we learned that in order to find the possible stationary states of a bound quantum system, and, thus, also the possible outcomes of an energy measurement, we must solve the equation

$$\hat{H}\psi = E\psi \quad . \tag{3.1}$$

This equation, which is the eigen value equation for the energy operator $\hat{H}$, is known as the *time-independent Schrödinger equation.* It is hard to guess how much time and effort researchers have been spent in obtaining solutions to this equation for various physical and chemical systems over the years. But its a lot, really a lot.

With one particle in one dimension the equation reads

$$\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x) \right] \psi(x) = E\psi(x) \quad . \tag{3.2}$$

3.1 Quantization

Suppose the potential V is such that it is negative in some region and that it vanishes asymptotically, $V(x) \to 0$ when $|x| \to \infty$. In that case, a particle with positive energy, $E > 0$, is able to escape, while a particle with negative energy, $E < 0$, may not – it is confined by the potential. We say that it is *bound*.

3.1.1   Exercise: Bound states of a rectangular well

a) For the purely rectangular well, Eq. 2.25 with $V_0 < 0$, we may find the
negative eigen energies by (almost) purely analytical means. This may be
done following this recipe:

   1. Choose adequate numerical values for how deep, $-V_0$, and wide, w, the
      well should be. (You will not need these values right away, however;
      treat them algebraically for now.)
   2. Divide the domain into three regions: Region 1: $x < -w/2$, region 2:
      $|x| \leq w/2$ and region 3: $x > w/2$.
   3. Write up the general solutions of the time-independent Schrödinger
      equation 3.2 in each of the three regions separately. Rembember that
      the energy E is supposed to be negative; we are interested in *bound
      states*. In this context it is convenient to introduce $\kappa \equiv \sqrt{-2E}$ in regions
      1 and 3 and $k \equiv \sqrt{2(E - V_0)}$ in region 2. (Both κ and k are real; do
      apply our usual units where $\hbar = m = 1$). We suggest that you write your
      expressions for the solution in terms of real, not complex, functions.
   4. You should now have a function contaning 6 indetermined parameters.
      Since the wave function must be finite and normalizable, the function
      must vanish as $|x| \to \infty$. In order to acheive this, two of these parameters
      must be set to zero right away. Moreover, since $V(x)$ is symmetric, the
      wave function has to be either even, $\psi(-x) = \psi(x)$, or odd, $\psi(-x) =
      -\psi(x)$. We will exploit this; let's choose an even solution for now. This
      will reduce your number of parameters to two.
   5. Impose the restrctions that both ψ and its derivative, $\psi'(x)$, is to be
      continous at $x = w/2$; with an even or an odd wave function, these
      restrictions are also fulfilled at $x = -w/2$. This will provide you with a
      homogenious set of two linear equations in two unknowns. Let's write
      this system as a matrix equation. Now, why must we insist that the
      determinant of the coefficient matrix is zero? And how does this impose
      restrictions on the energy E?
   6. Make a plot of the determinant from point 5) as a function of E and
      estimate which eigen energies E_n are admissible.
   7. Repeat from point 4) with an anti-symmetric wave function.

b) Use your implementation from last chapter to construct a numerical Hamil-
tonian for the system. Use either the potential of Eq. 2.25 or Eq. 2.26 with
rather sharp edges (a high s value). Use some numerical implementation to
find the eigen energies and eigen vectors of this Hamiltonian. How does the
negative eigen energies compare with the ones you estimated in a)?

c) Plot the wave functions, that is, the eigen vectors you found in b)[1]. Is there a pattern as you increas the energy? Do you see any parallels with the quantum guitar here?

What we just saw will happen to *any* quantum system which is bound: Its energy can only assume a set of discrete values. The energy is *quantized*. Note, again, that this quantum trait is not one we experience in our everyday lives. And, again, it has no classical analogue.

For the case of the confined electron in a hydrogen atom, the allowed energies follow a particularly simple pattern:

$$E_n = -\frac{B}{n^2} \quad \text{where the constant} \quad B = 2.179 \times 10^{-18} \text{ J} \quad , \quad (3.3)$$

and n, the so-called *principal quantum number*, *must* be a positive integer. This is the famous *Bohr formula*. It is predicted by the time-independent Schrödinger equation (in three dimensions) with the Coulomb potential:

$$V(r) = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r} \quad . \quad (3.4)$$

We will not derive it here, but you will find its derivation in virtually any other textbook on quantum physics.

Its validity was well known from experiment at the time Schrödinger published his famous equation. It bears Niels Bohr's name becaus he had earlier arrived at this expression based on a model for the hydrogen atom which is long since abandond. He was right about two things, though:

1. The energy of a bound atom is indeed quantized

2. The atomic system may "jump" from a state of lower energy to one of higher energy by *absorbing* a photon with energy corresponding to the energy difference, see Eq. 1.3. Correspondingly, it may "jump" to a lower laying state by *emitting* the excess energy in the form of a photon.

Now, what about situations where the systems isn't bound? Well, the energy is still supposed to be an eigen value of the Hamiltonian, but this time it may assume

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[1]In order to make sure that everything is right, you could compare your analytical solutions from a) with your numerical ones; for a more or less rectangular potential, they should not differ by more than an overall normalization factor and, possibly, a sign.

any value (as long as it corresponds being unbound, of course). In general, the set of eigen values, the *spectrum*, of a Hamiltonian will consist of both discrete values (bound states) and continous values (unbound states). Of course, it could be exclusively discrete, as would be the case when $V(x) \to \infty$ as $|x| \to \infty$, or the spectrum may be a pure continuum, as is the case when there is no potential at all.

3.1.2   Exercise: The Bohr formula

In Exercise 1.23 we cheated and played around with a three-dimensional hydrogen wave function as if it where one-dimensional. If we, once again, allow ourselves to take the same shortcut, we should be able to arrive at the same bound state energies as in Eq. 3.3. To this end, construct a numerical approximation of the Hamiltonian 1.26. Let r extend from 0 to some upper limit L. It is absolutely crucial that your implementation ensures that

$$\psi(0) = 0 \quad . \tag{3.5}$$

This is hard to achieve with your FFT version of the kinetic energy. Instead you could use a finite difference formula, Eqs. 2.10. Since $V(r)$ diverges as $r \to 0$, $r = 0$ should be omitted in your grid; you can still impose Eq. 3.5 in your finite difference representation of the kinetic energy.

This time, allow yourself to use atomic units exclusively, in which case the constant B in Eq. 3.3 is $1/2$.

To what extent does the eigen energies you obtain by numerical means conicide with the Bohr formula?

Do you see any relation between the quantum number n and the shape of the wave function? Does this compare to our silly quantum guitar?

For which n does you numerical eigen energies start deviating from the exact ones?

Is this onset manifested in the wave function somehow[2]?

How can we improve on the coincidence between the numerical and the exact eigen energies?

It's worth repeating that the measurement of *any* physical observable, not just the energy, will produce an eigenvalue of the corresponding operator as a result. Correspondingly, energy is not the only quantity which may be quantized. Take

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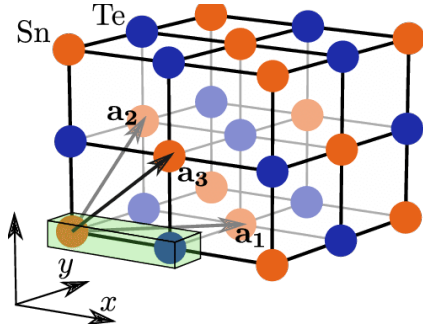[2]Since the question is posed in this way: Of course it is.

Figure 3.1: The figure illustrates a salt crystal – and its periodicity. We see that a translation along an integer multiple of any of the three vectors indicated will take you to a corresponding place in the crystal. In this particular case, the material is rocksalt, SnTe.

for instance the angluar momentum operator in three dimensions,

$$\hat{\mathbf{L}} = \mathbf{r} \times \hat{\mathbf{p}} = -i\hbar \mathbf{r} \times \nabla \quad ; \tag{3.6}$$

if we express it, or more conveniently, its square, in spherical coordinates, we will find that its eigen functions[3] only make sense physically if the eigen value of $\hat{\mathbf{L}}^2$ is $\ell(\ell+1)\hbar^2$, where $\ell = 0, 1, 2, \dots$.

3.2 Periodic potentials and band theory

The case of periodic potentials,

$$V(\mathbf{r}) = V(\mathbf{r} + \mathbf{p}_i) \quad , \tag{3.7}$$

merits particular attention. Here $\mathbf{p}_i$ is a one out of, possibly, several in which $V(\mathbf{r})$ is periodic. This could correspond to the potential an electron within a lattice sould experience, see Fig. 3.2 for an example. Here the nodes of the lattice would the part of the individual atoms, ions or molecules which are fixed in position; the electron we would consider is not bound to any particular of these. Obviously, this is a rather common situation; solid matter is, in fact, buit up of such regular patterns. Thus, very general lessons about solid matter may be learned from the case of periodic potentials.

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[3]These eigen function are called *spherical harmonics*, they appear frequently in quantum physics.

Figure 3.2: This is a plot of the periodic potential of Eq. 3.8 for $V_0 = -1/4$, $\sigma = 1$, $p = 10$. Although we have only plotted four periods here, it extends indefinitely.
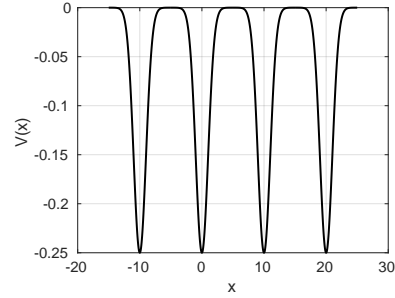
3.2.1   Exercise: Eigen energies for periodic potentials – bands

In this case we will investigate the eigen values of a periodic Gaussian potential in one dimension,

$$V(x) = -V_0 e^{-x^2/(2\sigma^2)} \quad \text{for} \quad x \in [-p/2, p/2] \quad \text{and} \quad V(x+p) = V(x) \quad . \tag{3.8}$$

It is illustrated in Fig. 3.2.1 for the case of $V_0 = -1/4$, $\sigma = 1$, $p = 10$.

a) With a periodic potential, the physics must reflect the periodicity. Specifically, we must insist that the solutions of the time-independent Schrödinger equation fulfill $|\psi_n(x)|^2 = |\psi_n(x+p)|^2$. Explain why this leads to this requirement:

$$\psi(x) = e^{i\chi(x)} u(x) \quad , \tag{3.9}$$

where $u(x)$ is periodic with period p and $\chi(x)$ is a real function.

b) Suppose the operator $\hat{T}(d)$ imposes a translation, $\hat{T}(d)\psi_n(x) = \psi_n(x+d)$. Then we will also have that $\hat{T}(d_2)\hat{T}(d_1)\psi_n(x) = \psi_n(x+d_1+d_2)$. Explain how this leads to the requirement that $\chi(x)$ in Eq. 3.9 must be a linear function, $\chi(x) = \kappa x + b$.

   The constant b only contributes with a global phase which we may safely ingore in the following.

c) With Eq. 3.9 and $\chi(x) = \kappa x$, explain how the time-indepenent Schrödinger equation may be re-written in terms of $u(x; \kappa)$ as

$$\left[-\frac{\hbar^2}{2m} \left(\frac{d}{dx} + i\kappa \right)^2 + V(x) \right] u(x; \kappa) = \varepsilon(\kappa) u(x; \kappa) \quad . \tag{3.10}$$
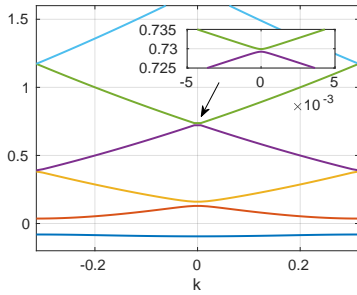
   Here u depends parametrically on κ.

Figure 3.3: The figure displays the first six eigenvalues of Eq. 3.10 for the periodic potential displayed in Fig. 3.2.1 as functions of κ.

d) The eigen energy now becomes a function of the wave number κ. Explain why it is periodic in κ. What is the period?

e) For a few of the lowest eigenvalues $\varepsilon_n(\kappa)$, find them numerically and plot them for one period of κ. The requirement that the eigen states $u_n(x; \kappa)$ is periodic in x should have a very specific implication on how we should implement the modified kinetic energy operator.
   Hint: $(d/dx + i\kappa)^2 u(x) = \mathscr{F}^{-1}\left\{(ik + i\kappa)^2 \mathscr{F}\{u\}(k)\right\}(x)$

f) Each of the eigen energies $\varepsilon_n(\kappa)$ occupy a specific interval of the energy axis if you include all possible values of κ. For each of the energies you plotted in e), determine the corresponding energy interval.

In Fig. 3.2.1 we have displayed the first six einvalues of Eq. 3.10 – as functions of κ. We see that each eigen value defines a range on the energy axis. In this context, such a range is called a *band*. In a one-dimensional system like this one, such bands do not overlap – although $\varepsilon_4(\kappa)$ and $\varepsilon_5(\kappa)$ comes close for $\kappa = 0$. Indenyably, the three-dimensional case is more relevant; with more dimentions, some bands will cross, and others won't; we will have a richer band structure. This divisions in bands and gaps does, to a large extent, determine the properties of the material at hand. It depends directly on how these bands are "filled up" with particles. If only bands of bound states, such as the lower one in Fig. 3.2.1, are populated by particles, we are dealing with an electrical insulator; there are no free electrons to carry current. However, if there are electrons in bands corresponding to unbound particles, the material is a couductor. Of course, this account is an oversimplification; we are using phenomenology for one single particle to try to "explain" phenomena which certainly belong in a many-particle context. The emergence of bands does, however, carry over from such an example involving a single particle in one dimension to more realistic ones.

We have here scracthed parts of the surface of the field of *solid states physics*.

Hopefully, you will enjoy submerging yourself fully in the sea that is solid state physics in the future.

3.3   The Spectral Theorem

There is an important result from linear algebra which is used *very* frequently in quantum physics. Actually, we already used it – in Eq. 2.18. As mentioned, the eigen values of the operator of a physical quantity generally form a combined set of both discrete and continuous values. For notational simplicity we will here, however, assume that the set is only discrete/countable, in which case we may write the eigen value equation for the energy, that is, the time-independent Schrödinger equation, as

$$\hat{H}\psi_n = E_n\psi_n \quad , \tag{3.11}$$

where the index n is an integer. Since the Hamiltonian is Hermitian, $\hat{H} = \hat{H}^\dagger$, its eigen vectors/functions form a orthogonal basis for the space in which the wave function lives. If we in addition require the eigen vectors/functions to be normalized under the inner product 1.18, we have *orthonormality*,

$$\langle \psi_m, \psi_n \rangle = \delta_{m,n} \quad , \tag{3.12}$$

where the Kronecker delta-function $\delta_{m,n}$ is one when $m = n$ and zero otherwise. The fact that the eigen vectors form a basis means that *any* (admissible) wave function may be written as a liner combination of these,

$$\Psi = \sum_n a_n\psi_n \quad . \tag{3.13}$$

Although this chapter is dedicated to the time-independent Schrödinger equation, we will still address time-dependence a bit. We have seen that eigenstates of a time-independent Hamiltonian are stationary in the sense that the wave function does not change in time – except for a trivial phase factor. However, suppose our initial state is not such an eigen state; in that case, this trivial phase factor cannot be disregarded anymore.

3.3.1   Exercise: Trivial time evolution

Suppose that the normalized set of eigen functions of the Hamiltonian, $\psi_1, \psi_2, \ldots$ is known and that your initial state is $\Psi(t=0) = \sum_n a_n\psi_n$.

a) Why must we insist that $\sum_n |a_n|^2 = 1$?

b) Explain why $a_n = \langle \psi_n, \Psi(t=0) \rangle$.

c) Explain why

$$\Psi(t) = \sum_n a_n e^{-i/\hbar E_n t} \psi_n \quad . \tag{3.14}$$

3.3.2 Exercise: Glauber states

The potential

$$V(x) = \frac{1}{2} k x^2 \quad , \tag{3.15}$$

where k is some real constant, is called the *harmonic oscillator* potential. It emerges in classical physics when you want to describe a mass attached to a spring. In that case, the solution of Newton's second law is oscillating at angular frequency

$$\omega = \sqrt{k/m} \quad . \tag{3.16}$$

In quantum physics, this potential is also given much attention – for several reasons. Many of these, in turn, are related to the fact that the eigen energies of the Hamiltonian with this potential are such that the difference between neighbouring energies are always the same[4]:

$$E_n = (n+1/2)\hbar\omega \quad , \tag{3.17}$$

where n is a non-negative integer. Note also that the energy is never zero.

In the following we will set $m = 1$, as usual, and $k = 1$.

a) Implement the Hamiltonian with the potential in Eq. 3.15 numerically and find its eigen values and eigen states. Choose a domiain size L and a number of grid points n large enough to reproduce the exact energies, Eq. 3.17, for the first 100 energies or so.

b) Construct some linear combination of the eigen states,

$$\Psi(t=0) = \sum_{n=0}^{n_{\max}} a_n \psi_n \quad , \tag{3.18}$$

that is, just pick some values a_n for a bunch of n values. Then, simulate the corresponding evolution of the absolute squared of your wave function as dictated by Eq. 3.14.

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[4]We say that they are *equidistant*.

c) Linear combinations of this particular form are called *coherent states* or *Glauber states*[5]:

$$\Psi_{\text{Glauber}} = e^{-|\alpha|^2/2} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} \psi_n \quad . \tag{3.19}$$

Here, α is any complex number.

Choose a real and positive α and repeat exercise b) with this particular linear combination.

Two issues are crucial for the numerical version to work:

1) Of course, in a finite space, such as our numerical representation, we cannot sum up to infinity. Moreover, we may get into trouble numerically if we use *all* our numerical eigen states. We suggest that you use the comparison between your numerical eigen values with the exact ones to determine a reasonable truncation in your numerical version of Eq. 3.19; by that we mean that we set all a_n to zero for some maximum value of n. Since the coefficients fall off quite rapidly due to the factorial in the denominator, this should be quite admissible.

2) As long at the eigen states are constructed by a numerical implementation of diagonalization, we do not control the over all sign of the eigen vectors. However, in order for us to construct the conherent state, we need to control the phase convention of the ψ_n-s. This may be acheived by insisting that the largest value of $\psi_n(x)$ for positive x is always positive. After your numerical diagonalization, you can run through your eigen states and flip the sign of them if necessary.

Notice anything special about this particular linear combination? Try playing around with other values of α, also complex and purely imaginary ones. Use a finer grid and/or a larger domain if you have to.

It could also be interesting to simulate the solution for a classical particle along with the quantum mechanical one, as in Exercise 2.4.2. In doing so, you would set the initial conditions to be $x(t = 0) = \sqrt{2}\,\text{Re}(\alpha)$ and $v(t = 0) = \sqrt{2}\,\text{Im}(\alpha)/m$.

The above notation in terms of countable set, Eq 3.13, is always adequate when we represent the wave function in a discretized manner, Eq. 2.8. In this case the wave function is just an array in $\mathbb{C}^n$ and all operators are square, Hermitian

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[5]Roy J. Glauber was a theoretical physicist from the USA. He made significant contributions to our understanding our light. For this he was awarded the 2005 Nobel prize in physics. His choerent states, Eq. 3.19, certainly hade something to do with that.
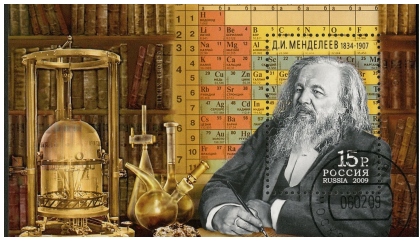
Figure 3.4: This Russion stamp portrays Dimitri Mendeleev, who in 1869 explained how all elements fit very nicely into his famous *periodic table*. It took some time until scientist could figure out how this periodicity came about. In order to do so, the time-independent Schrödinger equation, which was published about 55 years later, was necessary.

matrices. Such a discription does not, of course, support any actual continuum – we have to settle for a so-called *pseudo continuum*. The proper description in terms of a infinte dimensional space within a basis which is not countable is not compatible with purely numerical representations. We will not enter into these complications here, save to say that often we may "get away" with considering the real physics as the limiting case where n and $b - a$ in Eq. 2.8 approach infinity. As mentioned, convergence in these numerical parameters is absolutely necesseary for calculations to make sense.

3.4 Finding the Ground State

Although a quantum system in principle could be found to have any of its admissible energys, or, as we say, be in any admissible *state*, they tend to prefer the state with the lowest energy – the *ground state*. In a somewhat superficial manner we may say that this is due to nature's desire to minimize energy. A slightly less superficial account: Eigen states are indeed stationary and a system which does not experience any distrubance, will remain in that state indefinitely. However, avoiding disturbances, such as the intearction with other atoms or at least *some* electromagntic radiation, is virtually impossible. Due to such distrubances, the eigen states are not really eigen states in the absolute sense; such small interactions cause the system to relax into a state with lower energy.

Calculating ground states is crucial for understanding the properties of the elements and how they form molecules. It wasn't until people started solving the time-independent Schrödinger equation and calculating ground states that the periodic table started to make sense; there was no doubt that Dimitri Mendeleev's arrangement of the elements was a meaningful one, but it took some time to learn *why*, see Fig. 3.4.

The spectral theorem provides two very powerful methods for estimating the wave function and the energy of the ground state:

3.4.1   Exercise: The variational principle and imaginary time

a) Suppose we start out with some arbitrary admissible wave function. Why can we be absolutely sure that the expectation value of its energy cannot be lower than the ground state energy?

How can this be exploited in order to estimate the ground state energy?

b) Again, suppose that we start out with some arbitrary wave function. Now we replace the time t in the time-dependent Schrödinger equation by the imaginary time $-it$. This corresponds to doing the same, $\Delta t \to -i\Delta t$, in Eq. 2.19. This will, in turn, lead to a "time evolution" in which the norm of the wave function is *not* conserved. To compensate for that, we will also renormalize our wave function at each time step when we resolve the "time evolution" in small steps of length Δt. In other words: At each time step we multiply our wave function with a factor so that its norm becomes one.

Why will this, in exponential time, turn virtually *any* initial state into the ground state?

How can the change in norm at each time step be used in order to calculate the energy?

Note that when we make the replacement $t \to -it$, this effectively turns the (time-dependent) Schrödinger equation into a sort-of *diffusion equation*.

Both methods alluded to here are frequently used within quantum physics and quantum chemistry – maybe the latter more than the former. The principle that the ground state is a lower bound to the expectation value of *any* admissible function is called the *variational principle*. We can exploit it by constructing some initial guess, a test function, with tunable parameters. The closer this initial guess is to including the actual ground state wave function, the better. And the more parameters to "tweek on", the more flexibity you have to achive a good estimate of the ground state energy; the lower energy you get, the closer you get to the ground state energy. On the other hand, the more parametres you have, the more cumbersome are the calcuations. Therefore it is crucial to chose your test functions as cleverly as possilble.

One of the pioneers when it comes to variational calculations is the Norwegian Egil Hylleraas, Fig. 3.4.1. In fact, he was head hunted, so to speak, by Max Born to show that the time-independent Schrödinger indeed produced the right ground state energy for the helium atom, not just the hydrogen atom. Of course, at a time when quantum phyics was not yet established as *the* proper framwork for
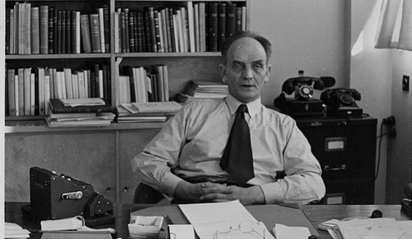
Figure 3.5: The picture shows the physics professor Egil Hylleraas in his office at the University of Oslo in 1954.

atomic and molecular physics, this was curcial. Hylleraas succeeded in doing so. The fact that he did so before researchers had access to computers does not make his acheivement any less impressive.

Let's do som variational calculations ourselves:

3.4.2 Exercise: One variable minimization

Let your potential be provided by Eq. 2.26 with $V_0 = -3$, $s = 5$ and $w = 8$. Also, take your test wave function to be a normalized Gaussian centered at the origin:

$$\psi_{\text{Test}} = \frac{1}{\sqrt[4]{2\pi\sigma^2}} \exp\left[-\frac{x^2}{4\sigma^2}\right] \quad . \tag{3.20}$$

Now, we calculate the energy expectation value,

$$E(\sigma) = \langle \psi_{\text{Test}}, \hat{H}\psi_{\text{Test}} \rangle \quad , \tag{3.21}$$

for various vales of σ. Do this numerically using the same implementation of the Hamiltonian as before and plot the expectation value of the energy as a function of σ. Try and read off its minimal value – and the corresponding σ.

In this case, actually obtaining the "correct" ground state energy is easy by means of direct diagonalization. Do this and compare the ground state energy to the upper bound you just found. Also, compare the actual (numerical) ground state with your test function, Eq. 3.20, with the σ that minimizes $E(\sigma)$.

3.4.3 Exersise: Imaginary time propagation

For the same potential as in Exercise 3.4.2, implement the method in Exercise 3.4.1 a), in which an arbitrary initial state is propagated in imaginary time and the wave function is normalized at each time step:

$$\psi_{n+1} = e^{-\hat{H}\Delta t}\psi_n, \quad \psi_{n+1} \to \psi_{n+1}/\sqrt{\langle \psi_{n+1}, \psi_{n+1} \rangle} \quad . \tag{3.22}$$

Choose a reasonably small "time step" Δt and plot the renormalized, updated wave function at each step. Also, write the estimated energy to screen for each iteration.

How does this implementation compare to the variational principle implementation above? Were you able to reproduce the very same ground state energy as you found by direct diagonalization? Did that happen with the variational calculation in Exercise 3.4.2?

3.4.4   Exercise: Two-variable minimization, Steepest Decent

This time, let your intial "guess" be a Gaussian with *two* parameters, μ and σ:

$$\psi_{\text{Gauss}} = \frac{1}{\sqrt[4]{2\pi\sigma^2}} \exp\left[-\frac{(x-\mu)^2}{4\sigma^2}\right] \quad . \tag{3.23}$$

We will now estimate the ground state energy, or, strictly speaking, determine an upper bound for the ground state energy, for this potential:

$$V(x) = V_{\text{s}}(z-1) + x^2/50 \quad , \tag{3.24}$$

where you fix the parameters $V_0 = -5$, $w = 6$ and $s = 5$ for V_{s} in Eq. 2.26.

As two parameters, μ and σ, are involved this time, minimization is not as straight forward as in exercise 3.4.2. In order to obtain values for both μ and σ which minimizes the expectation value of the energy, Eq. 3.21, we will apply the method of *gradient descent* or *steepest descent*[6]:

In order to minimize a multi-variable differential function[7], $F(\mathbf{x})$, you start out by choosing a starting point $\mathbf{x}_0$. Next, you move one step in the direction in which the function descends the most steeply[8]:

$$\mathbf{x}_{n+1} = \mathbf{x}_n - \gamma \nabla F(\mathbf{x}_n) \quad . \tag{3.25}$$

The factor γ, along with the length of the gradient at the point, determines the length of the step. For optimal performance, γ may be adjusted as you go along. However, with a sufficiently small γ value, this is not crucial in this case. The iterations of Eq. 3.25 are repeated as long as $F(\mathbf{x}_{n+1}) < F(\mathbf{x}_n)$. Finally, you should have arrived at some local minimum.

---

[6]This method is widely used within *machine learning*.

[7]In our case, this would be $E(\mu, \sigma)$.

[8]Put somewhat more precisely, you move in the direction in which the *tangent plane* descends the most.

When you have managed to minimize the expectation value of the energy – within reasonable precision, calculate the ground state energy by means of diagonalization and compare.

Finally, run this example through your imaginary time procedure, the one you implemented in Exercise 3.4.3, and compare.

Of course, when running a full diagonalization, that is, solving the time-independent Schrödinger equation, is feasible, as in the above exercises, it does not make much sense to apply the variational principle. However, as we depart from the simple scenario of one particle in one dimension, the hope of obtaining a full solution usually turns out to be just a pipe dream. For more realstic cases, the variational principle is actually a very useful one.

3.4.5 Exercise: Variational calculation in two dimensions

It is time we take a step outside our very small, one-dimensional world. We will minimize the energy of a potential which is an almost recangular well in two dimensions:

$$V(x,y) = \frac{V_0^2}{\left(e^{s(|x|-w_x/2)}+1\right)\left(e^{s(|y|-w_y/2)}+1\right)} \quad . \tag{3.26}$$

It is the product of two one-dimensional potential of type $V_s(x)$, see Eq. 2.26. Here, we have set the debth V_0 and the smoothness s to be the same for both the x and the y-part of the potential while the respective widths, w_x and w_y, differ. Specifically, take $V_0 = 1$, $s = ???$, $w_x = 2$ and $w_y = 3$. The corresponding Hamilton reads

$$H = -\frac{1}{2}\frac{\partial^2}{\partial x^2} - \frac{1}{2}\frac{\partial^2}{\partial y^2} + V(x,y) = T_x + T_y + V(x,y) \tag{3.27}$$

in our usual units.

We will use test-functions wich are products of purely x and y-dependent functions,

$$\psi_{\text{Test}}(x,y) = \psi_x(x)\,\psi_y(y) \quad . \tag{3.28}$$

a) Explain why the expecation value of the energy may now be estimated as

$$\langle E \rangle = \langle \psi_x, T\,\psi_x \rangle + \langle \psi_y, T\,\psi_y \rangle + \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} V(x,y)|\psi_x(x)\psi_y(y)|^2\,dxdy \quad . \tag{3.29}$$

b) Use your steepest decent implementation from exercise exercise 3.4.4, with suitable adjustments, to minimize the energy expectation value with Gaussian test functions, $\psi_x(x) \sim \exp(-x^2/(4\sigma_x^2))$ and $\psi_y(y) \sim \exp(-y^2/(4\sigma_y^2))$ in Eq. 3.28. The proper normalizaton factors are provided in Eq. 3.23, in which we have set $\mu = 0$ for both the x and the y-part.

c) Repeat b) with cosine-functions,

$$\psi_x(x) = \begin{cases} \sqrt{\frac{\pi}{2a_x}}\cos(a_x x), & -\frac{\pi}{2a_x} \le x \le \frac{\pi}{2a_x} \\ 0, & \text{otherwise} \end{cases} \tag{3.30}$$

and correspondingly for ψ_y.

Which guess gives the best estimate?

Does this conclusion seem to depend on the debth V_0?

3.4.6   Exercise: Variational calculation with two particles

In this exercise, we will return to our restricted one dimensional world. We will, however, finally dare to challenge the curse of dimenstionality and make a small departure from the realm of just a single particle.

Suppose **two particles** are trapped in the same potential as in Exercise 3.4.4, that is, the potential of Eq. 3.24. In addition, assume that the particles interact via this potential:

$$W(x_1, x_2) = \frac{W_0}{\sqrt{(x_1 - x_2)^2 + 1}} \quad, \tag{3.31}$$

where x_1 is the position of the first particle and x_2 is the position of the second. We take the interaction strength W_0 to be one in this case. As in exercise 3.4.5, the wave function has two variables. This potential is a repulsive one; the energy increases as the two particles approach eachother. In classcal physics, we would say that this leads to a repulsive *force* between the particles.

Take your two-particle test function to be a product state of two identical Gaussians – one for each of the particles[9],

$$\psi_{\text{TwoPart}} = \psi_{\text{test}}(x_1)\,\psi_{\text{test}}(x_2) \quad, \tag{3.32}$$

---

[9]Suppose that these particle are of the same kind – they could be two electrons, for instance. In this case, their wave function *must* reflect that they are identical – in the fundamental sense. Consequently, $|\Psi(x_1, x_2)|^2$ cannot depend on the ordering of x_1 and x_2. This, in turn, requires that $\Psi(x_1, x_2) = \pm\Psi(x_2, x_1)$. This principle, which extend to any number of identical particles, is called the *Pauli principle*. You are welcome to check that Eq. 3.32 actually fulfills it.

where $\psi_{\text{test}}(x)$, which depends parametrically on the mean position μ and width σ, is of the form of Eq. 3.23.

Again, use the method of gradient descent to determine the values of μ and σ which minimises the energy expectation value:

$$E(\mu,\sigma) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} [\Psi_{\text{TwoPart}}(x_1,x_2)]^* \hat{H} \Psi_{\text{TwoPart}}(x_1,x_2) \, dx_1 dx_2 \quad . \tag{3.33}$$

In this case, the Hamiltonian is a two-particle operator,

$$\hat{H} = \hat{h}_1 + \hat{h}_2 + W(x_1,x_2) \quad , \tag{3.34}$$

where $h_i = \hat{p}_i^2/2m + V(x_i)$ is the one-particle part for particle number i and the interaction W is given in Eq. 3.31. For our product state test function, Eq. 3.32, the one-particle parts of Eq. 3.33 can be reduced to one-variable integrals. The interaction part, however, remains a double integral.

Replace this exercise with the one we had in the project: Harmonic potential, translated gaussians.

Of course, the method of gradient decent can be applied to problems with more than two parameteres. And the more parameters you include in your expression for the approximate wave function, the lower is the upper bound you get to your true ground state energy – at least if the functional form you guess is a reasonable one. In Fig. 3.4.6 we have illustrated how the method, step by step, approaches the minimum energy for the particular case of Exercise 3.4.6. The minimum is found at $\mu = 1.74$, $\sigma = 1.05$.

### 3.4.7 Exercise: Self-consistent field

Here we revisit the problem of Exercise 3.4.6. We will again assume that the ground state can be written as product state with two identical wave functions[10], Eq. 3.32. But instead of fixing the the shape of the one-particle wave function as a Gaussian, we will here determine it in an iterative manner.

First, suppose that one particle "feels" the interaction from the other as a static charge distribution provided by the wave function of the second particle. This motivates an additional one-particle potential:

$$V_{\text{eff}}(x) = \int_{-\infty}^{\infty} |\psi_{\text{test}}(x_2)|^2 W(x,x_2) \, dx_2 \quad , \tag{3.35}$$

---

[10]It can't.

Figure 3.6: The surface plot illustrate the expectation value of the energy, $\langle E \rangle$ in Eq. 3.33, as a function of the two variables μ and σ. These variables are the mean position and width, respectively, of the Gaussian used in the two particle wave function assumption in Eq. 3.32. Here we have plotted how the gradient decent method approaches the minimum – step by step. We have done so for three different starting points.
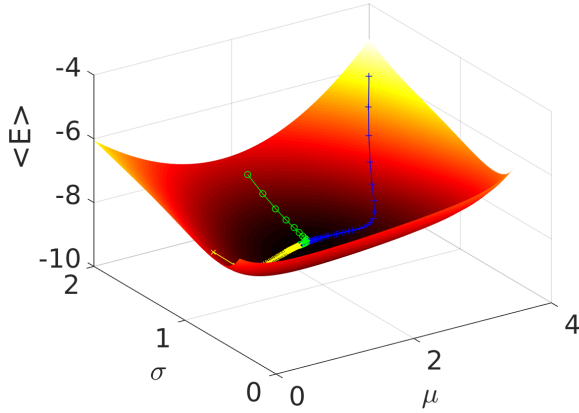
where the interaction W is given in Eq. 3.31. With this, we can set up our Hamiltonian with this addition, diagonalize it and replace our initial guess for ψ_{test} with the ground state of this effective one-particle system. In other words, we solve the effective one-particle Scrhödinger equation

$$[h + V_{\text{eff}}(x)]\,\psi(x) = \varepsilon\,\psi(x) \quad . \tag{3.36}$$

Note that this is not actually a linear problem since V_{eff} in fact depends on ψ_{test}. Of course, when we replace one ψ_{test} with another, we also alter the effective potential Eq. 3.35, which, in turn, alters ψ_{test} and so on. So how do make sense out of that? We iterate! We "guess" on an initial ψ_{test}, calculate the corresponding V_{eff}, solve Eq. 3.36 and choose the "grond state" as our new ψ_{res}, update V_{eff} and so on. We repeat this iteration procedure until the system is *self-consistent* – until ψ_{res} does not change anynomore. We can monitor the effective ground state, the lowest eiegenvalue in Eq. 3.36, in order to check convergence.

Finally, when we are pleased with our ψ_{test}, the energy expectation value of our two-particle test function may, as before, be calculated as

$$\langle E \rangle = \langle \psi_{\text{TwoPart}}, (\hat{h}_1 + \hat{h}_2 + W)\,\psi_{\text{TwoPart}} \rangle \quad . \tag{3.37}$$

For the sake of clarity: The one-particle parts of the Hamiltonian, $\hat{h}_1$ and $\hat{h}_2$, which, respectively, affect particle one and two exclusively, do not contain the effective potential in Eq. 3.35 – these are the actual one-particle Hamiltonians[11].

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[11]Having said this, we should also say that the expression in Eq. 3.37 *could* be written rather compactly using V_{eff}.

We repeat this until the effective potential is, in fact, consistent with the new ψ_{test} – until it's *self consistent*. This convergence can be monitored by comparing consecutive energy estimates, Eq. 3.37.

Implement this iteration procedure and use it to estimate the two-particle ground state energy. As your starting choice for the one-particle wave function ψ_{test} you may very well choose a (normalized) Gaussian centred around $x = 0$. In our usual grid represantation, the effective potential V_{eff} is represented as a diagonal matrix – just like the "ordinary" potential V. For each diagonal element of the V_{eff}-matrix, you must calculate an integral.

Is the energy estimate you found lower or higher than the estimate you found in Exercise 3.4.6? Does this alone enable you to say which estimate is the best[12]?

The approach of Exercise 3.4.7 a very simple example of a *Hartre-Fock* calculation.

Of course, the assumption, or *ansatz*, in Eq. 3.32 is somewhat naive; by construction we "force" the probability of finding both particles to be at the same spot to be high. Since they actually repel eachother, see Eq. 3.31, this is rather inacurate – at best. However, if the external confinement is strong, and the repulsion is week, the error intriduced by this assumtion is rather small. For weak confinement and strong repulsion, however, it's just wrong.

The wave functions shown in Fig. 3.7 illustrate the situation: The result from the method of Exercise 3.4.4 and Exercise 3.4.7 suggest that the two particles are likely to be found close to $x \approx 1.5$ – simultaniously. The density of the "exact" solution to the right shows, however, that, although there is a certain probability for the particles to be on top of eachther, they are most likely to be a bit separated.

By minimizing the energy by varying the mean position μ and the width σ of the Gaussians that makes up the plot to the left in Fig. 3.7, we arrive at an energy estimate, or rather, an upper bound of -8.807. The self consistent field approach, the middle plot, does slightly better: -8.851. The reason for this is that this approach does not confine the approximate ground state wave function to be Gaussians. This flexibility enables us to obtain a lower, and, thus, better estimate. Specifically, we see a rather sharp edge in the middle plot, corresponding to the near-rectangular shape of the confining potential. The actual ground state energy is -8.885. That's a relative error of less than half a percent for the self consistent field approach, which may seem odd if you compare the approximate wave function in Fig. 3.7 with the correct one.

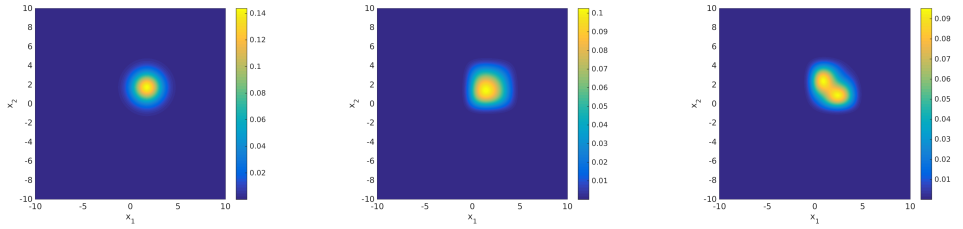[12]Provided that the numerics are good enough, that is.

Figure 3.7: The figure to the left shows the wave function obtained in Exercise 3.4.6. This approximate wave function is a product of two identical Gaussians – one for each particle. The middle figure shows the approximate wave function found in Exercise 3.4.7. Also in this case, the two particle wave function is assumed to be the product of two identical one particle wave functions. This assumption implies that the two particles are most likely to be found more or less on top of eachother. This does not seem reasonable since they actually repel each other, see Eq. 3.31. The proper solution, which is shown to the right, accounts for this; we see this from the fact that there are two peaks off the "diagonal" line $x_1 = x_2$.

Actually, this is rather typical – the ground state energy estimate is surprisingly good altough the test wave function is a bit off. Is there any particular reason why it should be so? Should the energy expectation value be less sensitive to adjustments of the wave function for the ground state than any other state? What does the variational principle say on the matter?

Appendix A

The Postulates of Quantum Physics

In the previous chapters we have played around with the various oddities of quantum physics numerically and addressed the necessary foundations rather superficially as we went along. It could, however, be useful to have the fundamental postulates listed. While these may be formulated in a rather general manner, we will here formulate them in terms of position coordinates. Here goes:

The state of a quantum system consisting of n particles is completely determined by its wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_n; t)$ where $\mathbf{r}_i$ is particle number i and t is time. The evolution of the wave function is determined by the Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t}\Psi = \hat{H}\Psi \quad , \tag{A.1}$$

where $\hat{H}$ is the Hamiltonian of the system.

The wave function must be normalized,

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}|\Psi|^2\,\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2\cdots\mathrm{d}\mathbf{r}_n \quad = 1 \quad , \tag{A.2}$$

continuous and continuosly differentiable[1] on the entire domain.

For any phyiscal quantity, there is a linear, Hermitian operator. For position $\mathbf{r}$, this operator is simply multiplication with the poistion vector, $\hat{\mathbf{r}} = \mathbf{r}$, while the momentum operator is $\hat{\mathbf{p}} = -i\hbar\nabla$. If the classical physical quantity depends on position and momentum in some way, say $F = F(\mathbf{r}, \mathbf{p})$, its operator depends on the position and momentum operators in the same way[2], $\hat{F} = F(\hat{\mathbf{r}}, \hat{\mathbf{p}})$.

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[1]This last requirement applies only where the potential is finite.

[2]There are also quantum physical quantities which cannot be constructed from any classical expression. The *spin* is an example of such.

If we are to measure a physical quantity, say F, the result will necessarily be one of the eigen values of the corresponding operator $\hat{F}$. The probability of a particular outcome, say f_n, is given by the projection of the wave function onto the eigen function corresponding to f_n;

$$P(f_k) = \left| \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \varphi_k^* \Psi \, d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_n \right|^2 \quad , \tag{A.3}$$

where

$$\hat{F} \varphi_k(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_n) = f_k \varphi_k(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_n) \quad . \tag{A.4}$$

Direclty after measurement, the wave function will be the eigen function corresponding to the outcome of the measurement[3]; $\Psi = \varphi_i$.

The outcome of many repeated measurments of the quantity F on several identically prepared quantum systems, will produce a distribution with expectation value

$$\langle F \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \Psi^* \hat{F} \Psi \, d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_n \tag{A.5}$$

and width

$$\sigma_F = \sqrt{\langle F^2 \rangle - \langle F \rangle^2} \quad . \tag{A.6}$$

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[3]That is to say, at this point it does *not* follow the Schrödinger equation; it starts over with the eigen state as the new initial condition for Eq. A.1.

Appendix B

Suggestions for Further Reading

This course has been somewhat superficial when it comes to the more formal aspects of quantum physics. And the have, without exception, been limited to one dimensional examples and, with few exceptions, only one particle. If you want a more general introduction, there is a vast selction of books you could read. For instance, if you read Norwegian, I can highly recommend "Kvantemekanikk" by P. C. Hemmer (Tapir). The book "Introduction to Quantum Mechanics" by D. J. Griffiths (Prentice Hall) is quite readable as well, but is slightly wanting when it comes to some of the formal aspects. And virtually all tekstbooks on the subject is wanting when it comes to numerical implementations.

The book "Computation in Modern Physics" by W. R. Gibbs (World Scientific), on the other hand, certainly takes numerics seriously. It does not, however, have a very general approach to quantum physics. "Coputational Physics – Lecture Notes Fall 2015" by M. H. Jensen, on the other hand, provides a rather complete introduction to computations in physics, including quantum physics. Neither of these books are limited to quantum physics, however.

In popular litterature I can highly recommend the book "Fearful Symmetry" by A. Zee (Princeton). It is primarily concerned with how modern physisc tends to use the concept of symmetry in order to try and discover the fundamental laws of nature. Also, in his book "Seven Brief Lessons on Physics" (Penguin Books), C. Rovelli gives a beautiful overview on quantum physics in Chapters two and four. The two last chapters of this book are, however, highly speculative and, quite frankly, rather weak.

If you are interested in the problematic sides of the traditional interpetation of quantum physics, you may find the book "What Is Real" by A. Becker (Basic Books) interesting. If you are interested in a more spiritual take on the interpretation of modern physics, "The Tao of Physics" by F. Capra (Shambala

Publications) may be of interest, although large parts of it are somewhat far fetched.

This very brief list of books is, of course, by no means exhaustive.