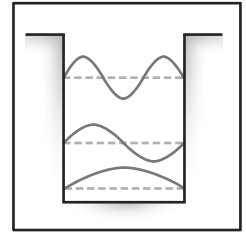


## Project 1

# Rectangular Finite Quantum Well – Stationary Schrödinger Equation in 1D



In this project, participants utilise the procedure of finding roots of functions to solve the eigenvalue problem of a rectangular quantum well (QWELL code). When considering the rectangular quantum well as the simplest model of a hydrogen atom, the code can be applied to determine its first two to three energy levels, which is the primary exercise in the project. The eigenvalue problem itself, appearing in various areas of physics (such as vibration mechanics, wave optics, and quantum mechanics), will be the subject of a separate project (Project 6) and one of the advanced projects (Project 12), where a rectangular quantum well partially filled with electrons is examined. It is somewhat paradoxical that despite employing the simplest mathematical operations in the current project, it is based on advanced physical concepts, such as quantum mechanics, often unfamiliar to first-year students. Learning the basics of quantum mechanics typically requires a 30-hour course and knowledge of advanced mathematics. Therefore, we will only introduce its fundamental and most straightforward ideas here, just enough to enable the conscious execution of the project.

## 1.1 Physics Background: Chosen Ideas of Quantum Mechanics

In quantum mechanics, while the physical quantities of interest, such as position or momentum of a particle, remain the same as in classical physics, their representation is entirely different. Focusing on the problem of a single particle, the central object is the quantum state rather than the coordinates in the chosen system (as it would be in classical physics). In the so-called position representation, the quantum state is a particular function of the position variable  $\psi(r)$ , which, from a mathematical perspective, must meet special conditions of differentiability and integrability. The function itself does not have a physical interpretation, but its squared modulus  $|\psi|^2$  does – it represents the

probability density of finding the particle at a given point in space, that is becomes a probability when multiplied by the volume element (the Born probabilistic interpretation). Here lies the main difference between classical and quantum physics – the probabilistic nature of the latter, with the concept of probability being inherent to the theory. When measuring a physical quantity, the outcome can only be predicted with a certain probability. The deterministic nature of phenomena, justified in classical physics, no longer holds, and this fact was challenging for many physicists to accept during the early stages of quantum theory development. For instance, Albert Einstein proposed the hidden variables hypothesis, suggesting that there are unknown variables that determine the measurement results. Modern interpretations, such as the Copenhagen Interpretation, go even further, positing that a particle can simultaneously exist in multiple positions with different probabilities (which is entirely impossible in the classical world), and only the act of measurement localises it to a specific position (e.g. the role of the measurement instrument is played by the screen in the ‘electron diffraction on a double slit’ experiment). The same concept applies to other physical quantities, meaning that quantum systems can simultaneously exist in various states of a particular quantity (with different probabilities), and during the measurement, the system selects one of these states. Currently, quantum mechanics is a coherent and complete theory, with the Copenhagen Interpretation being widely accepted, and no scientific evidence has emerged to challenge its validity.

The central and historically first equation for evaluating the state function is the Schrödinger equation

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \psi(r, t) = i\hbar \frac{\partial \psi(r, t)}{\partial t}, \quad (1.1.1)$$

where  $\hbar = h/2\pi$ ,  $h$  is Planck’s constant,  $m$  mass of the particle,  $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$  is Laplace’s operator, and  $V(r)$  the particle potential energy.

The equation resembles a wave equation, which is why the function  $\psi(r)$  is also called the wave function. As we can see, this is a function of both space and time variables. However, when the left-hand side of the equation (potential energy) does not explicitly depend on time, the function can be represented as a product of a space variable and time-dependent parts, with the latter having a known form  $\psi(r)e^{i(\omega t)}$  (using the Euler representation of complex numbers, see Appendix A.1). A similar situation has been described (with respective derivation) in Project 6 for the case of a standing wave. If we substitute the factorised

function into Eq. 1.1.1, we can easily eliminate the time-dependent part, which leads to the stationary Schrödinger equation

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \psi(r) = \varepsilon \psi(r), \quad (1.1.2)$$

where  $\varepsilon = \hbar\omega$ .

This equation is a starting point of the project. From a mathematical point of view it is an eigenvalue problem, the solution to which is a set of pairs: eigenvalues and corresponding eigenfunctions obeying the imposed boundary conditions,  $\{(\varepsilon_n, \psi_n(r))\}$ . The solutions are indexed with the integer  $n$  called the quantum number. The operator appearing on the left-hand side represents the total energy of the particle (Hamiltonian), and the eigenvalue problem leads to eigenenergies and eigenfunctions of the particle. From this an interpretation follows – the quantum system (a particle in a potential well, for example, an electron in the Coulomb potential of a proton) can have only strictly established energies and can occupy corresponding states described by the eigenfunctions. The modulus squared of these functions describes the spatial distribution of probability of finding the particle. It should be added that in quantum mechanics all physical quantities are represented by operators having certain mathematical properties, and the associated eigenvalue problems lead to eigenvalues (possible results of the measurement) and corresponding states. The measurement leads to a collapse of a quantum state into an eigenstate of a given quantity.

Two facts should be pointed out. First, the time-dependent part of the wave function, although it has been separated out, is still present in the full solution, but it does not affect the probability distribution of and eigenstate since its modulus squared equals 1. However, the situation changes if we consider a state being a superposition of a few eigenstates. Then we must not forget about time-dependent parts, and their presence results in time evolution of the probability distribution. The second issue is the normalisation of the wave function, which is necessary since its modulus squared multiplied by the volume element is the probability, and the probability of finding a particle overall must be equal to 1. From mathematical point of view this means that the integral of the modulus squared over the whole considered space must be equal to 1. Such normalisation is always possible since the Schrödinger equation is linear, that is any function being its solution when multiplied by a number still remains the solution.

## 1.2 Problem: Eigenenergies and Eigenfunctions in Rectangular Finite Quantum Well

In this project we will use the stationary Schrödinger equation (1.1.2) to find eigenvalues and eigenstates of an electron in a rectangular finite quantum well. This is not purely an academic problem since such systems are used to model, for example, semiconductor heterostructures. We describe the system as quasi one-dimensional because the changes of important physical characteristics appear in one direction only. Here, however, we will treat the quantum well as the simplest possible 1D model of the hydrogen atom. Thus Eq. 1.1.2 takes the form

$$\left[ -\frac{\hbar^2}{2m_e} \frac{d^2}{dx^2} + V(x) \right] \psi(x) = \varepsilon \psi(x), \quad (1.2.1)$$

where potential is equal (Figure 1.1)

$$V(x) = \begin{cases} -V_0 & \text{if } -a/2 \leq x \leq a/2, \\ 0 & \text{if } x < -a/2 \text{ or } x > a/2. \end{cases}$$

In Hartree atomic units,  $\hbar = m_e = e = 1$

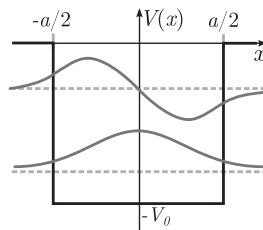
$$\left[ \frac{d^2}{dx^2} + k^2(x) \right] \psi(x) = 0, \quad (1.2.2)$$

where  $k^2(x) = 2(\varepsilon - V(x))$ .

The analytical solutions fall into three categories, two inside the well (Figure 1.1), which differ in symmetry (even and odd), and the third category are the corresponding solutions outside the well

$$\psi(x) = \begin{cases} A \cos(kx) & \text{for } -a/2 \leq x \leq a/2 \quad (\text{even}), \\ A \sin(kx) & \text{for } -a/2 \leq x \leq a/2 \quad (\text{odd}), \\ B \exp(\mp \kappa x) & \text{for } x < -a/2 \text{ or } x > a/2. \end{cases} \quad (1.2.3)$$

As one can see, the solutions are parametrised by two parameters:  $k$  – the wave number (inside the well) and  $\kappa$  – the rate of exponential decrease (outside). It will be shown in the next section



**Figure 1.1** A potential well and its solution: the even (lower) and the odd (upper)

that the numerical method will consist of finding the values of these parameters for consecutive eigenstates (thus they will become indexed).

It is worth noting that the eigenfunction (thus also its modulus squared) has finite values outside the well, that is in the region where the kinetic energy of electron is negative. In classical physics a particle must not have negative kinetic energy and that is why we call such a region ‘classically forbidden’ and the phenomenon ‘quantum tunnelling’.

### 1.3 Numerical Methods: Finding Roots of Characteristic Functions

The condition for the eigenvalue is that the two solutions (inside and outside the region of the well) must join smoothly (Figure 1.2), that is they must have equal values and equal values of their first derivatives at  $a/2$  (because of the symmetry of the system it is sufficient to consider only one border). Thus, we have, for even solutions

$$\begin{cases} \pm A \cos(ka/2) = \pm B \exp(-\kappa a/2), \\ \mp Ak \sin(ka/2) = \mp B\kappa \exp(-\kappa a/2), \end{cases} \tag{1.3.1}$$

and for odd solutions

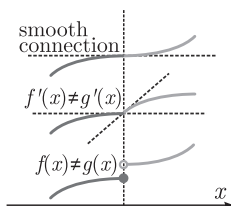
$$\begin{cases} \pm A \sin(ka/2) = \pm B \exp(-\kappa a/2), \\ \pm Ak \cos(ka/2) = \mp B\kappa \exp(-\kappa a/2), \end{cases} \tag{1.3.2}$$

where  $k = \sqrt{2(\varepsilon + V_o)}$  and  $\kappa = \sqrt{-2\varepsilon}$ .

Dividing the first equation by the second one in the above systems, we obtain two conditions, for even (symmetric) and odd (antisymmetric) solutions:

$$\begin{cases} F_{even}(\varepsilon) = \sin(ka/2) - \kappa/k \cdot \cos(ka/2) = 0 \quad (even), \\ F_{odd}(\varepsilon) = \sin(ka/2) + k/\kappa \cdot \cos(ka/2) = 0 \quad (odd). \end{cases} \tag{1.3.3}$$

The eigenvalues  $\varepsilon$  are found by solving these equations.



**Figure 1.2** The solutions inside and outside the well ( $f(x)$  and  $g(x)$ , respectively) must have same values and equal derivatives at the well border

## 1.4 Exercises

### *Obligatory*

1. Using the QWELL code, tabulate functions  $F_{\text{even}}(\varepsilon)$  and  $F_{\text{odd}}(\varepsilon)$ . These functions correspond to even and odd solutions, respectively, whose zeros are energies of quantum levels. Visualise the functions  $F_{\text{even}}(\varepsilon)$  and  $F_{\text{odd}}(\varepsilon)$  in one figure. Repeat the calculation and visualisation of  $F_{\text{even}}(\varepsilon)$  and  $F_{\text{odd}}(\varepsilon)$  for three significantly different values of the well parameters,  $a$  and  $V_0$  (e.g. wide and shallow well, deep and narrow, intermediate).
2. (Square finite quantum well as a model of the hydrogen atom). Try to fit the first two energy levels to the ones of the hydrogen atom through variation of the parameters  $a$  and  $V_0$ , by a trial and error method. (Hint: In the beginning set the values  $a = 3\text{Bohr}$  and  $V_0 = 1\text{Hartree}$ .) What is the value of the third energy level? One might try also to fit the first and the third levels. What would be the value of the second level then? Would it be very different from the true value? (Note that in atomic units the energy levels should be  $\varepsilon_n = -1/(2n^2)$ ; since the well is a two-parameter system, it should be possible, in principle, to fit any two levels.)

### *Challenge*

1. Try to construct an algorithm and write a code which automatically finds the parameters of a quantum well with energy levels close to those of the hydrogen atom with arbitrarily low uncertainty.
2. For the found eigenenergies plot the corresponding eigenfunctions and their moduli squared, with the picture of the well in background (do not normalise the functions). Note the effect of quantum tunnelling.