5. One-dimensional problems

In order to analyze quantum mechanical problems we need to find the solution of the time-dependent Schrödinger equation for the specific problem:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x,t)\,\Psi(x,t) = i\hbar \frac{\partial^2 \Psi(x,t)}{\partial t^2}$$

The solution $\Psi(x,t)$ contains all information about the particle (system). Itself it does however not have a physical meaning. We can retrieve information e.g. via

$$|\Psi(x,t)|^2 \quad : \quad \text{probability density}$$

$$<\Psi(x,t)> \quad : \quad \text{expectation (average) value.}$$

We will consider problems with $V(x,t) = V(x)$, i.e. the potential is independent of time. This is not a big restriction, indeed for most quantum mechanical problems the potential is time-independent. For example, the Coulomb potential for charged particles inside an atom or a molecule is time-independent.

In this case $\left(V(x,t) = V(x)\right)$ it can be shown that the solution is always written as:

$$\Psi(x,t) = \Psi(x) \; \phi(t)$$

i.e. the solution separates in a product in which one function $(\Psi(x))$ depends on position only, while the other $(\phi(t))$ depends on time only. We call this also separation of variables.

Furthermore : $\phi(t) = \exp\left(-iEt/\hbar\right)$

where E is the total energy of the particle (system).

On the other hand, $\dagger(x)$ is solution of the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2 \dagger(x)}{dx^2} + V(x) \dagger(x) = E \dagger(x)$$

and it is our task to solve this differential equation for a given problem. Erwin Schrödinger was able to do so for the hydrogen atom and got the energy values, that are in agreement with the Balmer series.

5.1 Solving the (time-independent) Schrödinger equation

We will now study the general concept to find a solution of the Schrödinger equation for a given quantum mechanical problem. We will separate this general strategy into several steps:

Step 1: Analyze the system and determine a potential energy function $V(x)$.

This is an important first step since $V(x)$ is needed to establish the Schrödinger equation. In order to find a solution we often need to make simplifying assumptions, This is needed

since it is difficult to solve the Schrödinger equation.
Indeed, an analytical solution can be found in
a few rare cases only. For example, a solution
can be found for the hydrogen atom but there
is no solution known for any other atom or
molecule.

Simplifying assumptions let us find solution and
learn about the physics behind quantum mechanical
systems.

Step 2 : Establish boundary conditions.

Since the Schrödinger equation is a differential
equation, we need boundary conditions to find
a specific solution.

There are general boundary conditions, e.g.

- $\Psi(x)$ is a continuous function, since otherwise
  $|\Psi|^2$ is not continuous and cannot be
  interpreted as probability density.

- $\Psi(x) \to 0$ for $x \to \pm\infty$, since otherwise
  we cannot normalize the wave function
  (Mathematically: $\int_{-\infty}^{\infty} |\Psi|^2 dx$ does not converge
  if $\Psi(x)$ does not go to zero
  for $x \to \pm\infty$)

and specific boundary conditions, given by
restriction due to the specific form of $V(x)$
in a given problem.

Step 3 : Solve time-independent Schrödinger equation

Now we need to solve the Schrödinger equation. This can be done ...

(i) mathematically (in few cases, for some potentials)

(ii) numerically, on the computer with high precision for some problems.

(iii) by making a physically informed guess and then checking the guessed solution.

In this way, we find a general solution for the given problem. Usually, this will be a set of solutions with undetermined parameters.

Step 4 : Fulfill boundary conditions and normalization.

The solution needs to fulfill both boundary condition and normalization (to interpret the square of solution as probability density).

Usually, this determines the open parameters and therefore we get a specific solution.

Step 5 : Multiply with $\exp(-iEt/\hbar)$

We have found $\Psi(x)$ in the previous four steps and get the full time-dependent solution as

$$\Psi(x,t) = \Psi(x) \exp\left(-iEt/\hbar\right)$$

5.2 Infinite square well

We will study the method to solve the Schrödinger equation for an example, namely the infinite square well. This can be seen as a (rough) approximation for electrons in a metal wire. A realistic potential for this scenario would be
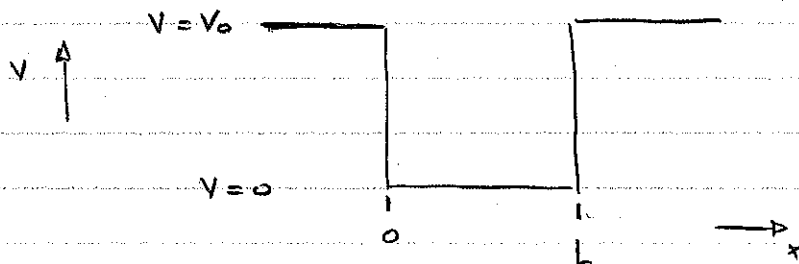

length of wire L
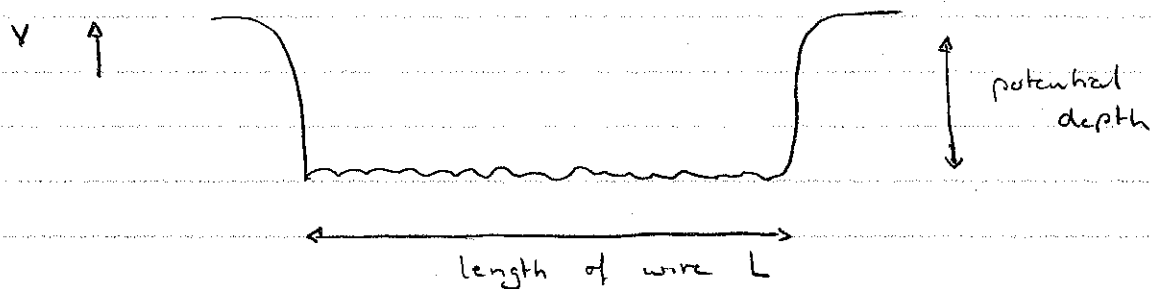
The Schrödinger equation for this potential could be only solved numerically. We will therefore
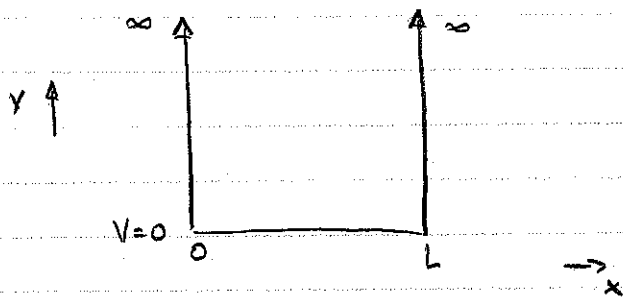
Step 1 : Make simplifying assumptions

To this end, we will approximate the potential by either a finite potential well

_or_   an infinite   square   well

We will first consider the _infinite_ square well, since it is easier to solve.

Step 2 : Establish boundary conditions

Obviously, the mathematical solution of the Schrödinger equation in the regions $x < 0$ and $x > L$ is

$$\Psi(x) = 0 \qquad \text{for } x < 0 \quad \text{and } x > L$$

since $V(x) = \infty$. This is the solution for any total energy.

Since the wavefunction has to be continuous we have as boundary conditions

$$\Psi(x) = 0 \qquad \text{at } x = 0$$

$$\text{and } \Psi(x) = 0 \qquad \text{at } x = L$$

Step 3: Solve Schrödinger equation (in region $0 \leq x \leq L$)

In this region we have to solve

$$-\frac{\hbar^2}{2m} \frac{d^2 \Psi(x)}{dx^2} + 0 = E \Psi(x) \qquad \text{for } E > 0$$

$$\Rightarrow \frac{d^2 \Psi(x)}{dx^2} = -\underbrace{\frac{2mE}{\hbar^2}}_{=k^2} = -k^2 \Psi(x)$$

Solutions are $\Psi_1(x) = A \sin(kx)$ and
$\Psi_2(x) = B \cos(kx)$

and therefore the general solution is

$$\Psi(x) = A \sin(kx) + B \cos(kx)$$

$$\text{with } k = \frac{\sqrt{2mE}}{\hbar}$$

Step 4: Boundary conditions and normalization.

This allows us to determine A and B and find the possible energies.

$$\Psi(x=0) = 0 \qquad \Rightarrow \qquad B = 0$$

$$\Rightarrow \qquad \Psi(x) = A \sin(kx)$$

$$t(x=L) = 0 \quad \Rightarrow \quad A \sin(kL) = 0$$

$$\Rightarrow \quad k_n L = n\pi \quad \text{with } n = 0, 1, 2, 3, \ldots$$

$$\Rightarrow \quad k_n = \frac{n\pi}{L}$$

This is the mathematical solution! We have however to exclude $n = 0$, since this leads to $t(x) = 0$ which can<u>not</u> be normalized.

$$\Rightarrow \quad k_n = \frac{n\pi}{L} \quad \text{with } n = 1, 2, 3, 4, \ldots$$

And, finally, the normalization of

$$t(x) = A \sin\left(\frac{n\pi}{L} x\right) \quad \text{for } 0 \leq x \leq L$$

$$\text{and} \quad t(x) = 0 \quad \text{otherwise}$$

$$\int_{-\infty}^{\infty} |t(x)|^2 \, dx = 1$$

$$\Rightarrow \quad \int_{0}^{L} A^2 \sin^2\left(\frac{n\pi}{L} x\right) dx = 1$$

$$\Rightarrow \quad A = \sqrt{\frac{2}{L}} \quad \text{(after some algebra)}$$

Step 5 : Full time-dependent solution

Putting everything together we get :

$$\Psi(x,t) = \Psi(x) \exp\left(-i \frac{Et}{\hbar}\right) \qquad \text{for} \quad 0 \leq x \leq L$$

$$= \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right) \exp\left(-i \frac{E_n t}{\hbar}\right)$$

$$\text{where} \quad \frac{2m E_n}{\hbar^2} = k_n^2 = \frac{n^2 \pi^2}{L^2}$$

$$\Rightarrow E_n = n^2 \frac{\pi^2 \hbar^2}{2m L^2}$$

This is the mathematical solution of the Schrödinger equation for the infinite square well.

Now, we can interpret the physics of this solution :

- There are only certain stationary states with discrete total energies possible, namely

$$E_n = n^2 \frac{\pi^2 \hbar^2}{2m L^2} \qquad \text{with} \quad n = 1, 2, 3, 4, \dots$$

This is in contrast to a classical counterpart in which the particle could have any energies.