Chapter 5
Two Simple Solutions of the Schrödinger Equation

The infinite potential well is the simplest model case for a discrete energy spectrum. We see that the eigenfunctions form a complete orthonormal system. Free motion is the simplest model case for a continuous spectrum. In both cases, we solve the initial-value problem. We make our first contact (within the analytical approach) with the interpretation of probability and measurements.

This chapter deals with the solutions of the SEq for two simple but important one-dimensional systems. First, we consider the *infinite potential well* as a simple model of a bounded system, then *force-free unlimited motion* as a simple model of an unbounded system. Here, 'bounded motion' means basically that the system is confined to a finite region, in contrast to unlimited motion.

The two examples in this chapter are of interest not only in view of our current state of knowledge in this course, but also because they provide further information. At the same time, they are mathematically so simple that they are treated as specific cases even at the school level. Among other things, we will see below that the striking differences between the two solutions can be attributed to 'just' their different boundary conditions.[1]

5.1 The Infinite Potential Well

We imagine a ping-pong ball which bounces back and forth between two fixed, infinitely rigid walls, whereby friction and gravity are switched off. We can represent the two walls by infinitely high potential barriers at $x = 0$ and $x = a$; for $0 < x < a$, the potential energy is zero. Classically, the ping-pong ball can have any speed or kinetic energy (it has no potential energy). This means that in Fig. 5.1, the ball can fly at any height (the height in the figure corresponds to the ball's kinetic energy, not to its position!).

[1] See also the exercises for Chap. 3.

J. Pade, *Quantum Mechanics for Pedestrians 1*, Undergraduate Lecture Notes in Physics, https://doi.org/10.1007/978-3-030-00464-4_5

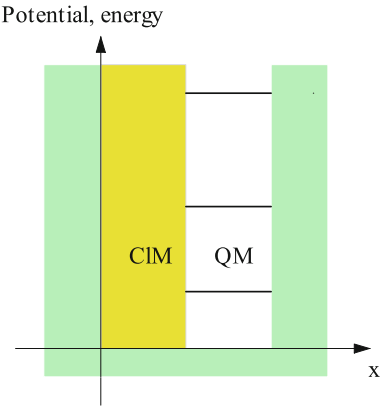

Fig. 5.1 Infinite potential well. In classical mechanics (*left*), all energies are allowed. In quantum mechanics, only discrete energy levels are allowed

In contrast, the quantum-mechanical ping-pong ball can occupy only certain 'energy levels', as we will see below.[2] In other words, its energy is quantized. This system, which represents the prototype of a bounded problem in quantum mechanics, is called the *infinite potential well*:

$$V = \begin{cases} 0 \text{ for } 0 < x < a \\ \infty \text{ otherwise .} \end{cases} \tag{5.1}$$

5.1.1 Solution of the Schrödinger Equation, Energy Quantization

The stationary SEq is given for $0 < x < a$ by:

$$E\varphi(x) = -\frac{\hbar^2}{2m}\varphi''(x) \tag{5.2}$$

Outside the infinite potential well and at its edges (walls), the wavefunction vanishes identically

$$\varphi(x) \equiv 0 \text{ for } x \leq 0 \text{ and } a \leq x. \tag{5.3}$$

Hence, the problem is described by (5.2) with the *boundary conditions*[3]

[2] Indeed, the quantum-mechanical ping-pong ball is quite a peculiar ball, namely an object described by a standing wave.

[3] A conclusive argument for these boundary conditions is given in Chap. 15, Vol. 2. For now, one might think (in an intuitive analogy to the wavefunction) of a rope which is clamped at both ends (although the question remains open as to what a rope has to do with this quantum-mechanical situation). Alternatively, one might consider a continuity requirement for the wavefunction at the walls to be plausible.

$$\varphi(0) = 0; \quad \varphi(a) = 0. \tag{5.4}$$

We write (5.2) in the form

$$\varphi'' = -\frac{2mE}{\hbar^2}\varphi. \tag{5.5}$$

In order to arrive at a more compact form, we make use of the de Broglie relation $p = \hbar k$ and obtain

$$E = \frac{p^2}{2m} = \frac{\hbar^2}{2m}k^2; \tag{5.6}$$

it then follows that

$$\varphi'' = -k^2\varphi. \tag{5.7}$$

This is the familiar differential equation for the classical harmonic oscillator, with the solutions

$$\varphi = Ae^{ikx} + Be^{-ikx}; \quad 0 < x < a; (A, B) \neq (0, 0), \tag{5.8}$$

where we assume without loss of generality that $k > 0$.[4] At this point, the energy E (and hence k) is not yet determined; we will find them in the next step.

The solution (5.8) contains the three free variables A, B and k, two of which can be fixed by the boundary conditions:

$$\begin{aligned} 0 &= \varphi(0) = A + B \\ 0 &= \varphi(a) = Ae^{ika} + Be^{-ika}. \end{aligned} \tag{5.9}$$

This is a homogeneous system of equations for A and B. It follows that:

$$\begin{aligned} A &= -B \\ 0 &= Ae^{ika} - Ae^{-ika}. \end{aligned} \tag{5.10}$$

This yields for $A \neq 0$[5]:

$$e^{ika} - e^{-ika} = 0, \tag{5.11}$$

or, equivalently[6]:

$$\sin ka = 0. \tag{5.12}$$

Only when this condition is met does the system (5.9) have a nontrivial (i.e. physical) solution. Equation (5.12) can be satisfied only for certain values of k, namely $ka = n\pi$, $n \in \mathbb{N}$. Thus, there exist only discrete values for k:

[4] We have $k \neq 0$, since for $k = 0$, only the trivial solution is obtained.

[5] For $A = 0$, we would obtain the trivial solution.

[6] We recall that $\sin x = \frac{e^{ix} - e^{-ix}}{2i}$.

$$k = \left\{ \frac{\pi}{a}, \frac{2\pi}{a}, \frac{3\pi}{a}, \frac{4\pi}{a} \ldots \right\} = \{k_n\}\,;\, k_n = \frac{n\pi}{a};\ n \in \mathbb{N}. \tag{5.13}$$

Accordingly, there are countably infinitely many solutions (= eigenfunctions) of the SEq, namely

$$\varphi_n(x) = 2iA \sin k_n x. \tag{5.14}$$

Due to the linearity of the SEq, one can choose the amplitude freely. With the choice[7]

$$2iA = \sqrt{\frac{2}{a}}, \tag{5.15}$$

we arrive at

$$\varphi_n(x) = \sqrt{\frac{2}{a}} \sin k_n x. \tag{5.16}$$

Because of the relation $E = \frac{\hbar^2 k^2}{2m}$, the energy can also assume only discrete values. These energy eigenvalues are given by:

$$E_n = \frac{\hbar^2}{2m} k_n^2 = \frac{\hbar^2}{2m} \frac{\pi^2}{a^2} n^2. \tag{5.17}$$

Since the SEq (5.2) has solutions only for certain eigenfunctions φ_n or energy levels E_n, one often writes the eigenvalue problem from the outset as

$$E_n \varphi_n(x) = -\frac{\hbar^2}{2m} \varphi_n''(x)\,. \tag{5.18}$$

Thus, we have a *discrete* energy spectrum, which occurs whenever the quantum object is bounded or localized.

As is well known, the quantization of energy means the following: If we look at the energy of a quantum object in the infinite potential well, we always detect one of these eigenvalues, but never any intermediate values. In other words, the possible measured (energy) values are the eigenvalues of the (energy) operator, i.e. the Hamiltonian. We have already encountered the same situation in the algebraic approach in Chap. 4, where we saw that the possible measured polarization values are determined by the eigenvalues of the corresponding polarization operators. In fact, this is a general aspect of quantum mechanics: Physical quantities are represented by operators, and the eigenvalues of those operators are the experimentally measurable quantities.

Two more comments on the eigenfunctions:

1. The amplitude in (5.16) is chosen to give the greatest simplicity of the result. In principle, also the form

[7] This special choice will be justified below.

$$\varphi_n(x) = \sqrt{\frac{2}{a}} e^{i\delta_n} \sin k_n x \tag{5.19}$$

is possible, where $\delta_n \in \mathbb{R}$ is a phase shift. In order to avoid unnecessary restrictions, we will use the eigenfunctions in their complex form (5.19) in the following exemplary considerations, wherever appropriate.

2. If we take into account the time dependence (see below), a state of definite energy E_n is given by $\varphi_n(x)\, e^{-i\omega_n t} \sim \sin k_n x \cdot e^{-i\omega_n t}$, i.e. it is a *standing wave*.

5.1.2 Solution of the Time-Dependent Schrödinger Equation

How would a total solution for the wavefunction Ψ look? In Chap. 3, we started with the separation *ansatz*:

$$\Psi(x,t) = \varphi(x) e^{-i\omega t} \quad \text{with} \quad E = \hbar\omega. \tag{5.20}$$

The eigenfunctions $\varphi_n(x)$ are solutions of the stationary SEq with the eigenvalues E_n or ω_n. Therefore, *each* of the functions $\varphi_n(x)\, e^{-i\omega_n t}$ is a particular solution of the time-dependent SEq. Due to the linearity of the SEq, we obtain the general solution by superposition of *all* the particular solutions. It follows that[8]:

$$\Psi(x,t) = \sum_n c_n \varphi_n(x)\, e^{-i\omega_n t} \tag{5.21}$$

with

$$c_n \in \mathbb{C}\,;\ \varphi_n(x) = \sqrt{\frac{2}{a}} e^{i\delta_n} \sin k_n x;\ \omega_n = \frac{E_n}{\hbar} = \frac{\hbar k_n^2}{2m}. \tag{5.22}$$

Thus, we have integrated the SEq in closed form. We note that this is one of the few examples where this is possible.[9]

The coefficients c_n in (5.22) are determined by the particular choice of the system. If all the c_n vanish except for one, the system is in a definite energy state; otherwise, it is in a superposition of several states. With the last equations, the problem 'infinite potential well' is completely determined—we know, in closed form, all the eigenvalues, the corresponding eigenfunctions and thus the general form of the time-dependent solution. From (5.21), we see explicitly that the solutions $\Psi(x,t)$, as discussed in Chap. 3, are elements of a vector space $\mathcal{V}$. It holds for example that with

[8] We recall that we are using a shorthand notation for the summation $\sum_n$. The range of values of n must be clear from the context. Here, it would be $n = 1, \ldots \infty$ or $\sum_{n=1}^{\infty}$.

[9] The form (5.21) for the general solution applies just as well to other potentials besides the infinite potential well considered here, although of course the eigenfunctions are then not the same as those in (5.22).

$$\Psi(x,t) = \sum_n c_n \varphi_n(x)\, e^{-i\omega_n t} \quad \text{and} \quad \Phi(x,t) = \sum_n d_n \varphi_n(x)\, e^{-i\omega_n t}, \tag{5.23}$$

every linear combination $\Theta = \alpha\Psi + \beta\Phi$ may be written as

$$\Theta(x,t) = \sum_n (\alpha c_n + \beta d_n)\, \varphi_n(x)\, e^{-i\omega_n t} = \sum_n b_n \varphi_n(x)\, e^{-i\omega_n t}, \tag{5.24}$$

and thus is also a solution.

However, one can still learn a lot more from this example. This is due to special properties of the eigenfunctions, whereby—and this is the salient point—these relationships are valid in general and not only for the infinite potential well. Thanks to these properties, the inclusion of the initial-value problem (and thus the proof that the solution of the SEq is determinate) is relatively easy, as we shall see in a moment.

5.1.3 *Properties of the Eigenfunctions and Their Consequences*

An essential property of the eigenfunctions (5.19) is their so-called *orthonormality*. As one can show,[10] the functions are *normalized*:

$$\int_0^a \varphi_n^*(x)\, \varphi_n(x)\, \mathrm{d}x = 1 \tag{5.25}$$

and *orthogonal*:

$$\int_0^a \varphi_m^*(x)\, \varphi_n(x)\, \mathrm{d}x = 0; \;\; m \neq n. \tag{5.26}$$

Written compactly, they are *orthonormal*[11]:

$$\int_0^a \varphi_m^*(x)\, \varphi_n(x)\, \mathrm{d}x = \delta_{nm}. \tag{5.27}$$

Here, we integrate the product $\varphi_m^* \varphi_n$ and not $\varphi_m \varphi_n$, so that the expression is independent of the phase which occurs in (5.19). Because the wavefunctions vanish outside of the interval $[0, a]$, the integration can extend from $-\infty$ to ∞. We thus obtain the general formulation:

[10] See the exercises for this chapter.

[11] This explains also the choice which we made in (5.15) or (5.19).

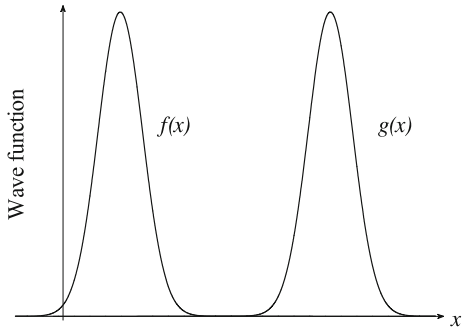

Fig. 5.2 Example sketch of two functions $f(x)$ and $g(x)$ which are orthogonal in the sense of (5.28)

$$\int_{-\infty}^{\infty} \varphi_m^*(x)\,\varphi_n(x)\,\mathrm{d}x = \delta_{nm}. \tag{5.28}$$

In fact, the eigenfunctions of *all* the Hamiltonians we consider possess this important property, provided the corresponding eigenvalues are discrete. Here, it is of course assumed that the integrals exist, which means that the functions are *square-integrable*.[12]

So far, we have used the term *orthonormal* in connection with 'usual' vectors, such as column or row vectors or kets and bras, e.g. in Chap. 4 in the form $\langle\varphi_i \,|\varphi_j\rangle = \delta_{ij}$. That now also *functions* such as (5.21) are deemed orthonormal may seem surprising at first. It is due to the fact that, as mentioned above, these functions are *also* elements of the vector space $\mathcal{V}$ of the solutions of the SEq,[13] and as such (i.e. as *vectors*), they can be orthogonal to each other. Indeed, the form on the left side of (5.28) is a scalar product, as is shown explicitly in Chap. 11. Hence, one has to distinguish between two aspects: On one hand, $\varphi_n(x)$ is a function of x; on the other hand and simultaneously, it is an element of the vector space $\mathcal{V}$ and in this sense a vector.[14] The orthogonality of two functions to each other does not mean that the graphs of these two functions intersect only at right angles or something similar; but rather that they, as members of $\mathcal{V}$, behave as described in (5.28). This may appear as shown in Fig. 5.2.

By the way, an even function is always orthogonal to an odd one (with symmetric limits of integration).

In addition to their orthonormality, the eigenfunctions (5.19) have the property of *completeness*. Intuitively, this means that it is possible to formulate any solution of the SEq for the infinite potential well as a superposition of these eigenfunctions, as we have already noted in (5.21). Concerning their orthonormality, we use very

[12] Square-integrable (or quadratically integrable) over the interval $[a, b]$ are those functions $f(x)$ for which $\int_a^b |f(x)|^2\,\mathrm{d}x < \infty$ holds. The short notation reads $f(x) \in L^2[a, b]$. For $a = -\infty$ and $b = \infty$, the notation $L^2[\mathbb{R}]$ is common.

[13] Hence the often undifferentiated use of the terms eigenfunction and eigenvector.

[14] This use of the term vector has of course nothing to do with arrows or with the properties of transformation behavior (polar and axial vectors).

similar formulations in both the algebraic and the analytic approaches, with

$$\langle \varphi_n \, | \varphi_m \rangle = \delta_{nm} \quad \text{or} \quad \int_{-\infty}^{\infty} \varphi_m^* \, (x) \, \varphi_n \, (x) \, \mathrm{d}x = \delta_{nm}. \tag{5.29}$$

The question of an analogous comparison for the completeness, which reads $\sum_n |\varphi_n\rangle \langle \varphi_n| = 1$ in the algebraic approach, will be taken up again only in Chap. 11. But here, we can already state that the eigenfunctions of the infinitely-deep potential well form a complete orthonormal system, a CONS.

5.1.4 *Determination of the Coefficients c_n*

Back to the example of the infinite potential well: For the general solution of the time-dependent SEq (i.e. the total wavefunction), we found the expression

$$\Psi \, (x, t) = \sum\nolimits_n c_n \varphi_n \, (x) \, e^{-i\omega_n t}. \tag{5.30}$$

The eigenfunctions and eigenvalues are defined by the physical problem (i.e. the shape of the potential), while the actual behavior in time is determined by the choice of the coefficients c_n. If we know all the coefficients, we have uniquely determined the time dependence of $\Psi \, (x, t)$. On the other hand, the SEq is a differential equation of first order in time, which means that the specification of the initial condition $\Psi(x, 0)$ determines the temporal behavior. In other words, knowledge of the initial condition $\Psi(x, 0)$ gives the same information as knowledge of all the coefficients c_n.[15] So it must be possible to calculate: (i) $\Psi(x, 0)$ from knowledge of all the c_n's, and (ii) all the coefficients c_n from knowledge of $\Psi(x, 0)$.

This is trivial in the first case, since we have $\Psi \, (x, 0) = \sum_n c_n \varphi_n \, (x)$. For the other direction, we use the orthonormality of the eigenfunctions (5.27). An additional technical note: We always assume that the functions considered here are sufficiently well-behaved, that all series converge, and that we can interchange any limiting processes such as derivatives, integrals, and infinite sums. Of course, this must be shown explicitly for particular cases, but we will save ourselves some trouble and leave this job to others, and accept their results. Some remarks on this are given in Appendix D, Vol. 1.[16]

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[15] At first sight, it may seem strange that one can compute *infinitely* many complex numbers c_n from *one* initial condition $\Psi(x, 0)$. But in fact, with $\Psi(x, 0)$ we have *uncountably* many values.

[16] "Physicists usually have a nonchalant attitude when the number of dimensions is extended to infinity. Optimism is the rule, and every infinite sequence is presumed to be convergent, unless proven guilty." A. Peres, *Quantum Theory*, p. 79.

We begin with

$$\Psi(x,0) = \sum\nolimits_n c_n \varphi_n(x). \tag{5.31}$$

Multiplying this equation from the left by $\varphi_m^*(x)$ and integrating yields:

$$\int_0^a \varphi_m^*(x)\Psi(x,0)\,\mathrm{d}x = \int_0^a \sum_n c_n \varphi_m^*(x)\varphi_n(x)\,\mathrm{d}x. \tag{5.32}$$

Interchanging the integration and the summation and using the orthonormality (5.27) of the eigenfunctions leads to:

$$\sum_n c_n \int_0^a \varphi_m^*(x)\varphi_n(x)\,\mathrm{d}x = \sum_n c_n \delta_{n,m} = c_m \tag{5.33}$$

or, compactly,

$$c_m = \int_0^a \varphi_m^*(x)\Psi(x,0)\,\mathrm{d}x. \tag{5.34}$$

Thus, the specification of the initial condition allows us to calculate uniquely all of the coefficients. It follows that

$$\Psi(x,t) = \sum_n \left(\int_0^a \varphi_n^*(x')\Psi\left(x',0\right)\mathrm{d}x' \right) \varphi_n(x)\, e^{-i\omega_n t} \tag{5.35}$$

gives an expression for the solution of the time-dependent SEq. We can read off from this equation directly that specifying the initial condition uniquely determines the time behavior of $\Psi(x,t)$ for all times.

5.2 Free Motion

As a second simple model system, we consider force-free unbounded motion. It is also described by the SEq[17]

$$i\hbar\dot{\Psi}(x,t) = -\frac{\hbar^2}{2m}\Psi''; \tag{5.36}$$

but here we assume that there are no limits on the motion. The quantum object is not localized and can move throughout all space.

[17] This equation is very similar to the heat equation $\dot{f} = \lambda\nabla^2 f$—apart from i in the SEq. As is well known, this 'small difference' is the mother of all worlds.

5.2.1 General Solution

As we know, special (particular) solutions of the problem are plane waves of the form

$$\Psi_{\text{part}}(x,t) = e^{i(kx-\omega t)}. \tag{5.37}$$

Since each $k \in \mathbb{R}$ is allowed, and thus also any energy $E = \frac{\hbar^2 k^2}{2m}$, we have a *continuous* energy spectrum. This case *always* occurs if the quantum object is not localized (i.e. is unbounded).

The general solution is the superposition of particular solutions, that is[18]

$$\Psi(x,t) = \int_{-\infty}^{\infty} c(k) e^{i(kx-\omega t)} \mathrm{d}k. \tag{5.38}$$

At $t = 0$, we obtain

$$\Psi(x,0) = \int_{-\infty}^{\infty} c(k) e^{ikx} \mathrm{d}k. \tag{5.39}$$

The specification of this initial condition determines the time evolution here, also, since the SEq is a differential equation of first order in time. Consequently, it must be possible to compute the coefficients $c(k)$ uniquely from $\Psi(x,0)$. This indeed works; by means of Fourier transformation,[19] we obtain immediately

$$c\,(k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \Psi(x,0) e^{-ikx} \mathrm{d}x, \tag{5.40}$$

so that we can, in principle, determine the solution for any given initial distribution. Thus, we have again integrated the SEq in closed form. In a compact notation, the solution reads:

$$\Psi(x,t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \left(\int_{-\infty}^{\infty} \Psi(x',0) e^{-ikx'} \mathrm{d}x' \right) e^{i(kx-\omega t)} \mathrm{d}k \quad \text{with} \quad \omega = \frac{\hbar k^2}{2m}. \tag{5.41}$$

Again in this case, we see immediately that the wavefunction is determinate.

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[18] Integral and not sum, because k is a continuous 'index'. The integration variable k may of course also assume negative values here.

[19] Some basics on Fourier transformation can be found in Appendix H, Vol. 1.

5.2.2 Example: Gaussian Distribution

A concrete standard example is based on the initial condition

$$\Psi(x,0) = \frac{1}{\left(\pi b_0^2\right)^{\frac{1}{4}}} \exp\left(-\frac{x^2}{2b_0^2}\right) e^{iKx}, \tag{5.42}$$

where we assume $K > 0$ without loss of generality.[20] Without the factor e^{iKx}, the center of the distribution would be stationary, i.e. it would remain at the same position. For the following discussion, we concentrate on the absolute square of the wavefunction. Initially, it is given by

$$\rho(x,0) = |\Psi(x,0)|^2 = \frac{1}{\sqrt{\pi} b_0} \exp\left(-\frac{x^2}{b_0^2}\right). \tag{5.43}$$

This function has the form of a Gaussian bell curve with its maximum $\rho_{\max} = (\sqrt{\pi} b_0)^{-1}$ at $x = 0$. The width of the curve is given by $2b_0$; it is measured between the points where the curve has the value $\rho = \rho_{\max}/e$.[21]

In this example, one can determine $\Psi(x,t)$ exactly, but the calculation is tedious and will be omitted here.[22] One arrives eventually at

$$\rho(x,t) = |\Psi(x,t)|^2 = \frac{1}{\sqrt{\pi} b(t)} \exp\left(-\frac{\left(x - \frac{\hbar K}{m} t\right)^2}{b^2(t)}\right), \tag{5.44}$$

where $b(t)$ is given by

$$b(t) = \sqrt{b_0^2 + \left(\frac{\hbar t}{b_0 m}\right)^2} \tag{5.45}$$

with $b(0) = b_0$. Obviously, the function $b(t)$ increases monotonically with t and tends towards $\frac{\hbar t}{b_0 m}$ for $t \to \infty$.

Equation (5.44) again represents a Gaussian curve, with its maximum at $x = \frac{\hbar K}{m} t$ and width $2b(t)$. This means that the curve becomes wider and wider with increasing t, while its maximum moves with constant velocity $v = \frac{\hbar K}{m}$ to the right. Its height is given by $\rho_{\max}(x,t) = (\sqrt{\pi} b(t))^{-1}$, i.e. it decreases continuously due to the monotonic form of $b(t)$. In short, the distribution $\rho(x,t)$ becomes steadily wider and flatter—it 'goes fuzzy' or becomes 'smeared out'; see Fig. 5.3.

This concludes our mathematical findings. However, the question remains as to what this 'smearing out' means physically. One thing is clear: It cannot mean that the

[20] The quite specific form of the coefficients is due to the normalization.

[21] Occasionally, this width is referred to as the halfwidth, although the function has dropped not to $1/2$, but to $1/e$ of its maximum value.

[22] A slightly more detailed analysis can be found in Appendix D, Vol. 2 (wave packets).

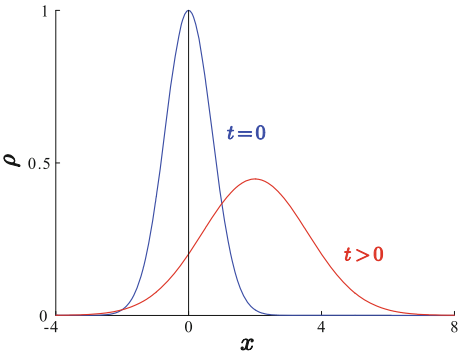

Fig. 5.3 Spreading of the density distribution (5.44). Arbitrary units; maximum at $t = 0$, normalized to 1

object (electron, etc.) is itself smeared out—an electron is, within the framework of our considerations, always an (indivisible) point object. We will discuss this point in more detail in Chap. 7. Here, we simply mention in anticipation that the question boils down to the interpretation of $\rho(x, t)$ as a *probability density*. It allows us by means of $\int_a^b \rho(x, t)$ to calculate the probability of finding the quantum object in the interval $[a, b]$. Describing the spreading of the Gaussian curve means that the wavefunction from which the probability is calculated spreads out (and not the quantum object itself). In other words, the uncertainty with which we can determine the location of a quantum object, $\Delta x \approx b(t)$, increases over time. With this interpretation of $\rho(x, t)$, we have introduced the term 'probability' also into the analytical approach.

However, this concept makes sense only if the effects are noticeable (i) very strongly for microscopic objects, and (ii) nearly not at all for macroscopic objects. Everyday things around us do not have a spreading probability of being found at a particular location, in contrast to objects in the microscopic world. In order to arrive at a numerical estimate, we compute the time t_{2b_0} after which the width of a bell-shaped curve, initially b_0, has doubled, that is $b\left(t_{2b_0}\right) = 2b_0$. It follows that:

$$\sqrt{b_0^2 + \left(\frac{\hbar t_{2b_0}}{b_0 m}\right)^2} = 2b_0 \quad \text{and thus } t_{2b_0} = \sqrt{3}\frac{m}{\hbar}b_0^2. \tag{5.46}$$

We calculate this doubling time t_{2b_0} for two examples ($\hbar \approx 10^{-34}$ kg m^2/s):

1. A 'Grain of sand': $m = 1$ g, $b_0 = 1$ mm:

$$t_{2b_0,\text{grain}} = 1.7 \cdot \frac{10^{-3}}{10^{-34}} 10^{-6}\text{s} = 1.7 \cdot 10^{25}\text{s} \approx 5.4 \cdot 10^{17}\text{years}; \tag{5.47}$$

2. An 'Electron', $m = 10^{-30}$ kg, $b_0 = 10^{-10}$ m:

$$t_{2b_0,\text{electron}} = 1.7 \cdot \frac{10^{-30}}{10^{-34}} 10^{-20}\text{s} \approx 1.7 \cdot 10^{-16}\text{s}. \tag{5.48}$$

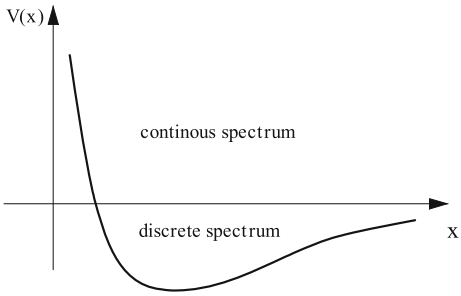

Fig. 5.4 Characterization of the energy spectrum for an arbitrary potential, depending on the localizability of the quantum object

We see clearly the difference between a macroscopic and a microscopic object. We note that this calculation is only about orders of magnitude, not 'exact' values, and that the results apply only if the objects are completely isolated during the time t_{2b_0} (i.e. they do not interact with anything else in the universe). And of course we know that the 'grain of sand' with $m = 1$ g is a many-particle system with internal interactions.

5.3 General Potentials

A few words about the nature of the energy spectrum are in order. We have found that the energy spectrum of the infinite potential well is discrete, whereas it is continuous for unlimited motions. That does not mean that every system has either a discrete *or* a continuous energy spectrum. Consider, for example, the hydrogen atom, i.e., proton plus electron. When the electron is in a bound state, we have discrete energies. If we ionize the atom, thus separating the electron from the nucleus so that it can move freely and without limit, then it can move with *any* kinetic energy—we have a continuous energy spectrum in this range. The situation is shown schematically in Fig. 5.4. In short, there are many systems whose energy spectrum has both a discrete and a continuous part.[23]

We will take up the formal treatment of this question later, where we will also see that continuous systems are mathematically more difficult than discrete ones. To circumvent these problems, one can resort to a 'trick', which helps to ensure that the *entire* spectrum is discrete.

We outline the basic idea: For this we start from an arbitrary (sufficiently well-behaved) potential $V(x)$ that vanishes at infinity. Now let us imagine that we put the system under consideration *in addition* into a potential well with infinitely high potential walls on all sides, see Fig. 5.5. The walls should be so far away that we can assume that their existence has no measurable influence on the 'local' physics

[23] In fact, it may also be the case that discrete and continuous spectra overlap, or that discrete levels are embedded in the continuum, as we shall see using the example of the helium atom in Chap. 23, Vol. 2.

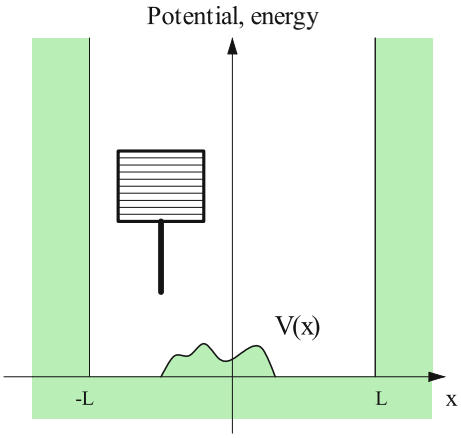

Fig. 5.5 At sufficiently high resolution, the apparent continuum of energy eigenvalues proves to consist of closely-spaced individual levels

(i.e. in our lab). In particular, the potential V is negligible (zero) at the location of the walls. The stationary SEq $E\varphi(x) = -\frac{\hbar^2}{2m}\varphi''(x) + V(x)\varphi(x)$ is a *second-order* differential equation with respect to x and accordingly has *two* linearly-independent fundamental solutions, $\varphi_1(kx)$ and $\varphi_2(kx)$, with $k^2 = 2mE/\hbar^2$. For the following argument, it does not matter exactly what form these functions take, it is sufficient that they exist. Each solution of the stationary SEq for the energy E can be expressed as a linear combination $\varphi(x) = A\varphi_1(kx) + B\varphi_2(kx)$. If we now imagine infinitely high potential walls at $x = \pm L$, then $\varphi(x)$ must vanish there. It follows that

$$\begin{aligned} A\varphi_1(-kL) + B\varphi_2(-kL) &= 0 \\ A\varphi_1(kL) + B\varphi_2(kL) &= 0. \end{aligned} \tag{5.49}$$

This is a homogeneous system of equations for the quantities A and B. This system is solvable[24] if

$$\varphi_1(-kL)\varphi_2(kL) - \varphi_2(-kL)\varphi_1(kL) = 0 \tag{5.50}$$

applies. This equation can be satisfied only for certain values of kL. For a given L, this is therefore a determining equation for k, with countably infinitely many solutions k_n. Hence the energy is discrete.

[24] Moreover, it follows from (5.49) for instance that

$$B = -\frac{\varphi_1(kL)}{\varphi_2(kL)}A$$

and so

$$\Phi(x) = A\left[\varphi_1(kx) - \frac{\varphi_1(kL)}{\varphi_2(kL)}\varphi_2(kx)\right],$$

leaving only *one* remaining free constant (and one *must* remain because of the linearity of the SEq).

The larger L is, the closer the energy levels lie together. We can visualize this by the fact that for sufficiently large n, the influence of the potential $V(x)$ is small (i.e. the main influence arises from the infinite potential well) and the energy levels are given approximately by

$$E_n \approx \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 \pi^2}{2m} \frac{n^2}{L^2}. \tag{5.51}$$

The difference between these energy levels is

$$E_n - E_{n-1} \approx \frac{\hbar^2 \pi^2}{2m} \frac{2n-1}{L^2}. \tag{5.52}$$

For sufficiently large L, one can reduce this difference to below any measurable value. In other words, we have in this case discrete energy eigenvalues, but they are so dense that they look to us like a (quasi-)continuum; cf. Fig. 5.5.

A numerical example: If the potential walls were a light year apart, then the differences between two neighboring energy levels for an electron are of the order of 10^{-50} eV (see exercises).

Finally, we note that another 'trick' for the discretization of the spectrum is the introduction of *periodic boundary conditions* of the form $\varphi(x + L) = \varphi(x)$. In this way, one can model solids, or also motions on a cylinder or a torus. Two examples can be found in the exercises.

5.4 Exercises

1. Given the free stationary SEq

$$E\Phi(x) = -\frac{\hbar^2}{2m}\Phi''(x), \tag{5.53}$$

   formulate the corresponding equation for the Fourier transform of Φ.
2. Given the stationary SEq

$$E\Phi(x) = -\frac{\hbar^2}{2m}\Phi''(x) + V(x)\Phi(x), \tag{5.54}$$

   formulate the corresponding equation for the Fourier transform of Φ.
3. The Hamiltonian has discrete nondegenerate eigenvalues $E_n, n = 1, 2, \ldots$. What is the general solution of the time-dependent SEq?
4. Infinite potential well: Show that the eigenfunctions in the form $\varphi_n(x) = \sqrt{\frac{2}{a}} e^{i\delta_n} \sin(k_n x)$ constitute an orthonormal system of functions ($\int_0^a \varphi_m^*(x)\varphi_n(x) = \delta_{mn}$). Hint: The integrals can be calculated for example by means of

$\sin x \sin y = \frac{\cos(x-y)-\cos(x+y)}{2}$ or the exponential representation of the sine functions.

5. Infinite potential well: Formulate the general solution of the time-dependent SEq and verify that specification of the initial condition determines the wave function. Concretize the considerations to the special cases ($C \in \mathbb{C}$ is an arbitrary complex constant):

   (a) $\Psi(x, t = 0) = C\delta(x - \frac{a}{2})$;
   (b) $\Psi(x, t = 0) = C$;
   (c) $\Psi(x, t = 0) = Ce^{iKx}$.

6. Given the three-dimensional SEq $E\psi(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r})$, which energy eigenvalues are allowed if one imposes the following periodic boundary conditions: $\psi(x, y, z) = \psi(x + L_x, y, z) = \psi(x, y + L_y, z) = \psi(x, y, z + L_z)$?
7. An electron is located between the two walls of an infinite potential well, which are one light year apart. Calculate roughly the magnitude of the difference between two adjacent energy levels.
8. Find examples for functions which

   (a) are integrable, but not square-integrable;
   (b) are square-integrable, but not integrable.

9. Given the stationary SEq

$$E\varphi(x) = -\frac{\hbar^2}{2m}\varphi''(x) + V(x)\varphi(x), \tag{5.55}$$

   rewrite this equation for a dimensionless independent variable.
10. A short outlook into string theory (compactified or rolled-up dimensions): String theory assumes that the elementary building blocks of nature are not point objects, but rather one-dimensional objects (strings) with a certain energy—comparable to an object in a one-dimensional potential well. Strings have a spatial extension of order of the Planck length and live in higher-dimensional spaces (e.g. dim = 10 or dim = 26), where only four dimensions are not rolled up (compactified)—quite similar to our following simple example.[25]
    For the formal treatment, we take the two-dimensional SEq

[25] When a writer like Terry Pratchett couples the idea of rolled-up dimensions with other physical paradigms, it reads like this: "..and people stopped patiently building their little houses of rational sticks in the chaos of the universe and started getting interested in the chaos itself—partly because it was a lot easier to be an expert on chaos, but mostly because it made really good patterns that you could put on a T-shirt.

And instead of getting on with proper science, scientists suddenly went around saying how impossible it was to know anything, and that there wasn't really anything you could call reality to know anything about, and how all this was tremendously exciting, and incidentally did you know there were possibly all these little universes all over the place but no-one can see them because they are all curved in on themselves? Incidentally, don't you think this is a rather good T-shirt?" Terry Pratchett, in *Witches Abroad*, A Discworld Novel.

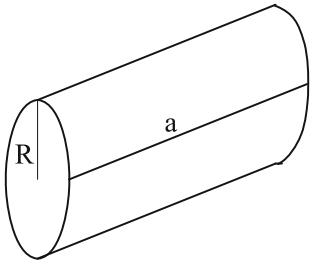

Fig. 5.6 The 'cylinder world' of our toy string

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}\right)=E\psi \tag{5.56}$$

as starting point. In the x direction, we have an infinite potential well

$$V=\begin{cases}0 \quad \text{for} \quad 0<x<a\\ \infty \text{ otherwise}\end{cases} \tag{5.57}$$

and for the y coordinate we postulate

$$\psi(x,y)=\psi(x,y+2\pi R)\,. \tag{5.58}$$

So we have a combination of two different boundary conditions: In the x direction, $\psi(0,y)=\psi(a,y)=0$ applies, while in the y direction the periodic boundary condition $\psi(x,y)=\psi(x,y+2\pi R)$ is valid. In other words, the quantum object 'lives' on the surface of a cylinder of length a and of radius R, see Fig. 5.6. The problem is now to calculate the possible energy levels. Discuss in particular the situation when $R \ll a$.

11. Given the free one-dimensional SEq (5.36) and the function $\Phi(x)$, show that

$$\Psi(x,t)=A\frac{1}{\sqrt{t}}\int_{-\infty}^{\infty} e^{\frac{im}{2\hbar}\frac{(x-y)^2}{t}}\Phi(y)\,\mathrm{d}y \tag{5.59}$$

is a solution (A is a normalization constant).