# Practice Work 3

The introduction might look quite long and maybe difficult, but excercises are quite straight forward.

## Introduction

### Part 1

Hydrogen atom consist of proton and electron. They have opposite electric charge and thus attractive force between them. In classical physics the dynamics of the system could be derived from *Hamiltonian function*

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} - \frac{e^2}{4\pi\epsilon_0|\mathbf{r}_1 - \mathbf{r}_2|} \tag{1}$$

where $\mathbf{p}_i$, $\mathbf{r}_i$ and $m_i$ are momentum, location and mass of proton and electron. Terms $p_i^2/2m$ describe the kinetic energies and

$$V = \frac{e^2}{4\pi\epsilon_0|\mathbf{r}_1 - \mathbf{r}_2|} \tag{2}$$

is *Coulomb's potential energy* ($\epsilon_0$ is vacuum permittivity). In general the 0-level of the potential energy could be chosen arbitrarily. Here it is chosen to be $V(\infty) = 0$. Also, electron must be bounded to the proton i.e. values of the energy are *negative.*

In quantum mechanics location and momentum are replaced with *operators*. Let's define *Hamiltonian operator*, whose *eigenfunctions* describes the probability distribution of proton and electron (the point-like particles are replaced with wave-like ones).

Eigenvalue equation of the Hamiltonian operator (*Schrödinger's eq.*) is

$$-\frac{\hbar^2}{2m}\nabla_1^2\Psi(\mathbf{r}_1,\mathbf{r}_2) - \frac{\hbar^2}{2m}\nabla_2^2\Psi(\mathbf{r}_1,\mathbf{r}_2) - \frac{e^2}{4\pi\epsilon_0|\mathbf{r}_1 - \mathbf{r}_2|}\Psi(\mathbf{r}_1,\mathbf{r}_2) = E_t\Psi(\mathbf{r}_1,\mathbf{r}_2) \tag{3}$$

where $\nabla_i$ is a gradient with respect to $\mathbf{r}_i$. The motion of the center of mass and the relative motion of electron and proton could be separated. The center of mass is moving with constant velocity and the relative motion is

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) - \frac{e^2}{4\pi\epsilon_0}\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{4}$$

where $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and $E = E_t - E_c$, where $E_c$ is the kinetic energy of the center of mass.

Let's solve (4). First, change to the *natural* unit system:

$$r \to a_0 r \tag{5}$$

$$E \to \frac{\hbar^2}{2ma_0^2} E \tag{6}$$

and we choose

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} \tag{7}$$

which is the radius of the ground state of the hydrogen atom predicted by *Bohr model*. Above-mentioned formula could be derived from equation of the circular motion with assumption that the radius of the electron must be whole wavelength of matter wave of electron. Unit of energy is *Rydberg* (= 13.606eV)

$$\frac{m}{2\hbar^2}\frac{e^4}{(4\pi\epsilon_0)^2} \equiv 1\,\mathrm{Ryd} \tag{8}$$

and the Schrödinger's eq. becomes

$$\nabla^2\psi(\mathbf{r}) + \left(\frac{2}{r} + E\right)\psi(\mathbf{r}) = 0 \tag{9}$$

Next, separation of variables: Let's denote $\psi(\mathbf{r}) = u(r)w(\phi, \theta)$, where $r$, $\phi$ and $\theta$ are variables in spherical coordinate system. When former is substituted in eq. (9), we get two independent equations for $u$ and $w$. $u$ is the *radial-* and $w$ is the *angular part* of the wave function. If denoted $u(r) = y(r)/r$, we get quite simple differential equation for $y$

$$y''(r) + \left(E + \frac{2}{r} - \frac{l(l+1)}{r^2}\right)y(r) = 0, \tag{10}$$

where $l$ is quantum number related to *angular momentum.*

## Part 2

Let's derive the *boundary conditions* for $y$:
If $r$ is large, $2/r$ and $l(l+1)/r^2$ are small. Therefore we get

$$y''(r) + Ey(r) = 0 \tag{11}$$

and solution of the form

$$y(r) \sim e^{-\sqrt{-E}r}, \quad r \to \infty \tag{12}$$

If $r$ is small, the $l(l+1)/r^2$ dominates and we get

$$y''(r) - \frac{l(l+1)}{r^2}y(r) = 0 \tag{13}$$

and solution is of the form

$$y(r) \sim r^{l+1}, \quad r \to 0 \tag{14}$$

Here we restrict only to eigenfunctions where $l = 0$ (spherically symmetric). Therefore $w(\phi, \theta) = 1$, i.e wave function becomes $\psi(\mathbf{r}) = u(r) = y(r)/r$.

Differential equation to be solved is thus

$$y''(r) + \left(E + \frac{2}{r}\right) y(r) = 0 \tag{15}$$

with boundary conditions (12) ja (14) mentioned above and taking into account that $l = 0$.

The boundary conditions determine the *asymptotic behaviour* of $y$ at origin and at infinity. Note that there is two unknown: wave function $y$ and eigenvalue $E$. This could be solved analytically: eigenvalues are form of

$$E_n = -\frac{1}{n^2}, \quad n = 1, 2, \ldots \tag{16}$$

and the functions could be presented with help of Laguerre polynomial.

# Introduction to assingment

In this practice work you task is solve equation (15) numerically. You have to find the eigenvalues $E$ and corresponding eigenfunctions $y$. In practical, you must first guess $E$ and then test if there is corresponding eigenfunction $y$ for that $E$.
Note: $y$ must satisfy eq. (15) with all values of $r$, so it must be *continuous and differentiable.*

The procedure is similar to excercise 11 (standing wave). First you define the boundaries $r_0$ and $r_\infty$numerically. Divide the range in two parts $I_0 = [r_0, r_i]$ and $I_\infty = [r_i, r_\infty]$ and solve the eq. separately in both areas. Apply the boundary condition (14) in $I_0$ and boundary condition (12) in $I_\infty$ (i.e the value of function and its derivative at $r_0$ and $r_\infty$ follows from the boundary conditions).

Fit solutions together at $r_i$. Function and its derivative must be continuous i.e.

$$\frac{y_0'(r_i)}{y_0(r_i)} = \frac{y_\infty'(r_i)}{y_\infty(r_i)}$$

If $y$ satisfy that condition, it is good enough for solution and $E$ is corresponding eigenvalue.

When you have found the eigenvalue, calculate the wave function $u(r) = y(r)/r$ and normalize it to the unity.

## Task

1. Solve four lowest energy states of the hydrogen atom. Derive values of energy (eigenvalues) and corresponding wave functions. Normalize wave-functions and plot them. Don't use (16) when solving eigenvalues. Write your own eigenvalue-finding-algorithm. Note: Your algorithm could find point of discontinuity! You can use Mathematica's `NDSolve` to find the solution of differential eqs.

2. When hydrogen atom moves from the excited state to some lower state it emits a photon. The wavelength of the photon is

$$\lambda = \frac{hc}{\Delta E} \tag{17}$$

   where $\Delta E$ is the difference of energy states, $c$ is speed of light and $h$ Planck' s constant. Calculate the wavelengths of the photons when hydrogen atom moves from higher state to the ground state i.e. calculate the wavelengths corresponding transitions $2 \to 1$, $3 \to 1$ and $4 \to 1$

## Some hints

- When finding the values of energy, do not start very far from zero. For example energy $-3$Ryd corresponds classical radius $0.1 \cdot 10^{-11}$ m, which is already quite small!)

- When the energy of the state becomes larger, the electron wave function extends farther from the proton. Hence you must increase the parameter $r_\infty$, when finding higher states.