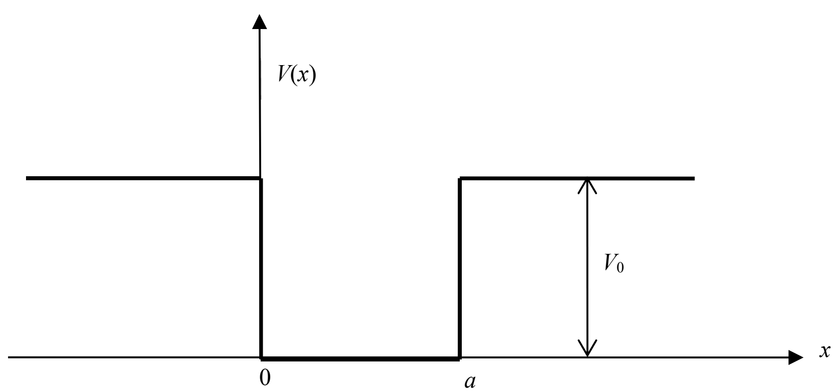
Quantum Chemistry
Exercises 2B

1. 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.