Quantum Chemistry
Exercises 2B

1. One can use numerical matrix based methods to solve the Schrodinger equation. The accuracy of this method depends on the number discretization steps used.

a. Using the Matlab code provided, investigate how the accuracy of the numerical solutions of the energy for the particle-in-a-box problem depend on the number of discretization steps, N. In the calculations use:

Mass of the particle:	m=me (mass of an electron)
Size of the box:	a=1.0 Å
Minimum x value for discretization:	xmin=-0.5 Å
Maximum x value for discretization:	xmax=1.5 Å
Value of the potential:	V0=1· 10^{12} eV (representing infinity)

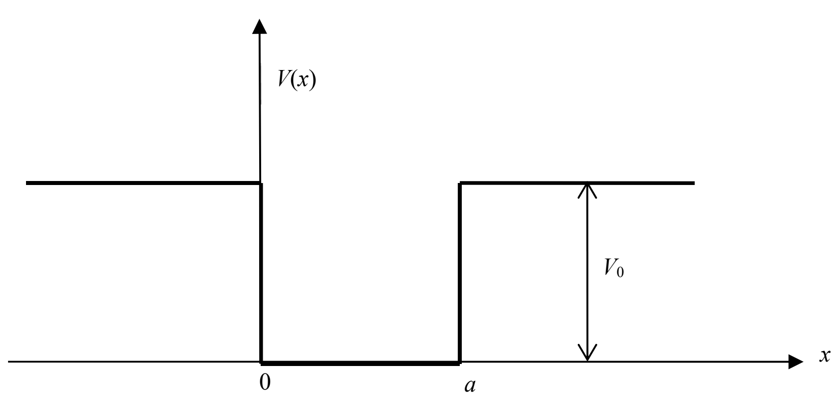
Plot the time it takes to perform the calculations and the relative deviation from the exact results for the energy levels n=1,2 and 5 for the values of N=20,21,50,51,100,101,102,200,201,500,501,1000,1001, 2000,2001, 5000 and 5001 (depending on your computer you can try even larger values)

Discuss the results, paying special attention to the differences between similar values of N.

2. In exercise session 2A you have calculated the energy levels and the corresponding transition frequencies of butadiene, $H_2C=CH–CH=CH_2$, assuming that the π electrons can be described by a particle-in-a-box model. In that exercise, the potential outside the box was assumed to be infinite. Consequently, the electrons cannot be found outside of the box. This implies that this molecule cannot be ionized, since this requires that one of the electrons is at a large outside the box. In order to allow for the ionization of the molecule the potential outside the box should not be infinite, but rather correspond to the ionization energy, V_0, that is required to remove an electron from the molecule.

One therefore should consider square well potential of the form:

$$V(x) = V_0 \qquad \text{for } x < 0 \text{ and } x > a$$
$$V(x) = 0 \qquad \text{for } 0 \le x \le a$$



a. Separate this problem into 3 regions and write down the Hamiltonian for each of these using classical observables.

b. Write down the Hamiltonian operator for each of these regions.

c. Find the general solutions (eigenfunctions) to the Schrodinger equations for each region.

d. Draw the eigenfunctions for each region.

e. Write down the boundary conditions for this problem.

g. Discuss how this problem and its solutions relate to the particle-in-a-box problem having infinite potential outside the box.

f. Now, ***without*** solving the resulting coupled equations, draw the eigenfunctions for the 3 lowest energy levels.

h. Use Matlab to solve the Schrodinger equation numerically and determine the energy levels of butadiene assuming an ionization energy of 12 eV. Calculate the corresponding transition wavelength and wavenumber and compare the results to those found for a box with infinite walls.