

Chapter 4

Time–Independent Schrödinger Equation

4.1 Stationary States

We consider again the time dependent Schrödinger equation (Prop. 2.1)

$$i\hbar \frac{\partial}{\partial t} \psi(t, x) = \left(-\frac{\hbar^2}{2m} \Delta + V(x) \right) \psi(t, x) = H \psi(t, x), \quad (4.1)$$

where the potential in the Hamiltonian is assumed to be time independent $V = V(x)$. We calculate the solutions of this equation by using the *method of separation of variables*, i.e. we make the following ansatz for the solution $\psi(t, x)$:

$$\psi(t, x) = \psi(x) f(t) \quad (4.2)$$

and insert it into the time dependent Schrödinger equation, Eq. (4.1),

$$\begin{aligned} i\hbar \psi(x) \frac{\partial f(t)}{\partial t} &= -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} f(t) + V(x) \psi(x) f(t) & | \cdot \frac{1}{\psi(x) f(t)} \\ i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} &= -\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{d^2 \psi(x)}{dx^2} + V(x). \end{aligned} \quad (4.3)$$

Since now the left hand side in Eq. (4.3) is only dependent on t and the right hand side only on x , both sides must be equal to a constant, which we will call E , and we can thus solve each side independently. The left side yields

$$\begin{aligned} i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} = E &\Rightarrow \frac{df}{f} = -\frac{i}{\hbar} E dt \\ \Rightarrow \ln(f) = -\frac{i}{\hbar} E t + \text{const.} &\Rightarrow f = \text{const.} e^{-iEt/\hbar}. \end{aligned} \quad (4.4)$$

The constant in Eq. (4.4) will later on be absorbed into $\psi(x)$.

Then multiplying the right side of Eq. (4.3) with $\psi(x)$ we get

$$-\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{d^2\psi(x)}{dx^2} + V(x) = E \quad \Rightarrow \quad \underbrace{-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)}_{H\psi(x)} = E\psi(x). \quad (4.5)$$

The operators on the left express the Hamiltonian H acting on $\psi(x)$, which represents the *time independent Schrödinger equation*.

Theorem 4.1 (Time-independent Schrödinger equation)

$$H\psi(x) = E\psi(x)$$

where $H = -\frac{\hbar^2}{2m}\Delta + V(x)$ is the Hamiltonian

Definition 4.1 A state is called **stationary**, if it is represented by the wave function

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

For such states the probability density is time independent

$$|\psi(t, x)|^2 = \psi^*(x)\psi(x) \underbrace{e^{iEt/\hbar} e^{-iEt/\hbar}}_1 = |\psi(x)|^2. \quad (4.6)$$

The expectation values of observables $A(X, P)$ are time independent as well

$$\begin{aligned} \langle A(X, P) \rangle &= \int dx \psi^*(x) e^{iEt/\hbar} A(x, -i\hbar \frac{\partial}{\partial x}) \psi(x) e^{-iEt/\hbar} \\ &= \int dx \psi^*(x) A(x, -i\hbar \frac{\partial}{\partial x}) \psi(x). \end{aligned} \quad (4.7)$$

Remark I: As a consequence, the eigenvalues of the Hamiltonian, which are the possible energy levels of the system, are clearly time independent.

To see it, just take $H(X, P)$ instead of $A(X, P)$ in Eq. (4.7) and use the time-independent Schrödinger equation (Theorem 4.1)

$$\langle H(X, P) \rangle = \int dx \psi^*(x) H\psi(x) = \int dx \psi^*(x) E\psi(x) = E \underbrace{\int dx \psi^*(x)\psi(x)}_{< \infty}. \quad (4.8)$$

Remark II: The normalization of the wavefunction will restrict the possible values of the constant E , the energy of the system, in the Schrödinger equation.

Two more interesting features about stationary states and the corresponding energies will be formulated here in the form of two lemmata, whose proofs we will leave as exercises.

Lemma 4.1 *For normalizable solutions $\psi(x)$ of the Schrödinger equation the energy E must be real, $E \in \mathbb{R}$.*

Lemma 4.2 *Solutions $\psi(x)$ of the time-independent Schrödinger equation can always be chosen to be real.*

Definition 4.2 *The **parity operator** \mathcal{P} acting on a function $f(x)$ changes the sign of its argument:*

$$\mathcal{P} f(x) = f(-x).$$

We conclude that even and odd functions are eigenfunctions of the parity operator

$$\mathcal{P} \psi_{\text{even}} = +\psi_{\text{even}} \qquad \mathcal{P} \psi_{\text{odd}} = -\psi_{\text{odd}}, \qquad (4.9)$$

which we will use in the following theorem that will be helpful later on.

Theorem 4.2
For a symmetric potential $V(x) = V(-x)$ a basis of states can be chosen, that consists entirely of even and odd functions.

$$\psi_{\text{even}}(x) = \psi(x) + \psi(-x) \qquad \psi_{\text{odd}}(x) = \psi(x) - \psi(-x)$$

The proof for this theorem will be left as an exercise too.

4.2 Schrödinger Equation as Eigenvalue Equation

A subject concerning the time-independent Schrödinger equation we have not yet touched is its interpretation as an eigenvalue equation. Clearly, from its form we see that stationary states $|\psi\rangle$ are eigenvectors/eigenfunctions of the Hamiltonian H with eigenvalues E

$$H |\psi\rangle = E |\psi\rangle . \quad (4.10)$$

It implies the exact determination of the energy E . A stationary state has a precisely defined energy. Calculating the expectation value of the Hamiltonian for a stationary system just gives

$$\langle H \rangle = \langle \psi | H | \psi \rangle = \langle \psi | E | \psi \rangle = E \langle \psi | \psi \rangle = E . \quad (4.11)$$

Consequently, there is no energy uncertainty ΔE for these states

$$\Delta E = \Delta H = \sqrt{\langle H^2 \rangle - \langle H \rangle^2} = \sqrt{E^2 - E^2} = 0 . \quad (4.12)$$

Generally eigenvalue equations for linear operators take the form

$$A |\phi\rangle = a |\phi\rangle , \quad (4.13)$$

where a is an eigenvalue of the linear operator A with corresponding eigenvector $|\phi\rangle$. For hermitian operators there exist important statements about their eigenvalues and eigenfunctions.

Theorem 4.3

The eigenvalues of hermitian operators are real and the eigenvectors corresponding to different eigenvalues are orthogonal.

The proof is easy and again left as an exercise. The above theorem is vitally important for the spectrum $\{E_n\}$ of the Hamiltonian, which is thereby guaranteed to be real

$$H |\psi_n\rangle = E_n |\psi_n\rangle . \quad (4.14)$$

Using our notation $|\psi_n\rangle \equiv |n\rangle$ the orthogonality and completeness relations (remember equations (3.25) and (3.26)) can be written as

$$\langle n | m \rangle = \delta_{nm} \quad \sum_n |n\rangle \langle n| = \mathbb{1} . \quad (4.15)$$

4.3 Expansion into Stationary States

Using the spectral theorem (Theorem 3.1) we can then expand a given state into a complete orthonormal system of energy eigenstates $|n\rangle$ exactly as outlined in Section 3.3.1

$$|\psi\rangle = \sum_n c_n |n\rangle \quad c_n = \langle n | \psi \rangle . \quad (4.16)$$

By inserting a continuous CONS of position eigenstates (Eq. (3.32)) into the transition amplitude the expansion coefficients c_n can be rewritten as

$$c_n = \langle n | \psi \rangle = \int dx \langle n | x \rangle \langle x | \psi \rangle = \int dx \psi_n^*(x) \psi(x) . \quad (4.17)$$

We can now extend the expansion from the time independent case to the time dependent one. We just remember the time dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \psi(t, x) = H \psi(t, x) , \quad (4.18)$$

with a particular solution

$$\psi_n(t, x) = \psi_n(x) e^{-i E_n t / \hbar} . \quad (4.19)$$

The general solution is then a superposition of particular solutions

$$\psi(t, x) = \sum_n c_n \psi_n(x) e^{-i E_n t / \hbar} . \quad (4.20)$$

The expansion coefficients can easily be computed by setting $t = 0$ and taking the scalar product with $\psi_m(x)$

$$\begin{aligned} \int dx \psi_m^*(x) \psi(0, x) &= \int dx \psi_m^*(x) \sum_n c_n \psi_n(x) \underbrace{e^{-i E_n 0 / \hbar}}_1 \\ \langle \psi_m | \psi(t=0) \rangle &= \sum_n c_n \underbrace{\int dx \psi_m^*(x) \psi_n(x)}_{\delta_{mn}} . \end{aligned}$$

Thus the expansion coefficients are given by

$$c_n = \langle \psi_n | \psi(t=0) \rangle . \quad (4.21)$$

Physical interpretation of the expansion coefficients:

Let's consider an observable A with eigenstates ψ_n and eigenvalues a_n

$$A | \psi_n \rangle = a_n | \psi_n \rangle . \quad (4.22)$$

If a system is in an eigenstate of this observable the expectation value (in this state) is equal to the corresponding eigenvalue

$$\langle A \rangle = \langle \psi_n | A | \psi_n \rangle = a_n \langle \psi_n | \psi_n \rangle = a_n . \quad (4.23)$$

Thus a measurement of the observable always produces the result a_n which implies that the uncertainty of the observable vanishes for this state $\Delta A = 0$. Furthermore the measurement leaves the state unchanged, the system remains in the eigenstate

$$|\psi_n\rangle \xrightarrow{A} |\psi_n\rangle. \quad (4.24)$$

If the system, however, is in a general state $|\psi\rangle$, which is a superposition of eigenstates, the expectation value is given by the sum of all eigenvalues, weighted with the modulus squared of the expansion coefficients

$$\begin{aligned} \langle A \rangle &= \langle \psi | A | \psi \rangle = \sum_n \sum_m \langle c_m \psi_m | A | c_n \psi_n \rangle \\ &= \sum_n \sum_m c_m^* c_n a_n \underbrace{\langle \psi_m | \psi_n \rangle}_{\delta_{mn}} = \sum_n |c_n|^2 a_n. \end{aligned} \quad (4.25)$$

The expansion coefficients $c_n = \langle \psi_n | \psi \rangle$ can thus be regarded as a probability amplitude for the transition from a state ψ to an eigenstate ψ_n when the corresponding observable is measured. The actual transition probability is given by its modulus squared $|c_n|^2$ – the *probability for measuring the result a_n* – which also obeys

$$\sum_n |c_n|^2 = 1. \quad (4.26)$$

So a measurement of an observable in a general state changes the state to one of the eigenstates of the observable. This process is often called the *reduction* or *collaps of the wave function*

$$|\psi\rangle \xrightarrow{A} |\psi_n\rangle. \quad (4.27)$$

4.4 Infinite Potential Well

Our goal in the next sections is to calculate the energy eigenvalues and eigenfunctions for several Hamiltonians, i.e. for several potentials. Let us begin with the infinite potential well, represented by the potential $V(x)$, as illustrated in Fig. 4.1, such that

$$V(x) = \begin{cases} 0 & \text{for } x \in [0, L] \\ \infty & \text{else} \end{cases} \quad (4.28)$$

This means that the quantum object is limited to a certain region between $x = 0$ and $x = L$ where it moves freely but cannot ever leave. Thus mathematically we have

$$\psi(x) = 0 \quad \text{for } x \notin [0, L]. \quad (4.29)$$

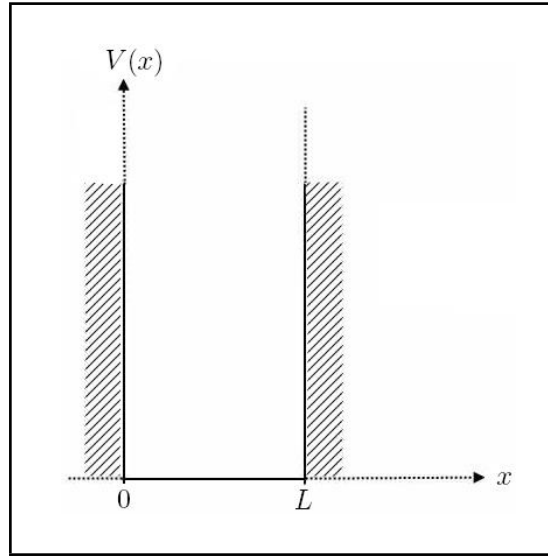


Figure 4.1: Infinite potential well: The potential is infinite outside the interval $[0, L]$, inside it vanishes. Therefore the only physically allowed region for a particle is inside the interval.

Furthermore, for the wave function to be continuous we have to require that it vanishes at the boundaries

$$\psi(0) = \psi(L) = 0. \quad (4.30)$$

The only region where particles are allowed is inside the well, where they behave like free particles, i.e. they are not exposed to a potential. Therefore we need to solve the free (time-independent) Schrödinger equation with the boundary conditions from Eq. (4.30)

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E \psi(x). \quad (4.31)$$

With the abbreviation

$$k^2 = \frac{2mE}{\hbar^2}, \quad k = \frac{\sqrt{2mE}}{\hbar} \quad (4.32)$$

the free Schrödinger equation takes the following form

$$\frac{d^2}{dx^2} \psi(x) = -k^2 \psi(x), \quad (4.33)$$

where the general solution is well known, and given by

$$\psi(x) = a \sin(kx) + b \cos(kx). \quad (4.34)$$

Here a and b are some constants that are yet to be determined by the boundary conditions, starting with $\psi(0) = 0$

$$0 = \psi(0) = a \underbrace{\sin(0)}_0 + b \cos(0) \quad \Rightarrow \quad b = 0. \quad (4.35)$$

Exploiting the second boundary condition $\psi(L) = 0$, leads to discrete values of k

$$0 = \psi(L) = a \sin(kL) \quad \Rightarrow \quad kL = n\pi \quad \Rightarrow \quad k = \frac{n\pi}{L}, \quad (4.36)$$

where $n = 1, 2, 3, \dots$ can be any natural number. Inserting our result into Eq. (4.32) and solving it with respect to E we see that the *energy is quantized*. Labeling the several energy levels by n we find

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}. \quad (4.37)$$

Finally, the value of the constant a follows from the normalization of the wave function

$$\int_0^L dx |\psi|^2 = 1 \quad \Rightarrow \quad |a|^2 \int_0^L dx \sin^2\left(\frac{n\pi}{L}x\right) = 1 \quad \Rightarrow \quad |a|^2 = \frac{2}{L}. \quad (4.38)$$

Thus the bound states of the infinite potential well, which form a CONS, are then given by

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right). \quad (4.39)$$

For $n = 1$ we get the ground state energy and wave function E_1, ψ_1 of the infinite potential well, the higher states with $n > 1$ are called *excited states*.

4.5 Finite Potential Well

We now study a similar problem as in Section 4.4, but with the change that the potential walls are no longer infinitely high. Classically, a particle is trapped within the box, if its energy is lower than the height of the walls, i.e., it has zero probability of being found outside the box. We will see here that, quantum mechanically, the situation is different.

The time-independent Schrödinger equation is again our starting point where we now insert the following potential $V(x)$ into our Hamiltonian

$$V(x) = \begin{cases} -V_0 & \text{for } |x| \leq L \\ 0 & \text{for } |x| > L \end{cases} \quad (4.40)$$

For the possible energy range $E > -V_0$ we consider separately the two energy regions, $-V_0 < E < 0$ for the *bound states* and $E > 0$ for the *scattered states*. We also split the whole x -range into the three regions I, II, and III, where we solve the equations separately.

4.5.1 Bound States

Region I: $x < -L$, $V(x) = 0$

Here we have again the free Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E \psi(x), \quad (4.41)$$

which we rewrite by substituting $\kappa = \frac{1}{\hbar} \sqrt{-2mE}$, where $\kappa > 0$ because $E < 0$,

$$\frac{d^2}{dx^2} \psi(x) = \kappa^2 \psi(x). \quad (4.42)$$

We already know that the general solution of Eq. (4.42) is given by

$$\psi(x) = A e^{-\kappa x} + B e^{\kappa x}, \quad (4.43)$$

where A and B are constants, yet to be determined. Since we are in the region where $x < -L < 0$ the exponent of the first term would ever increase for $x \rightarrow -\infty$. In order to keep the wave function normalizable we must demand that the constant A be identically zero, and we get as solution for region I

$$\psi(x) = B e^{\kappa x}. \quad (4.44)$$

Region II: $-L \leq x \leq L$, $V(x) = -V_0$

In this region acts the potential and we have

$$\text{Schrödinger equation:} \quad \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} - V_0 \right) \psi(x) = E \psi(x), \quad (4.45)$$

which, by introducing a new constant q , becomes the equation

$$\frac{d^2}{dx^2} \psi(x) = -q^2 \psi(x) \quad q = \frac{1}{\hbar} \sqrt{2m(E + V_0)} > 0, \quad (4.46)$$

with the general solution

$$\psi(x) = \bar{C} e^{-iqx} + \bar{D} e^{iqx} = C \sin(qx) + D \cos(qx). \quad (4.47)$$

Again, $C = i(\bar{D} - \bar{C})$ and $D = \bar{C} + \bar{D}$ are some constants.

Region III: $x > L$, $V(x) = 0$

Here we have the same case as in region I with the Schrödinger equation (4.41) and general solution

$$\psi(x) = F e^{-\kappa x} + G e^{\kappa x}. \quad (4.48)$$

But now, in order to keep the wave function normalizable we have to set $G = 0$ otherwise the corresponding exponent would ever increase for increasing x . We thus get as solution of region III

$$\psi(x) = F e^{-\kappa x}. \quad (4.49)$$

Summary: Let's summarize the solutions for the energy range $-V_0 < E < 0$. We have

$$\psi(x) = \begin{cases} B e^{\kappa x} & \text{in region I} \\ C \sin(qx) + D \cos(qx) & \text{in region II} \\ F e^{-\kappa x} & \text{in region III} \end{cases} \quad (4.50)$$

Remark: The motion of a classical particle with energy $E < 0$ is strictly confined to region II. A quantum mechanical particle, however, can penetrate into the classically forbidden regions I and III, i.e. the probability density is non-vanishing, $|\psi(x)|^2 \neq 0$. How far the particle can penetrate depends on the respective energy, it can reach a depth of about

$$\Delta x \propto \frac{1}{\kappa} = \frac{\hbar}{\sqrt{-2mE}} \longrightarrow 0 \text{ for } |E| \longrightarrow \infty, \quad (4.51)$$

which vanishes for large energies in deep potentials. Accordingly, there exists a momentum uncertainty which a classical particle would need to overcome the potential barrier

$$\Delta p \propto \frac{\hbar}{\Delta x} = \sqrt{-2mE}. \quad (4.52)$$

If we now remember Theorem 4.2 we can conclude that for the symmetric potential defined in Eq. (4.40) there is a family of even and odd solutions, which we will call $\psi^{(+)}(x)$ and $\psi^{(-)}(x)$, sketched in Fig. 4.2

$$\psi^{(+)}(x) = \begin{cases} B e^{\kappa x} & \text{I} \\ D \cos(qx) & \text{II} \\ B e^{-\kappa x} & \text{III} \end{cases} \quad \psi^{(-)}(x) = \begin{cases} -B e^{\kappa x} & \text{I} \\ C \sin(qx) & \text{II} \\ B e^{-\kappa x} & \text{III} \end{cases} \quad (4.53)$$

At the boundaries of the potential well the functions that are solutions in their respective areas need to merge smoothly into each other. Mathematically this means, that the total wave function needs to be smooth, i.e. the values as well as the first derivatives of the respective partly solutions must match at $\pm L$.

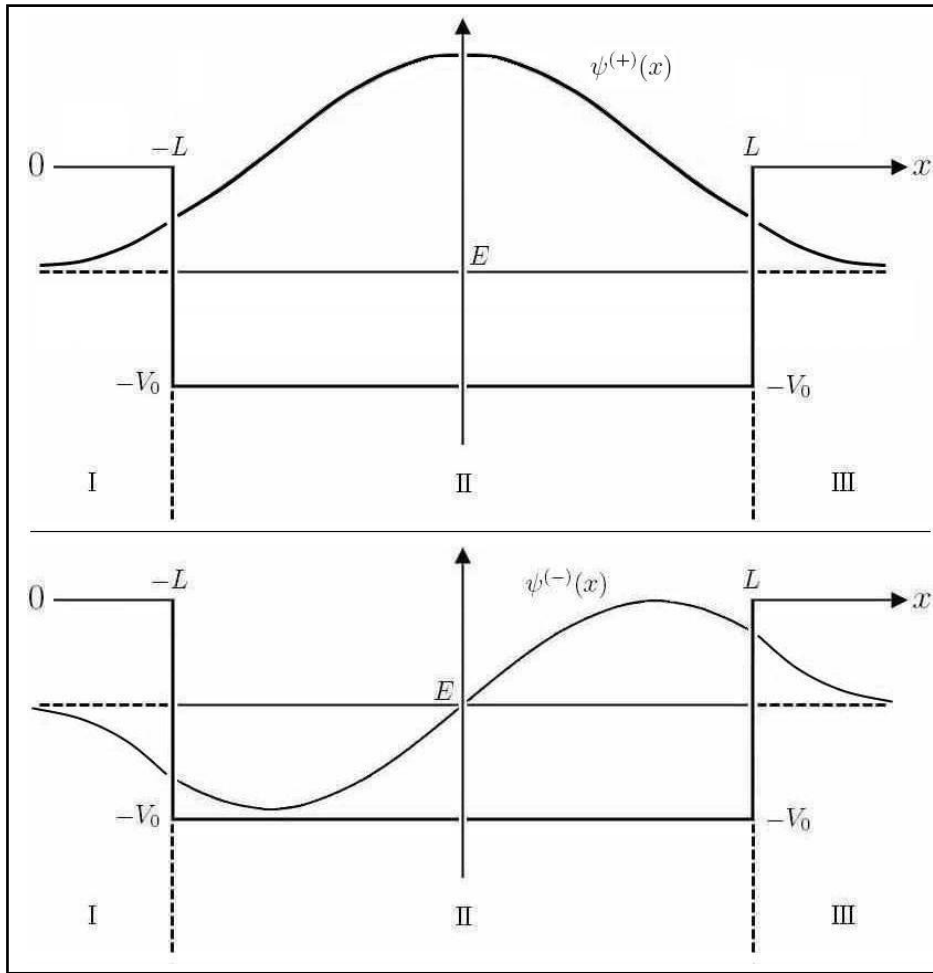


Figure 4.2: Bound state solutions: The bound states can be split into even and odd solutions, both solutions together with their first derivatives must be continuous with respect to x .

We can summarize these two requirements into the statement, that the *logarithmic derivative* of the wave function must be continuous

$$\text{logarithmic derivative: } \frac{d}{dx} \ln(\psi(x)) = \frac{\psi'(x)}{\psi(x)} \text{ continuous.} \quad (4.54)$$

For the even solutions¹ this translates to

$$\left. \frac{\psi^{(+)\prime}(x)}{\psi^{(+)}(x)} \right|_{x \rightarrow L} \Rightarrow \frac{-Dq \sin(qL)}{D \cos(qL)} = \frac{-B\kappa e^{-\kappa L}}{B e^{-\kappa L}}. \quad (4.55)$$

Eq. (4.55) can then easily be rewritten as

$$q \tan(qL) = \kappa. \quad (4.56)$$

¹It does not matter here whether one chooses the boundary between regions I and II or II and III, the result is the same.

Since κ and q depend on the energy E via

$$\kappa = \frac{1}{\hbar} \sqrt{-2mE} \quad , \quad q = \frac{1}{\hbar} \sqrt{2m(E - V_0)} \quad (4.57)$$

Eq. (4.56) becomes a formula for the permitted energies, a *quantization condition*.

The analogous calculation as in Eq. (4.55) can be done for the odd solutions, which then gives the corresponding condition for the odd states

$$q \cot(qL) = -\kappa. \quad (4.58)$$

Graphical solution: The two equations (4.56) and (4.58) are so called *transcendental equations*, which means that they can only be written in implicit form. Solutions to this group of equations can be found numerically or graphically, the latter of which we will do here, but not analytically. However before we do so, we will introduce new (dimensionless) variables z, z_0 to simplify the calculation

$$z := qL \quad , \quad z_0 := \frac{L}{\hbar} \sqrt{2mV_0}. \quad (4.59)$$

To relate our old variables κ and q to the new ones, we first look at

$$\kappa^2 + q^2 = \frac{-2mE}{\hbar^2} + \frac{2m(E + V_0)}{\hbar^2} = \frac{2mV_0}{\hbar^2}, \quad (4.60)$$

which we multiply with L^2 to get

$$\begin{aligned} \Rightarrow \kappa^2 L^2 + \underbrace{q^2 L^2}_{z^2} = z_0^2 &\Rightarrow \frac{\kappa^2 L^2}{q^2 L^2} = \frac{z_0^2 - z^2}{z^2} = \left(\frac{z_0}{z}\right)^2 - 1 \\ \Rightarrow \frac{\kappa}{q} = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1} &\Rightarrow \text{insert in Eq. (4.56)} \end{aligned} \quad (4.61)$$

$$\tan z = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1}. \quad (4.62)$$

We can now study this graphically by plotting both the left hand and the right hand function for given values of z_0 , e.g. for L, m and V_0 chosen such that², see Fig. 4.3,

$$z_0 = \frac{L}{\hbar} \sqrt{2mV_0} = 8. \quad (4.63)$$

²Keep in mind that z_0 is dimensionless.

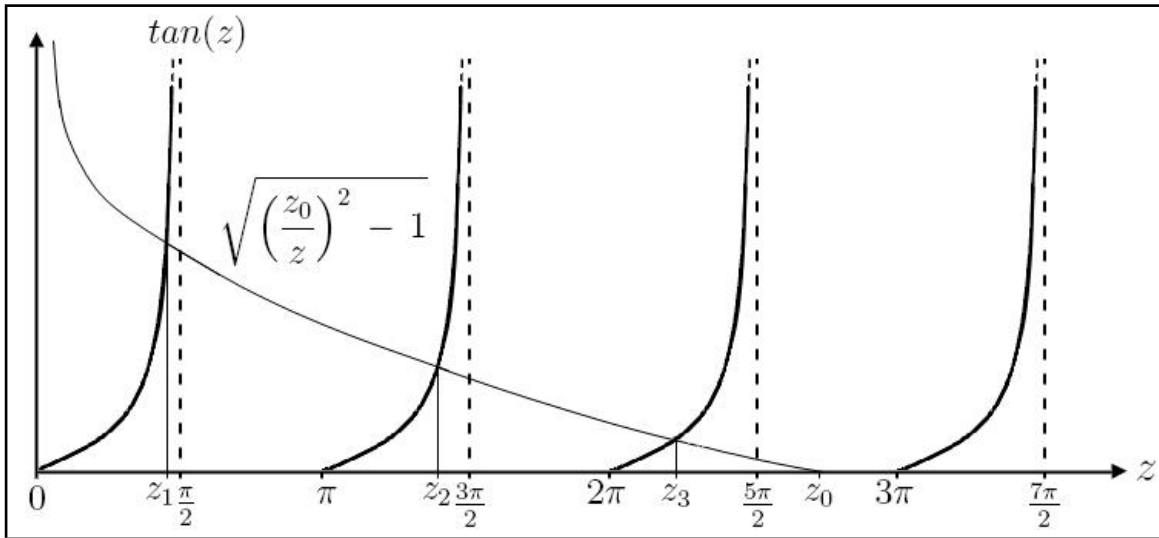


Figure 4.3: Graphic solution of transcendental equation (4.62): The equation cannot be solved analytically, thus both sides are plotted for the given parameter $z_0 = 8$. The intersections then lead to the allowed values of z .

For the chosen parameter we have three solutions $z_1 = 0,8 \times \frac{\pi}{2}$, $z_2 = 2,6 \times \frac{\pi}{2}$ and $z_3 = 4,25 \times \frac{\pi}{2}$ such that $E = E_n$, $n = 1, 2, 3$, from

$$z_n = q_n L = \frac{1}{\hbar} \sqrt{2m(E_n + V_0)}. \quad (4.64)$$

For increasing parameters L and V_0 the value of z_0 grows as well and we obtain more bound states. We could now repeat the same procedure for the odd states by replacing $\tan z$ with $-\cot z$ (recall Eq. (4.58)), which is the same function but shifted by $\frac{\pi}{2}$, so we will skip this calculation and use qualitative statements about the energies of the odd solutions later on.

Special cases: Let us now study some limits of the graphical solutions, where we can find analytical approximations to our problem.

Case I: Broad & deep potential well: For big values for L and V_0 the quantity z_0 also reaches higher values and the intersections with the tangens-curves get even closer to the singularities $(2k + 1)\frac{\pi}{2}$, where k is natural number

$$z_{2k+1}^2 \approx (2k + 1) \frac{\pi}{2}, \quad (4.65)$$

which turns into

$$z_{2k+1}^2 = (q_{2k+1} L)^2 \longrightarrow \frac{L^2}{\hbar^2} 2m(E_{2k+1} + V_0) \approx \frac{(2k + 1)^2 \pi^2}{4}. \quad (4.66)$$

Thus we can express the corresponding energies as

$$E_{2k+1} + V_0 \approx \frac{(2k + 1)^2 \pi^2 \hbar^2}{2m(2L)^2}. \quad (4.67)$$

Since we already concluded, that the feature of the odd solutions is to shift the tangens by $\frac{\pi}{2}$, we can easily deduce that in the limit of very large z_0 the intersections will get close to the singularities of the cotangens, which are given by integer multiples of π

$$\psi^{(-)} : \quad E_{2k} + V_0 \approx \frac{(2k)^2 \pi^2 \hbar^2}{2m(2L)^2}. \quad (4.68)$$

We can then summarize all solutions to the formula

$$E_n + V_0 \approx \frac{(n)^2 \pi^2 \hbar^2}{2m(2L)^2}, \quad (4.69)$$

which is the expression for the infinite potential well (see Eq. (4.37)), if we keep in mind that the energy scales we used differ by V_0 and the width of the potential well is here $2L$ instead of L .

Case II: Narrow & small potential well: We now consider small values for L and V_0 , which reduces z_0 as well and we finally push its value under $\frac{\pi}{2}$, see Fig. 4.4.

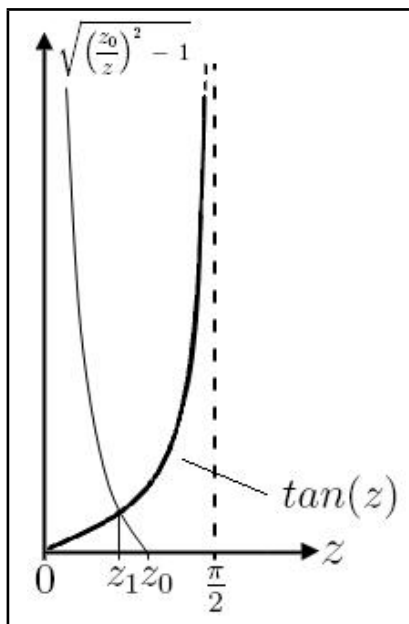


Figure 4.4: Graphic solution of small potential well: However small the parameter z_0 gets, an intersection of the functions always remains, thus always allowing at least one bound state.

Remark: The finite potential well in one dimension always has a bound state, but this is not generally the case for all dimensions. The 3-dimensional Schrödinger equation does not automatically allow for a bound state in such a problem. Though the equation can be rewritten in terms of the radius r , and thus get reduced to a 1-dimensional problem, the radius however is defined on \mathbb{R}^+ in contrast to $x \in \mathbb{R}$. The ground state then is an

odd wave function (see Fig. 4.5) which is the equivalent of the first excited state in our problem, and therefore can get "pushed" out if the parameters are too small.

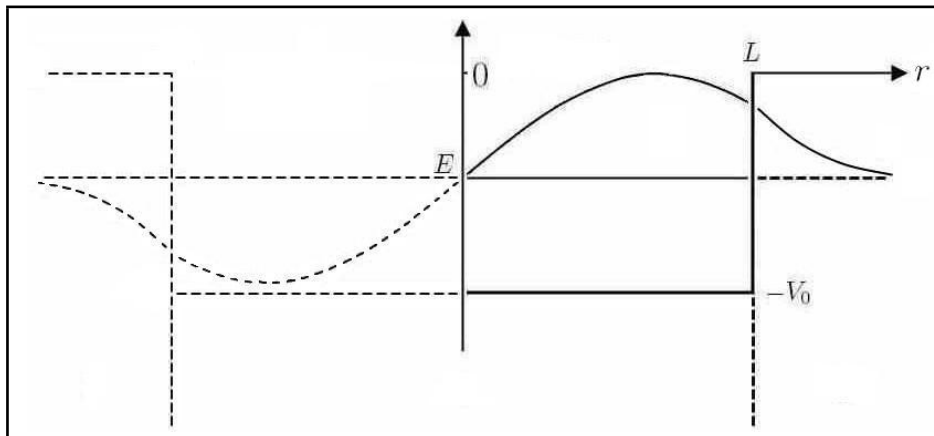


Figure 4.5: Potential well in three dimensions: The 3-dimensional problem can be reduced to a 1-dimensional problem in r , but the reduced wave function of the ground state then is an odd function, because r is only defined on \mathbb{R}^+ .

Let us now return again to the even and odd wavefunctions, Eq. (4.53), where we still have to determine the constants B , C and D . We first use the continuity at $x = L$ to get the equations

$$\psi^{(+)} : D \cos(q_n L) = B e^{-\kappa_n L} \quad , \quad \psi^{(-)} : C \sin(q_n L) = B e^{-\kappa_n L} \quad , \quad (4.70)$$

providing us with

$$D = B \frac{e^{-\kappa_n L}}{\cos(q_n L)} \quad , \quad C = B \frac{e^{-\kappa_n L}}{\sin(q_n L)} \quad . \quad (4.71)$$

Finally we obtain the constant B from the normalization

$$B_n = \frac{\cos(q_n L)}{\sqrt{1 + \kappa_n L}} e^{-\kappa_n L} \quad \Rightarrow \quad C_n = D_n = \frac{1}{\sqrt{1 + \kappa_n L}} \quad . \quad (4.72)$$

Physical interpretation of the finite potential well: An application for the finite potential well is the model for free electrons in metal, used in solid state physics. There the atoms of the metal crystal "share" the electrons which are thus free to move inside the metal, but face a potential barrier, which keeps them inside. Thus in a first approximation, the finite (square) potential well is a good model for the situation, see Fig. 4.6.

To release one electron from the metal, the energy W must be invested. This is the work function, we encountered in Section 1.2.3, which we can calculate³ with the formula

$$W = V_0 - E_n \quad , \quad (4.73)$$

³Keep in mind, that we rescaled the energy here in contrast to our previous calculations, the potential V_0 as well as the energies of the bound states are positive here.

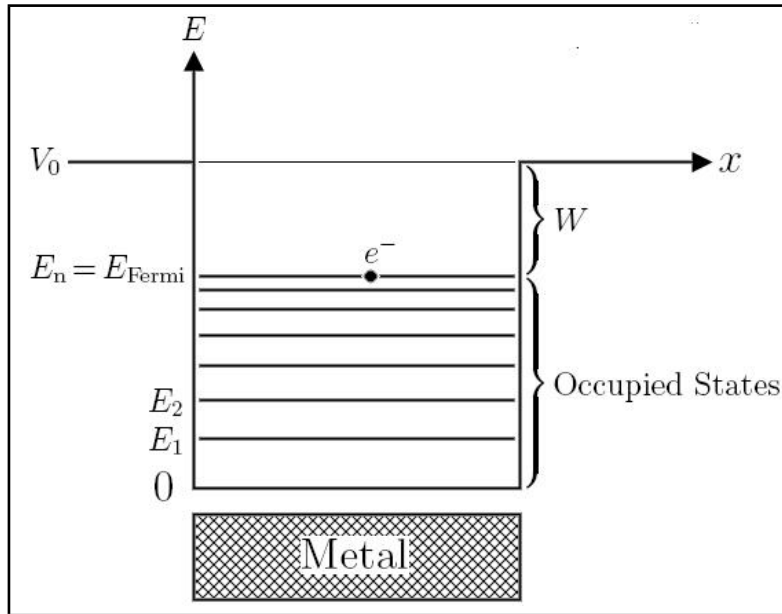


Figure 4.6: Potential model for electrons in metal: The electrons are free inside the metal, occupying the states up to a certain energy level E_n . In order to separate an electron from the metal, one needs to overcome the energy difference W , the work function.

where E_n is the highest⁴ occupied energy level.

4.5.2 Scattered States

We will now investigate the Schrödinger equation, including the potential from Eq. (4.40) for positive energies $E > 0$. We will assume that an initial plane wave travels from $x = -\infty$ to our potential and study the possible states that are not bound but scattered, i.e. transmitted or reflected by the potential, see Fig. 4.7. As before we will analyze our problem for the regions I, II and III separately before combining our results.

Region I: $x < -L$, $V(x) = 0$

In this region we have to solve the free Schrödinger equation

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi = -k^2\psi \quad \text{where} \quad k^2 = \frac{2mE}{\hbar^2}. \quad (4.74)$$

⁴The electrons in the metal are *fermions*, particles with half integer spin / antisymmetric wave function. Therefore they are subject to the *Pauli Exclusion Principle*, stating that no more than one of them can occupy the same quantum state. Thus at temperature $T = 0$ the states of the potential well are filled one by one from the bottom of the well to a certain energy level, named the *Fermi Energy*, creating the so called Fermi Sea.

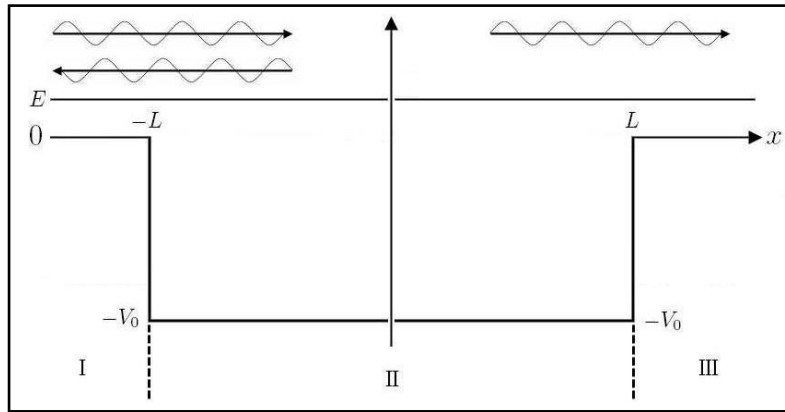


Figure 4.7: Scattered states of the finite potential well: The quantum mechanical potential well can either reflect or transmit an incoming state with energy $E > 0$, whereas classically only the transmission is possible.

Like in Eq. (4.46) we can write down the general solution to this equation as

$$\psi(x) = \underbrace{A e^{i k x}}_{\text{incoming}} + \underbrace{B e^{-i k x}}_{\text{reflected}} \quad \text{with} \quad k = \frac{1}{\hbar} \sqrt{2 m E} > 0. \quad (4.75)$$

Region II: $-L \leq x \leq L$, $V(x) = -V_0$

In total analogy to the case for bound states, Eq. (4.45), we get in region II

$$\psi(x) = C \sin(qx) + D \cos(qx) \quad q = \frac{1}{\hbar} \sqrt{2m(E + V_0)} > 0. \quad (4.76)$$

Region III: $x > L$, $V(x) = 0$

Here we have exactly the situation as in region I, and can thus easily write down the solution as in Eq. (4.75) with new constants F and G , but we set $G \equiv 0$ since we assume no reflection at infinity (the associated solution would represent a wave traveling from right to left).

$$\psi(x) = \underbrace{F e^{i k x}}_{\text{transmitted}}. \quad (4.77)$$

Summarizing our solutions we have

$$\psi(x) = \begin{cases} A e^{i k x} + B e^{-i k x} & \text{I} \\ C \sin(qx) + D \cos(qx) & \text{II} \\ F e^{i k x} & \text{III} \end{cases} \quad (4.78)$$

where the constants A , B and F now characterize the incoming, reflected and transmitted parts of our solution respectively. We then regard the boundary conditions, i.e. the

continuity of the wave function and its first derivative at the edges of the potential wall

$$\psi(x) \xrightarrow{x \rightarrow -L} A e^{-ikL} + B e^{ikL} = -C \sin(qL) + D \cos(qL) \quad (4.79)$$

$$\psi'(x) \xrightarrow{x \rightarrow -L} ik (A e^{-ikL} - B e^{ikL}) = q (C \cos(qL) + D \sin(qL)) \quad (4.80)$$

$$\psi(x) \xrightarrow{x \rightarrow +L} C \sin(qL) + D \cos(qL) = F e^{ikL} \quad (4.81)$$

$$\psi'(x) \xrightarrow{x \rightarrow +L} q (C \cos(qL) - D \sin(qL)) = ik F e^{ikL} . \quad (4.82)$$

Together with the normalization condition we thus have 5 equations for our 5 variables A , B , C , D and F . To solve this system of equations we start by calculating

$$\begin{aligned} \text{Eq. (4.81)} \cdot \sin(qL) + \text{Eq. (4.82)} \cdot \frac{1}{q} \cos(qL) &\Rightarrow \\ \underbrace{(\sin^2(qL) + \cos^2(qL))}_1 C &= C = \left(\sin(qL) + i \frac{k}{q} \cos(qL) \right) F e^{ikL} \end{aligned} \quad (4.83)$$

$$\begin{aligned} \text{Eq. (4.81)} \cdot \cos(qL) + \text{Eq. (4.82)} \cdot \frac{1}{q} \sin(qL) &\Rightarrow \\ \underbrace{(\cos^2(qL) + \sin^2(qL))}_1 D &= D = \left(\cos(qL) - i \frac{k}{q} \sin(qL) \right) F e^{ikL} . \end{aligned} \quad (4.84)$$

Then we insert the results for C and D into Eq. (4.79) and Eq. (4.80) to get A and B in dependence of F

$$\begin{aligned} A e^{-ikL} + B e^{ikL} &= -\text{Eq. (4.83)} \cdot \sin(qL) + \text{Eq. (4.84)} \cdot \cos(qL) \\ &= \left(-\sin^2(qL) - 2i \frac{k}{q} \sin(qL) \cos(qL) + \cos^2(qL) \right) F e^{ikL} . \end{aligned} \quad (4.85)$$

Using the following identities we can then rewrite Eq. (4.85)

$$\cos^2 x - \sin^2 x = \cos(2x) \quad , \quad 2 \sin x \cos x = \sin(2x) \quad (4.86)$$

$$\Rightarrow A e^{-2ikL} + B = \left(\cos(2qL) - i \frac{k}{q} \sin(2qL) \right) F , \quad (4.87)$$

and applying the same procedure for Eq. (4.80) gives

$$\begin{aligned} ik (A e^{-ikL} - B e^{ikL}) &= q (\text{Eq. (4.83)} \cdot \cos(qL) + \text{Eq. (4.84)} \cdot \sin(qL)) \\ &= \left(i \frac{k}{q} \cos^2(qL) + 2 \sin(qL) \cos(qL) - i \frac{k}{q} \sin^2(qL) + \right) F e^{ikL} \end{aligned} \quad (4.88)$$

$$\text{Eq. (4.86)} \Rightarrow A e^{-2ikL} - B = -i \frac{q}{k} \left(\sin(2qL) + i \frac{k}{q} \cos(2qL) \right) F . \quad (4.89)$$

At last we subtract Eq. (4.88) from Eq. (4.87) to get the coefficient B , which characterizes the reflection from the potential well

$$\text{Eq. (4.87)} - \text{Eq. (4.88)} = 2B = i \left(\frac{q}{k} - \frac{k}{q} \right) \sin(2qL) F \quad (4.90)$$

$$\Rightarrow \frac{B}{F} = i \frac{q^2 - k^2}{2kq} \sin(2qL) \quad \text{reflexion/transmission amplitude} . \quad (4.91)$$

This can be understood as a balance between the reflected and the transmitted part of the wave function. To get the probability for the reflection or transmission we have to normalize each part by the amplitude of the incoming wave and to take the modulus squared of each expression. We also want to express the quantities q and k by the more familiar constants m , \hbar and V_0 , using Eq. (4.75) and Eq. (4.76)

$$(q^2 - k^2)^2 = \frac{1}{\hbar^4} (2m(E + V_0) - 2mE)^2 = \frac{(2m)^2 V_0^2}{\hbar^4} \quad (4.92)$$

$$4q^2 k^2 = 4 \frac{1}{\hbar^4} (2m)^2 E(E + V_0) . \quad (4.93)$$

Thus we find for the **reflection coefficient** $R(E)$ describing the probability of reflection

$$R(E) = \frac{|B|^2}{|A|^2} = \frac{V_0^2}{4E(E + V_0)} \sin^2(2qL) \frac{|F|^2}{|A|^2} \neq 0 . \quad (4.94)$$

We conclude that there is a nonzero possibility for a reflection of the wave at the potential well, a purely quantum mechanical effect that is not possible classically.

The reflection, of course, is related to the transmission of the wave. Focussing on the transmission, we can calculate the *transmission coefficient* $T(A) = \frac{|F|^2}{|A|^2}$ which rates the transmitted against the incoming intensity. We first calculate the sum of Eq. (4.87) and Eq. (4.88) to get the *transmission amplitude*

$$\begin{aligned} \text{Eq. (4.87)} + \text{Eq. (4.88)} &= A e^{-2ikL} = 2 \left(\cos(2qL) - i \sin(2qL) \frac{1}{2} \left(\frac{q}{k} + \frac{k}{q} \right) \right) F \\ \Rightarrow \frac{F}{A} &= e^{-2ikL} \left(\cos(2qL) - i \frac{q^2 + k^2}{2kq} \sin(2qL) \right)^{-1} , \end{aligned} \quad (4.95)$$

and by taking the modulus squared and inserting the expressions for q and k (Eq. (4.75) and Eq. (4.76)) we obtain the **transmission coefficient** $T(E)$

$$T(E) = \frac{|F|^2}{|A|^2} = \left(1 + \frac{V_0^2}{4E(E + V_0)} \sin^2(2qL) \right)^{-1}. \quad (4.96)$$

Of course, both coefficients are related by

$$R(E) + T(E) = 1. \quad (4.97)$$

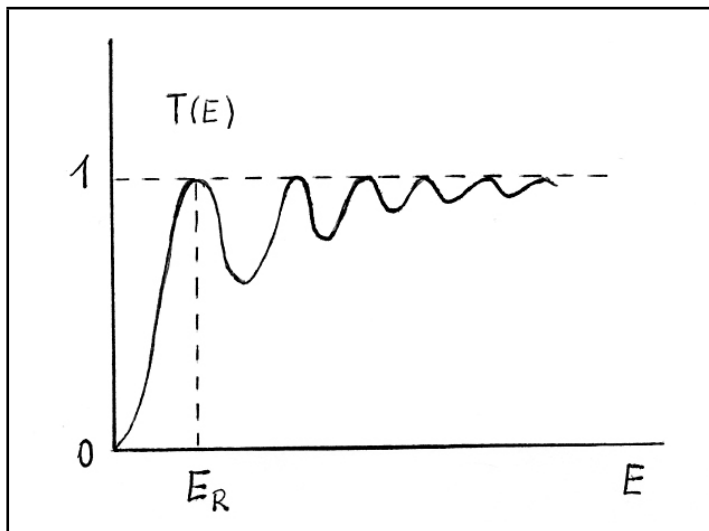


Figure 4.8: Transmission coefficient: The transparency of the well, Eq. (4.96), is plotted as a function of the energy showing the positions E_R of the resonances.

Studying the transmission coefficient we easily see that for some arguments the sinus function will be zero and thus the probability for transmission equal to one, $T = 1$, see Fig. 4.8. To find the corresponding energies we simply look for the roots of the sinus, finding the following condition

$$\sin(2qL) = 0 \quad \Rightarrow \quad \frac{2L}{\hbar} \sqrt{2m(E + V_0)} = n\pi, \quad (4.98)$$

where $n \in \mathbb{N}$ labels the energies. We thus get the positions of the **resonances** of a finite potential well, the energies for which it becomes transparent, as

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2m(2L)^2} - V_0. \quad (4.99)$$

These resonance positions, interestingly, happen to be precisely at the allowed energy levels of the infinite potential well (see Eq. (4.37) and the remarks accompanying Eq. (4.69)). Accordingly, the minima of transmission can be found by using the condition

$$\sin(2qL) = \pm 1 \quad \Rightarrow \quad \frac{2L}{\hbar} \sqrt{2m(E + V_0)} = (2n + 1) \frac{\pi}{2}. \quad (4.100)$$

We can also conclude, that the resonances become more distinct the deeper the potential.

At last let us study the transmission coefficient in the vicinity of the resonant energies. To this end we go back to the transmission amplitude Eq. (4.95), where we expand the denominator in a Taylor series around the resonant energies, calculating the first two terms of the expansion individually

$$\left(\cos(2qL) - i \frac{q^2 + k^2}{2kq} \sin(2qL) \right)_{E=E_R} = \cos(n\pi) = \pm 1. \quad (4.101)$$

We can easily see that, obeying the condition of Eq. (4.98), all terms containing $\sin(2qL)$ evaluated at $E = E_R$ vanish, while the cosine of this argument gives ± 1 . Also the second order can then be calculated easily

$$\begin{aligned} \frac{d}{dE} \left(\cos(2qL) - i \frac{q^2 + k^2}{2kq} \sin(2qL) \right)_{E=E_R} &= \\ &= \left(-i \frac{q^2 + k^2}{2kq} \frac{d(2qL)}{dE} \right)_{E=E_R} \underbrace{\cos(n\pi)}_{\pm 1} = \\ &= \mp i \left(\frac{q^2 + k^2}{2kq} \frac{d(2qL)}{dE} \right)_{E=E_R} =: \mp i \frac{2}{\Gamma}. \end{aligned} \quad (4.102)$$

Neglecting all higher terms the expansion of the denominator then is of the form

$$\pm 1 \mp i \frac{2}{\Gamma} (E - E_R) + \dots \approx \frac{2}{\Gamma} \left(\pm \frac{\Gamma}{2} \mp i (E - E_R) \right). \quad (4.103)$$

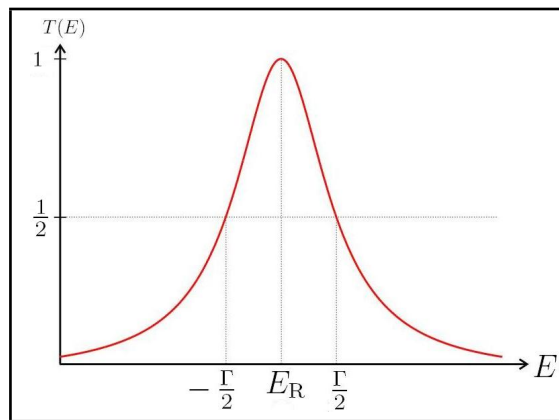


Figure 4.9: Breit–Wigner distribution: The distribution with height 1 and width Γ at half maximum is also known as Cauchy distribution in stochastics and as Breit–Wigner- or Lorentz distribution in physics; figure from http://de.wikipedia.org/w/index.php?title=Bild:Breitwig_fig.png&filetimestamp=20050622183322

Reinserting expression (4.103) as the denominator of Eq. (4.95) and taking the modulus squared to get the corresponding transmission coefficient we arrive at the expression valid near the resonances

$$T(E) = \frac{\frac{\Gamma^2}{4}}{(E - E_R)^2 + \frac{\Gamma^2}{4}}. \quad (4.104)$$

This is the well-known **Breit–Wigner distribution**, also known as Lorentz- or Cauchy distribution, which describes resonance phenomena⁵. The quantity Γ represent the width at half maximum of the distribution and is proportional to the inverse lifetime of the resonance, $\Gamma = \tau^{-1}$, see Fig. 4.9.

As a simple explanation of the resonances of the finite potential well, we may regard them as destructive interference between the waves reflected at $x = L$ and $x = -L$, sketched in Fig. 4.10.

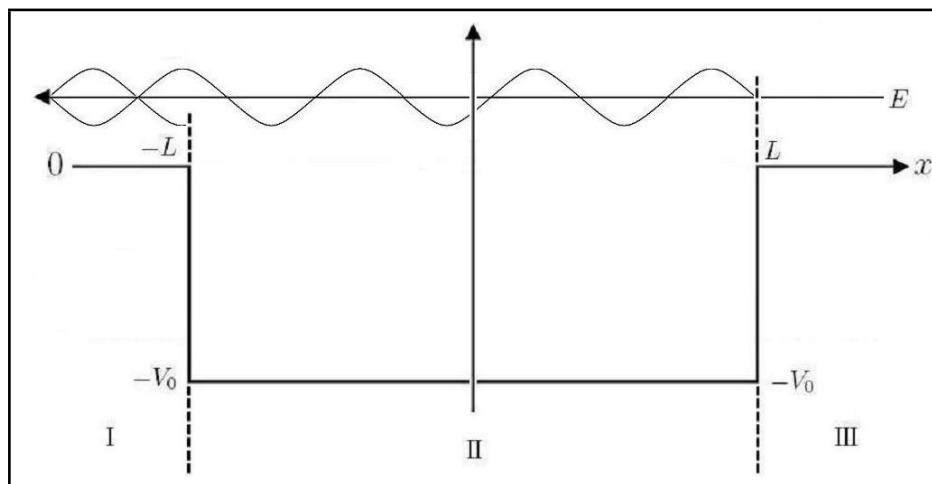


Figure 4.10: Interference of reflected waves: The resonances of the finite potential well can be regarded as interference of the reflected waves, thus permitting free transmission.

Experiment: Ramsauer–Townsend effect

The resonance of transmission can be nicely seen in the scattering of slow electrons in a noble gas (e.g. Ne, Ar, Xe) which has been studied independently by C. Ramsauer and J.S. Townsend in the 1920's. The probability for the electrons to collide with the gas particles, which classically should decrease monotonically for increasing energy, is observed to reach local minima for certain energies. This effect is in total agreement with the quantum mechanical prediction of the transparency of the potential well for the resonance energies.

⁵E.g. the forced resonance of a driven oscillator or energy resonances in particle physics describing unstable particles, where the lifetime is proportional to the inverse of the width.

4.6 Tunnel Effect

4.6.1 Finite Potential Barrier

The so-called tunnel effect of quantum mechanics can be derived from a special case of the potential well, by changing $-V_0$ into $+V_0$, thus creating a potential barrier, as seen in Fig. 4.11

$$V(x) = \begin{cases} V_0 & \text{for } |x| \leq L \\ 0 & \text{for } |x| > L \end{cases} \quad (4.105)$$

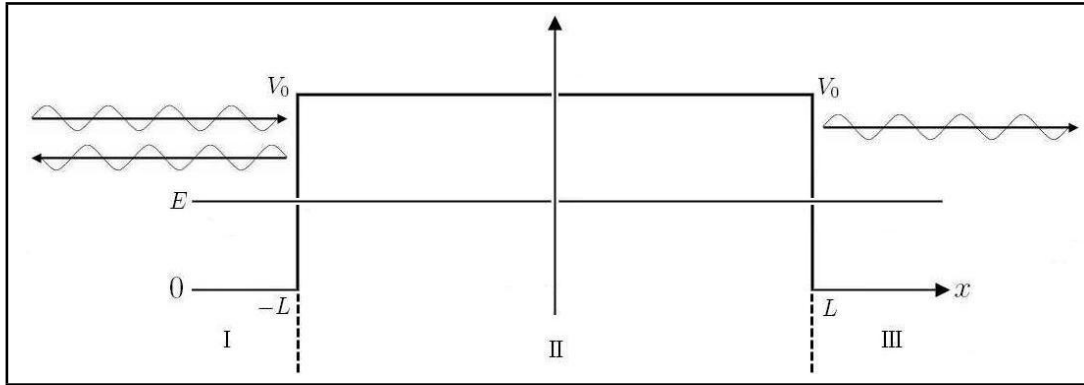


Figure 4.11: Tunnel effect: For a given potential barrier with height V_0 the solutions of the Schrödinger equation with energy $E < V_0$ still have a nonvanishing probability density in region III, which allows them to "tunnel" through the barrier although this would classically be forbidden.

Classically, a particle with less energy than the potential barrier could only be reflected. But in quantum mechanics, due to continuity the wave function decreases exponentially in the forbidden region II, resulting in a nonvanishing probability density in region III. It allows the particle to pass the barrier as if it was through a tunnel, this linguistic illustration gives rise to the name *tunnel effect*.

Mathematically, we can use the solutions from Section 4.5.2, where we replace the $-V_0$ into $+V_0$ changing the solutions in region II

$$\psi(x) = \begin{cases} A e^{i k x} + B e^{-i k x} & \text{I} \\ C e^{-q x} + D e^{q x} & \text{II} \\ F e^{i k x} & \text{III} \end{cases} \quad (4.106)$$

where

$$k = \frac{1}{\hbar} \sqrt{2 m E} > 0 \quad , \quad q = \frac{1}{\hbar} \sqrt{2 m (V_0 - E)} > 0 . \quad (4.107)$$

Since the exponent of the solution in region II is not imaginary anymore, we can replace the sinus and cosinus functions of Section 4.5.2 with their hyperbolic counterparts

$$\sin(2qL) \rightarrow \sinh(2qL) \quad , \quad \cos(2qL) \rightarrow \cosh(2qL) , \quad (4.108)$$

and calculate the missing constants from the continuity requirements as before, which we will however not do explicitly again.

4.6.2 Tunneling – Transmission Coefficient

For the transmission amplitude we get the result

$$\frac{F}{A} = e^{-2ikL} \left(\cosh(2qL) - i \frac{q^2 - k^2}{2kq} \sinh(2qL) \right)^{-1}, \quad (4.109)$$

which, using the identity

$$\cosh^2(x) - \sinh^2(x) = 1, \quad (4.110)$$

gives the transmission coefficient

$$T(E) = \frac{|F|^2}{|A|^2} = \left(1 + \frac{(k^2 + q^2)^2}{4k^2q^2} \sinh^2(2qL) \right)^{-1} \neq 0. \quad (4.111)$$

It can be simplified under the condition that $qL \gg 1$, which is a good approximation in most cases. Then

$$qL \gg 1 \Rightarrow \sin(2qL) \approx \frac{1}{2} e^{2qL}, \quad (4.112)$$

and we can rewrite Eq. (4.111) as

$$T \approx \left(1 + \underbrace{\frac{(k^2 + q^2)^2}{4k^2q^2} \frac{e^{4qL}}{4}}_{\gg 1} \right)^{-1} \approx \frac{16k^2q^2}{(k^2 + q^2)^2} e^{-4qL}. \quad (4.113)$$

We then use Eq. (4.107) to express the transmission coefficient by the energy and potential strength to get

$$T \approx \frac{16E(V_0 - E)}{V_0^2} e^{-4\frac{L}{\hbar} \sqrt{2m(V_0 - E)}}. \quad (4.114)$$

Using $e^x e^y = e^{x+y}$ we can write the whole coefficient as an exponential function

$$\Rightarrow T \approx \exp \left(-4\frac{L}{\hbar} \sqrt{2m(V_0 - E)} + \ln \left(\frac{16E(V_0 - E)}{V_0^2} \right) \right). \quad (4.115)$$

Since we required that qL be much bigger than one and the logarithm increases only very slowly we can conclude that the first term in the exponent outweighs the second one, which we therefore neglect to obtain

$$T \approx e^{-4\frac{L}{\hbar} \sqrt{2m(V_0 - E)}}. \quad (4.116)$$

We now have a good approximation for the transmission probability of a single potential step, constant in certain interval and vanishing outside. This potential is of course

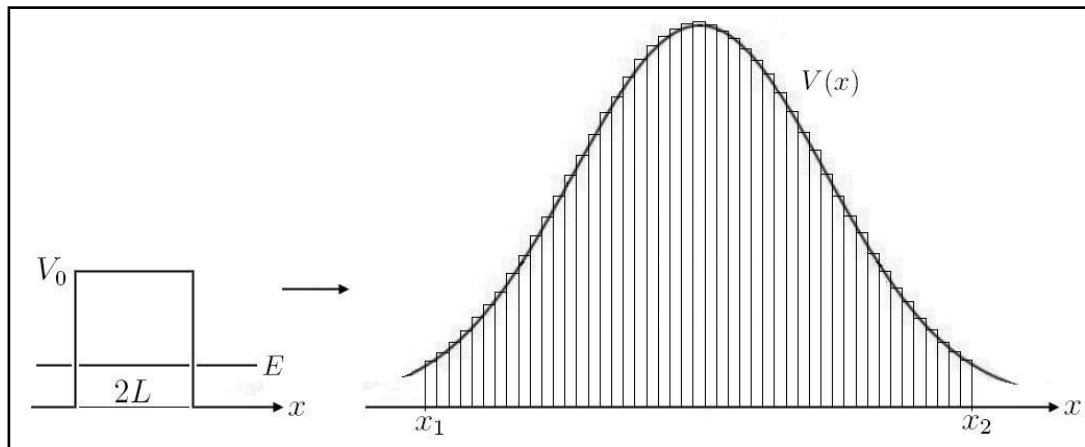


Figure 4.12: Calculation of Gamow factor: The generalization of the transmission coefficient, from a single constant potential barrier with width $2L$, to the incorporation of a function $V(x)$ is done straightforward by integration of infinitesimal potential barriers.

a very crude approximation of real life potentials, which usually are more complicated functions of x . To meet these concerns we can generalize the transmission coefficient of Eq. (4.116) to the so called **Gamow factor** by "chopping" a given potential in infinitesimal potential steps with constant values and integrating over a reasonable range $[x_1, x_2]$ for which the potential stays above a certain value, see Fig. 4.12.

$$T \approx e^{-\frac{2}{\hbar} \int_{x_1}^{x_2} dx \sqrt{2m(V(x) - E)}}. \quad (4.117)$$

4.6.3 Physical Examples of Tunneling

We will now briefly present some examples, where the tunnel effect explains the observed phenomena.

Tunneling between conductors: Imagine two conducting materials, separated by a thin insulating material, sketched in Fig. 4.13. The tunnel effect then allows the electrons to tunnel through that barrier, thus creating a current. This effect is also observed for superconducting materials, where it is named Josephson effect.

Cold emission: Electrons can be emitted from metals at very low temperatures, even without incident light if an exterior electric field is applied. Assuming that the electrons have a very low energy compared to the potential height, it is not very probable that an electron can tunnel through the potential barrier. Only if an electric field raises the energy of the electron, the transmission coefficient increases and the electron emission can be observed.

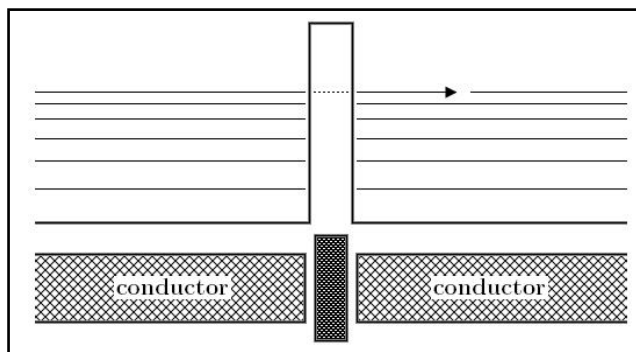


Figure 4.13: Tunneling through insulator: Between two conducting materials, separated by a thin insulating barrier, the tunnel effect creates a current.

Alpha decay: In nuclear physics the tunnel effect plays an important role in the process of alpha decay. In the nucleus two protons and two neutrons can form an alpha-particle, i.e. a ${}^4\text{He}$ nucleus, which due to the energy gain of the binding process, has the required energy to tunnel through the Coulomb-barrier, see Fig. 4.14. E.g. the alpha decay of polonium to lead

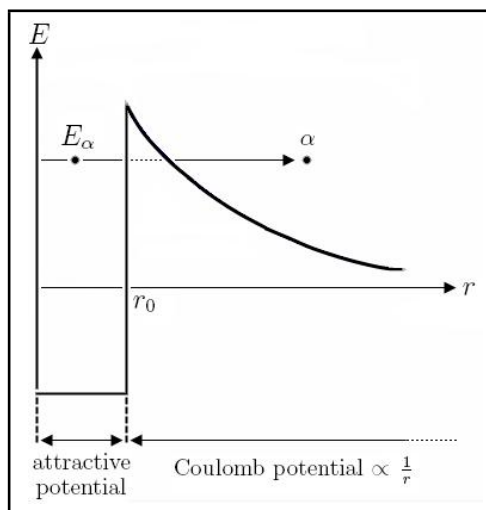


Figure 4.14: Alpha decay: The alpha particle formed in the nucleus has an energy boost due to the mass deficit of the binding process, which allows it to overcome the attractive strong force inside the nucleus and tunnel through the Coulomb barrier.