Linear Boundary Values Problems

In this project, we solve the time-independent Scrödinger equation (TISE) in one dimension. We will use the Numerov algorithm to integrate the second-order differential equation and the shooting method to find the eigenvalues and eigenfunctions.

I. LIST OF TASKS

1. Implement the (i) bracketing (ii) bisection, (iii) Numerov and (iv) shooting algorithms to numerically solve linear second-order boundary value problems with decoupled boundary conditions.
2. Numerically solve the Schrödinger equation for a number potentials including infinite and finite depth wells, double wells, the quantum harmonic oscillator, and a central potential.

II. INTRODUCTION

Many important differential equations in physics are linear second-order boundary value problems with decoupled boundary conditions:

$$\alpha_2(x)y''(x) + \alpha_1 y'(x) + \alpha_0 y(x) = f(x),\ x \in [a,b] \tag{1}$$

with the following boundary conditions:

$$\begin{aligned} A_0 y(a) + A_1 y'(a) &= \lambda_1,\ |A_0| + |A_1| \neq 0 \\ B_0 y(b) + B_1 y'(b) &= \lambda_2,\ |B_0| + |B_1| \neq 0 \end{aligned} \tag{2}$$

The TISE falls into the family of boundary problems described by Eqs. (1) and (2):

$$\frac{\hbar}{2m}\frac{d^2}{dx^2}\psi(x) + V(x) = \varepsilon\psi(x) \tag{3}$$

Eq. (3) has the form of an "eigenvalue" equation where $\psi(x)$ denotes the eigenfunctions and ε the eigenvalues. Let us label the solutions as $\psi_n(x)$ and ε_n , where n is integer and denotes the corresponding eigenvalues and eigenfunctions. The eigenfunctions must be normalized, i.e.:

$$-\int_{-\infty}^{+\infty} |\psi_n(x)|^2\, dx = 1 \tag{4}$$

III. NUMEROV ALGORITHM

Let us write a more general form of the linear second-order equation that is of interest in the current project:

$$\frac{d^2}{dx^2}y(x) + k^2(x)y(x) = S(x) \tag{5}$$

The equation above coincides with the TISE if $k^2(x) = \frac{2m}{\hbar}\left(\varepsilon - V(x)\right)$ and $S(x) = 0$.
Let us also consider the following homogeneous boundary conditions:

$$\begin{aligned} y(x=a) &= 0 \\ y(x=b) &= 0 \end{aligned} \tag{6}$$

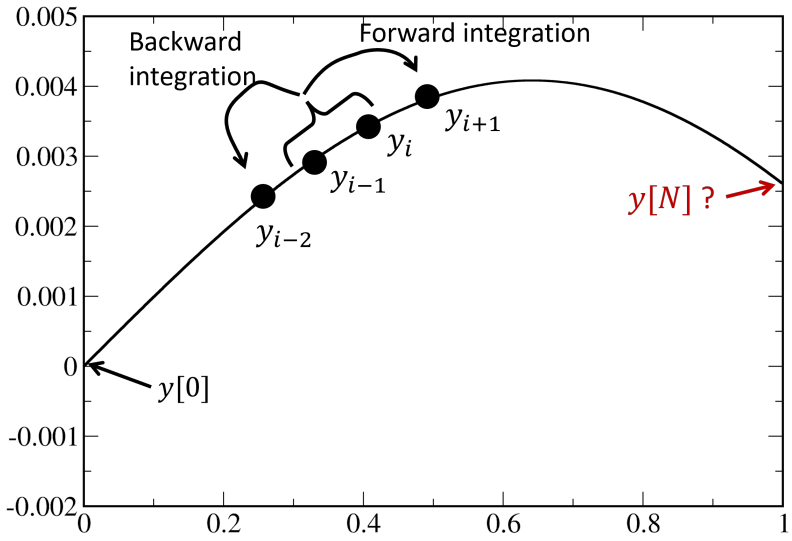

FIG. 1. Schematic representation of the firward andbackward integration in Numerov algorithm. In the forward integration we start from $i = 0$, i.e. $x = 0$, and we integrate up to $i = N$ ($x = b$).

In the finite difference approach (see slides uploaded in the eclass) Eq. (5) can be written as:

$$\begin{aligned} w_{i+1}y_{i+1} - w_i y_i + w_{i-1}y_{i-1} &= \frac{h^2}{12}\left(S_{i+1} + 10S_i + S_{i-1}\right) + \mathcal{O}(h^6) \\ w_{i+1} &= 1 + \frac{h^2}{12}k_{i+1}^2 \\ w_i &= 2\left(1 - \frac{5h^2}{12}k_i^2\right) \\ w_{i-1} &= 1 + \frac{h^2}{12}k_{i-1}^2 \end{aligned} \tag{7}$$

In Eq. (7) h should not be confused with the Planck constant $\hbar$. h is the "infinitesimal" interval:

$$h = \frac{b-a}{N} \tag{8}$$

where, $[a, b]$ is the interval to solve Eq. (5) and N is the mesh size[1].
Solving Eq. (7) for y_{i+1} allows to **forward** integrate Eq. (5) (forward integration is schematically shown in Fig. 1). On the other hand, solving for y_{i-1} allows to **backward** integrate Eq. (5).

IV. SHOOTING METHOD

A suitable strategy to solve Eq. (5) with the boundary conditions shown in Eq. (6) is to guess a trial eigenvalue and integrate the differential equation as an initial value problem, e.g., start from $x = a$ ($i = 0$) and integrate until $x = b$ ($i = N$) apllying the left boundary

[1] We consider $N + 1$ grid points, i.e., the index i takes the values $0, ..., N$ ($x_i = ih + a,\ x_0 = a,\ x_N = b$). Hence, we devide the interval $[a, b]$ into N "infinitisemal" intervals of length h.

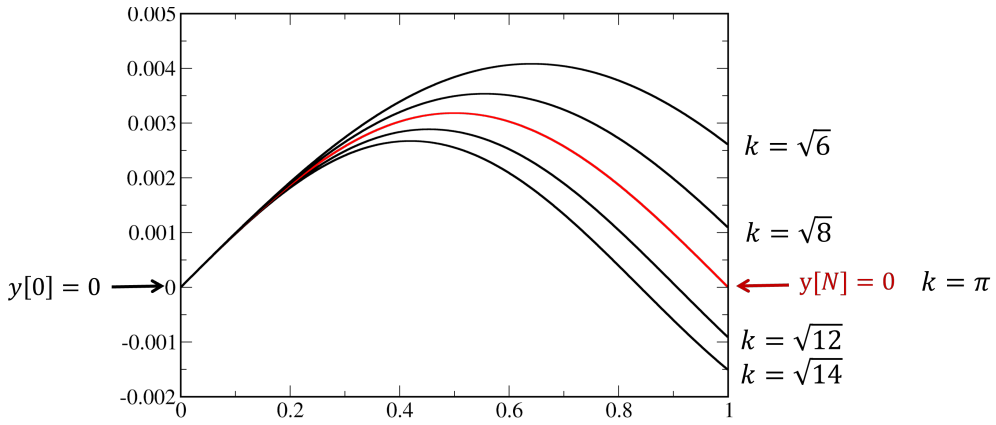

FIG. 2. Schematic representation of the shooting method to solve the differential equation $y'' + k^2 y = 0$ with the boundary conditions $y(x = 0) = y(x = 1) = 0$ ($y[0] = y[N] = 0$). Forward integration [see Eq. (7)] using different values of k are shown. $k = \pi$ is an eigenvalue and the corresponding eigenfunction is indicated by the red curve.

condition $y(x = a) = 0$ ($y_0 = 0$). Then repeat the process for different trial eigenfunctions until an eigenvalue is found for which the right boundary condition is satisfied, i.e., $y(x = b) = 0$ ($y_N = 0$).

The abovementioned procedure can be improved to allow for a systematic eigenvalue search. To achieve this, we define the following function:

$$f(\widetilde{k}) = y_N(\widetilde{k}) - y(x = b) \tag{9}$$

Where $\widetilde{k}$ is the trial eigenvalue,$y_N(\widetilde{k})$ is the numerically calculated value of the function at the right boundary and $y(x = b)$ is the imposed right boundary [for simplicity, we will consider $y(x = b) = 0$]. Therefore, the search for the eigenvalue/s is formally expressed as a search for a root of the function $f(\widetilde{k})$ (see Fig. 2).

A suitable method for root finding is the **bisection** method. In this method, a pair of trial values $\widetilde{k}_1$ and $\widetilde{k}_2$ that bracket the minimum is provided (i.e., $f(\widetilde{k}_1) \cdot f(\widetilde{k}_2) < 0$, and the root of the function is calculated. A significant advantage of this approach is that it can converge to a root if the function is continuous and changes sign over the interval $[\widetilde{k}_1, \widetilde{k}_2]$. Compared to other rootfinding methods like Newton's may be slow, but the bisection does not require the calculation of the first derivative of the function.

The basic idea of the bisection method is to repeatedly narrow down the interval in which the root lies by dividing it in half and checking which half contains the root. Details and pseudocode to implement the bisection method are provided in the slides (eclass). To use the bisection method, a pair of trial eigenvalues that bracket the root of the function f has to be provided. A simple **bracketing** algorithm can also be found in the slides.

V. TASKS (TOTAL: 250 POINTS)

In the following tasks, we adopt atomic units. Therefore, the TISE is written as:

$$-\frac{1}{2}\frac{d^2}{dx^2}\psi(x) + V(x)\psi(x) = \varepsilon\psi(x) \tag{10}$$

A. Particle in infinite square potential well. (50 pnts)

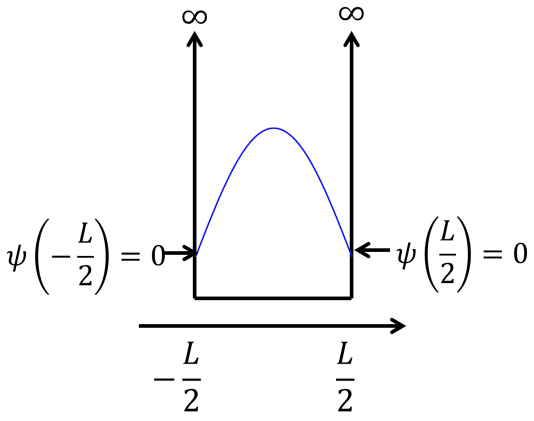

FIG. 3. Schematic representation of the infinitesquare well potential.

Write a program to solve for the stationary states of the infinite square potential well. Due to the infinite depth, the boundary conditions require the wavefunction to vanish at the edge of the well:

$$\psi\left(x = -\frac{L}{2}\right) = \psi\left(x = \frac{L}{2}\right) = 0 \tag{11}$$

or

$$\psi[0] = \psi[N] = 0 \tag{12}$$

Calculate the four lowest energy eigenvalues and eigenfunctions. Do not forget to normalize the wavefunctions.

Compare your results with the actual eigenvalues and eigenfunctions:

$$\begin{aligned} \varepsilon_n &= \frac{n^2}{L^2}\pi^2 \\ \psi_n(x) &= \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) \end{aligned} \tag{13}$$

B. Particle in infinite square potential well. (75 pnts)

A finite square potential well can be defined as follows:

$$V(x) = \begin{cases} 0, & |x| < \frac{L}{2} \\ V_0, & |x| > \frac{L}{2} \end{cases} \tag{14}$$

where V_0 is the depth of the well.

Unlike the case of the infinite well, the bound states, i.e., states with eigenvalues lower than the depth of the well, extend outside the well in the so-called classically forbidden region (see Fig. 4 for a schematic representation of the wavefunction of the ground state). Hence, different boundary conditions must be applied: The wavefunction does not vanish at the edge of the well, but it tends to zero as the distance from the well tends to infinite. To model this, we have to (i) construct a simulation box larger than the width of the well and (ii) modify the boundary conditions for the wavefunction to become zero at the edges of the box ($\psi[0] = \psi[N] = 0$, where the indices 0 and N correspond to the left and right edges of the simulation box, not the edges of the well).

The shooting method with the Numerov integration can also be applied to solve the present problem. However, the eigenfunctions exponentially vary outside the well and oscillate in

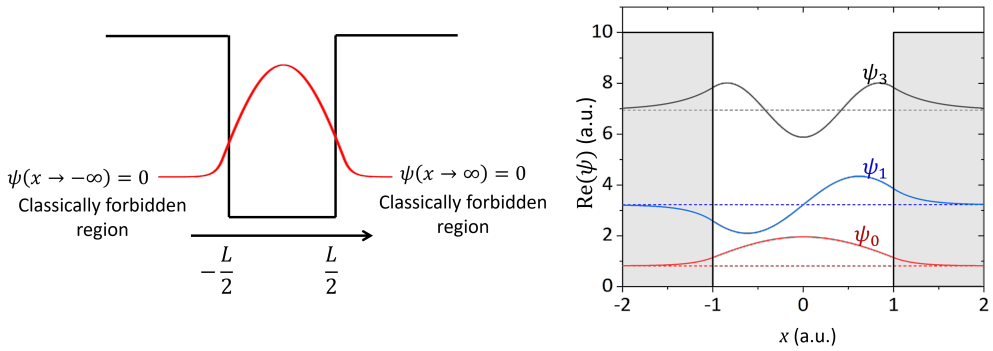

FIG. 4. Left: Schematic representation of a finite square well. Right: Eigenfunctions of the three lowest eigenstates.

the well (see Fig. 4). Let us assume that we start the numerical integration from the left edge and generate a solution ψL. Initially ψL increases exponentially through the classically forbidden region (gray shaded area in Fig. 4). Then, it oscillates in the classically allowed region. If, however, we continue integrating past the right turning point in the right-wing classically forbidden region, the integration would become numerically unstable. To tackle this problem, we can generate a second solution, ψR, by integrating from the right limit toward smaller x. To determine if the energy is an eigenvalue, we require that the left and right solutions, ψL and ψR, are equal at a matching point x_m and have equal derivatives. I.e.,

$$\psi L[m] = \psi R[m] \tag{15}$$

and

$$\frac{d\psi L[m]}{dx}|_{x=x_m} = \frac{d\psi R[m]}{dx}|_{x=x_m} \tag{16}$$

The first of the two conditions can be satisfied by rescaling ψL:

$$\psi L[:] = \frac{\psi R[m]}{\psi L[m]}\psi L[:] \tag{17}$$

The second condition defines the function for which we need to find the root:

$$\begin{aligned} f(\varepsilon) &= \frac{\text{derL} - \text{derR}}{\psi_{\max}} \\ \text{delL} &= \psi L[m+1] - \psi L[m-1] \\ \text{delR} &= \psi R[m] - \psi R[m-2] \end{aligned} \tag{18}$$

In the above equation $\psi_{\max} = \max\{|\psi L[0:m]|, |\psi R[m+1:N]|\}$. Here ψL has already been rescaled using Eq. (15).

A second problem that may occur and render the integration unstable is in large simulation boxes. In this case $\psi[i]$'s may take arbitrarily large values. To address this, we monitor if the absolute value of the wavefunction exceeds a threshold value, e.g., 1E6. If this happens, then we rescale all the calculated values, e.g., $\psi L = \psi L * 1E-6$ and/or $\psi R = \psi R * 1E-6$.

More infos and pseudocodes can be found in the slides (eclass). The slides of the course, provide information regarding the eigenvalues and eigenfunction of the finite potential well. Calculate the bounding eigenvalues and eigenstates and compare them with those in the slides.

NOTE How to choose the matching point x_m.
In principle, you can choose any value that allows for stable integration. A good choice is x_m to be near the left edge of the well.

C. Simplified and qualitative model of covalent bonding (25 points)

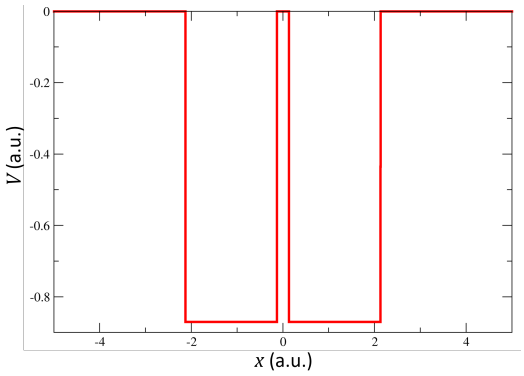

FIG. 5. Schematic representation of a double well potential.

You can use the code you have developed to solve the particle in a finite square potential well to qualitatively model the bonding in the single ionized Hydrogen molecule, H_2^+.

In the first step, construct a finite potential well with a width of 2 Bohr radius (we consider the size of the H atom to be roughly 1 Bohr radius). Adjust the depth of the potential well such that the first eigenvalue is -0.5.

In the second step, construct a double well. Each well has the depth you calculated in the previous step and 2 Bohr radius width. The distance between the centers of the two wells is 2.26 Bohr radius (see Fig. 5).

Calculate the eigenvalues and eigenfunctions of the ground state and the first excited state. What do you observe?

How does the total energy of the system depend on the distance between the two wells?

D. The Quantum Harmonic Oscillator (25 pnts)

Modify the program to calculate the eigenvalues and eigenfunctions of the quantum harmonic oscillator. The potential for the oscillator is the following:

$$V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2 x^2 \tag{19}$$

For simplicity, consider $m\omega^2 = 1$, i.e., $V(x) = \frac{1}{2}x**2$. Calculate the first few eigenvalues and eigenfunctions and verify that these are:

$$\varepsilon_n = n + \frac{1}{2} \tag{20}$$

E. The radial Schrödinger equation (75 pnts)

We aim to develop an algorithm that calculates the energies and charges of the bound states of a single electron in the central potential of a nucleus with charge Z. The problem that we are dealing with is to integrate the one-electron radial Schrödinger equation:

$$-u''(r) + \left(\frac{l(l+1)}{r^2} - \frac{2Z}{r}\right) = \varepsilon u(r) \tag{21}$$

where, $\psi_{lm}(\hat{r}) = \frac{u(r)}{r} Y_l m(\hat{r})$. The boundary conditions are:

$$\begin{aligned} u(0) &= 0 \\ u(\infty) &= 0 \end{aligned} \tag{22}$$

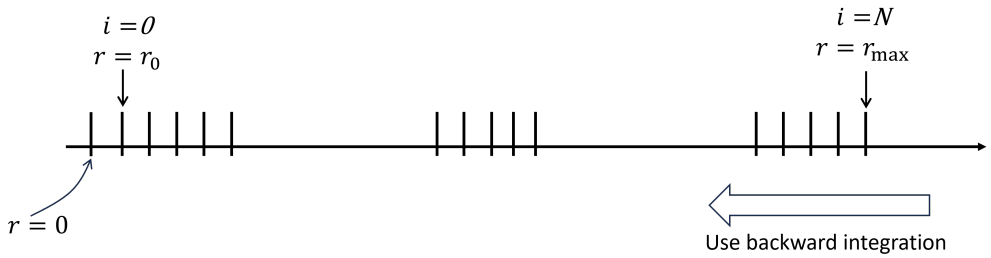

FIG. 6. Schematic representation of a the grid implemented to solve the Schr"odinger equation in a central potential. The boundary conditions we implement are $r_0 = 0$ and $r_{\max} = 0$. However, r_0 is not explicitly included in our grid.

The problem can be solved using the shooting and Numerov algorithms. However, there are two issues that require our attention:

1. Our central potential becomes infinite at $r = 0$, so $r = 0$ cannot be explicitly included into our routine.

2. Forward integration is unstable.

The second issue can be resolved by implementing backward integration, meaning we start from $r = r_{\max}$ and integrate toward $r = 0$. To address the first issue we do not explicitly include r_0 in our grid. Instead, we terminate the backward integration at r_0, where r_0 is a small value (e.g. 1E-6). However, to satisfy the boundary condition $u(r = 0) = 0$, we approximate the function $u(r)$ near the origin wit h the first two terms of its Taylor expansion arround r_0):

$$u(r) \approx u(r_0) + u'(r_0)(r - r_0) \tag{23}$$

In the above equation, the first derivative $u'(r_0)$ is computed using the finite difference method:

$$u'(r_0) = \frac{u[1] - u[0]}{h} \tag{24}$$

Here, $u[i]$ denotes the calculated eigenfunction at grid point i, and $h = (r_{\max} - r_0)/N$, and N is the number of intervals in our grid. Using Eqs. 23 and (25), we obtain: ‘

$$u(r = 0) \approx u[0] - \frac{u[1] - u[0]}{h} r_0 \tag{25}$$

Thus, the shooting algorithm consists of finfing the values of ε in Eq (21) that set $u(r = 0)$, i.e. the value in Eq. (refeq:fdDer) to zero. So, the shooting algorithm works as follows:

1. Start with a trial value of ε.

2. Perform backward integration from $r_{\max}$ down to r_0.

3. Use the Eq. (25) to estimate $u(r = 0)$.

4. Apply the bracketing and bisection methods to find the root/eigenvalue.

Calculate the three lowest eigenvalues and their corresponding eigenfunctions (see Fig. 7).

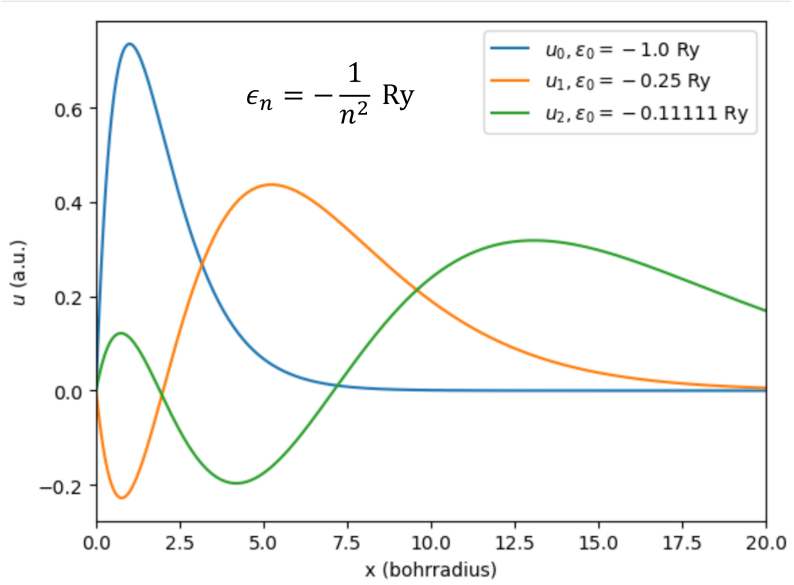

FIG. 7. Eigenfunctions corresponding to the three lowest eigenvalues of Eq. (21).