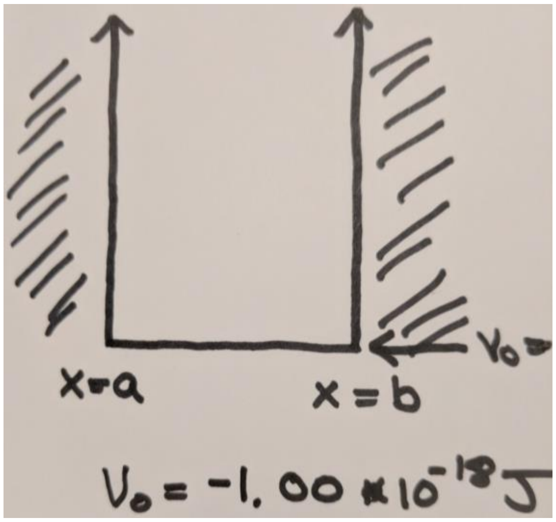
Worksheet 8.

There are many different ways to confine a particle to an infinite box. Consider the following scenario: an electron is put in a box whose bottom is at $-1.00\cdot10^{-18}$ J and which is located in the region $a < x < b$. That is, the potential is:

$$V(x) = \begin{cases} -1.00\cdot10^{-18}\,\mathrm{J} & a < x < b \\ +\infty & \text{otherwise} \end{cases}$$



1. Write an expression for the energy eigenvalues of this system.

The energy eigenvalues do not depend on where the box is located, only the size of the box. They do depend on the energy of the bottom of the box, however. So the energy eigenvalues are:

$$E_n = -1.00\cdot10^{-18}\,\mathrm{J} + \frac{h^2 n^2}{8m(b-a)^2}$$

If you want to solve this explicitly, write the Hamiltonian as:

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

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - 1.00\cdot10^{-18}\,\mathrm{J} + V_{\text{p-in-box}}(x-a)\right)\Psi(x) = E\Psi(x)$$

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V_{\text{p-in-box}}(x-a)\right)\Psi(x) = \left(E + 1.00\cdot10^{-18}\,\mathrm{J}\right)\Psi(x)$$

where the "traditional" particle-in-a-box potential is

$$V_{\text{p-in-box}}(y) = \begin{cases} 0 & 0 < y < b-a \\ +\infty & \text{otherwise} \end{cases}$$

The solutions to this equation can be constructed as:

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dy^2} + V_{\text{p-in-box}}(y)\right)\psi_n(y) = \varepsilon_n \psi_n(y)$$

$$\varepsilon_n = \frac{h^2 n^2}{8m(b-a)^2} \qquad \psi_n(y) = \sqrt{\frac{2}{b-a}}\sin\left(\frac{n\pi y}{b-a}\right)$$

Setting the left-hand-sides of the above to Schrodinger equations (which are the same thing, just written differently) to be equal, we obtain:

$$E_n + 1.00\cdot10^{-18}\,\mathrm{J} = \frac{h^2 n^2}{8m(b-a)^2}$$

$$E_n = -1.00\cdot10^{-18}\,\mathrm{J} + \frac{h^2 n^2}{8m(b-a)^2}$$

2. Write an expression for the eigenfunctions of this system?

This is the same system as the normal particle in a box, but the origin is shifted to $x = a$ and the length of the box is now $\ell = b - a$. Define $y = x - a$. The eigenfunctions are:

$$\psi_n(y) = \sqrt{\frac{2}{\ell}}\sin\left(\frac{n\pi y}{\ell}\right)$$

or in terms of *x*,

$$\psi_n(x) = \sqrt{\frac{2}{b-a}}\sin\left(\frac{n\pi(x-a)}{b-a}\right)$$

The following information is necessary for problems 6 and 7.

The lowest-energy absorption has a wavelength of 300. nm, corresponding to the excitation $n = 1 \to n = 2$.

3. Assume that *a* = –1.00 nm. What is *b*?

In terms of the length of the box, the excitation energy is

$$E = \frac{h^2(2)^2}{8m\ell^2} - \frac{h^2(1)^2}{8m\ell^2} = \frac{3h^2}{8m\ell^2} = h\nu$$

$$\ell^2 = \frac{3h^2}{8mh\nu} = \frac{3h}{8m\nu}$$

$$\ell = \sqrt{\frac{3h}{8m\nu}}$$

The frequency of the light is

$$\nu = c/\lambda = \left(3.00\cdot10^8\ \tfrac{\text{m}}{\text{s}}\right)/\left(300\cdot10^{-9}\,\text{m}\right) = 1.00\cdot10^{15}\,\text{s}^{-1}$$

and so

$$\ell = \sqrt{\frac{3\left(6.626\cdot10^{34}\ \frac{\text{kg}\cdot\text{m}^2}{\text{s}}\right)}{8\left(9.11\cdot10^{-31}\,\text{kg}\right)\left(1.00\cdot10^{15}\,\text{s}^{-1}\right)}} = \sqrt{2.727\cdot10^{-19}\,m^2} = 5.22\cdot10^{-10}\,\text{m} = 0.522\text{ nm}$$

b must be this distance from *a*. We have implicitly assumed that *b* > *a* so we have

$$b = -1.00\cdot10^{-9}\,\text{m} + 5.22\cdot10^{-10}\,\text{m} = -4.78\cdot10^{-10}\,\text{m} = -0.478\text{ nm}$$

but it is also possible to have

$$b = -1.00\cdot10^{-9}\,\text{m} - 5.22\cdot10^{-10}\,\text{m} = -1.52\cdot10^{-10}\,\text{m} = -1.52\text{ nm}$$

4. What is the kinetic energy of the first excited state of this system?

The kinetic energy does not depend on the position or the zero of energy of the box, so it is the same as "usual." For the first excited state, $n = 2$, one has:

$$T = \frac{h^2 (2)^2}{8m\ell^2} = \frac{\left(6.626 \cdot 10^{-34} \frac{\text{kg}\cdot\text{m}^2}{\text{s}}\right)^2 (4)}{8\left(9.11 \cdot 10^{-31} \text{ kg}\right)\left(5.22 \cdot 10^{-10} \text{ m}\right)^2} = 8.84 \cdot 10^{-19} \frac{\text{kg}\cdot\text{m}^2}{\text{s}^2} = 8.84 \cdot 10^{-19}\,\text{J}$$

One can also do this by explicitly evaluating the kinetic energy,

$$\int_a^b \left(\sqrt{\frac{2}{b-a}} \sin\left(\frac{2\pi x}{(b-a)}\right)\right) \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} \left(\sqrt{\frac{2}{b-a}} \sin\left(\frac{2\pi x}{(b-a)}\right)\right) dx$$

but this is much more tedious.

5. Problem 5 is just tedious substitution of the eigenfunctions into the Schrödinger equation.