Exercises 3

Exercise 3.1

A particle is confined in a linear box of length L surrounded by walls of infinite potential. The ground state of this system is described by the following wave function:

$$\Psi_1(x) = \sqrt{\frac{2}{L}} \times sin\left(\frac{\pi x}{L}\right)$$

a) What is the probability of finding the particle at a given position x?
b) At which position is the maximum probability density?
c) What is the total probability of finding the particle in the box?
d) If L = 10 nm, what is the probability that the particle is between 4:95 and 5:05 nm?

Note: Exercise 3.1 will be solved on the board during the exercise session this Friday, September 26, 2025.

a) As we saw, the probability density of finding the particle at a given position x is given by the square of the wavefunction:

$$\Psi_1(x)^2 = \left(\sqrt{\frac{2}{L}}\sin\left(\pi\frac{x}{L}\right)\right)^2 = \frac{2}{L}\sin^2\left(\pi\frac{x}{L}\right)$$

And the probability itself is calculated by integrating the probability density between two points. Therefore, if we calculate the probability of finding the particle at a single specific position x, the borders of the integral are the same:

$$\int_x^x \Psi_1(x)^2 dx$$

and consequently, the integral yields 0. The probability of finding the particle at a particular position x iequals zero.

b) The position with the highest probability corresponds to the maximum of the probability density functions $\Psi_1(x)^2$. A look at the graphical representation of the wavefunction shows a peak at the middle of the box ($x = \frac{L}{2}$), otherwise it can be calculated. When $\Psi^2{}_1$ is at its maximum, its first derivative must be equal to zero:

$$\begin{aligned} 0 = \Psi_1^2(x)' &= \left[\tfrac{2}{L}\sin^2\left(\tfrac{\pi x}{L}\right)\right]' \\ &= \left[\tfrac{1}{L} - \tfrac{1}{L}\cos\left(\tfrac{2\pi x}{L}\right)\right]' \\ &= \tfrac{1}{L}\sin\left(\tfrac{2\pi x}{L}\right)\cdot\tfrac{2\pi}{L} \quad \text{using, } \sin^2\alpha = \tfrac{1-\cos(2\alpha)}{2} \end{aligned}$$

Since $\sin\left(\frac{2\pi x}{L}\right) = 0$, then $\frac{2\pi x}{L} = 0 + k\pi$ with k a positive integer. Moreover since $x \in [0, L]$, $x = \frac{L}{2}$
.

$x = 0$ and $x = L$ also yield first derivative euqal to zero, however they correspond to mimima and not maxima. This can be easily verified by calculated the second derivative of $\Psi_1^2(x)$:

$$\Psi_1^2(x)'' = \left(\frac{2\pi}{L^2}\sin\left(\frac{2\pi x}{L}\right)\right)' = \frac{4\pi^2}{L^3}\cos\left(\frac{2\pi x}{L}\right)$$

Therefore, when $x = 0$ or $x = L$ the second derivative is positive whereas it's negative for $x = L/2$. A second derivative yielding negative values matches a maximum.

c) The particle is confined within the box so the total probability of finding the particle inside the box must be 1, this can be verified by integrating Ψ_1^2 from 0 to L:

$$\begin{aligned}\int_0^L \Psi_1^2(x)dx &= \int_0^L \frac{2}{L}\sin^2\left(\pi\frac{x}{L}\right)dx \\ &= \frac{2}{L}\int_0^L \frac{1-\cos(2\pi\frac{x}{L})}{2}dx \\ &= \frac{1}{L}\int_0^L dx - \frac{1}{L}\int_0^L \cos\left(2\pi\frac{x}{L}\right)dx \\ &= \frac{1}{L}(L-0) - \frac{1}{L}\frac{L}{2\pi}\left[\sin\left(2\pi\frac{x}{L}\right)\right]_0^L \\ &= 1 - \frac{1}{2\pi}\cdot(0-0) = 1\end{aligned}$$

by using: $\sin^2\alpha = \frac{1-\cos(2\alpha)}{2}$

d) Following the same procedure, with $L = 10$, we find:

$$\begin{aligned}P(4.95 \le x \le 5.05) &= \int_{4.95}^{5.05} \Psi^2(x)dx = \ldots \\ &= \frac{1}{10}(5.05-4.95) - \frac{1}{2\pi}\left\{\sin\left(2\pi\frac{5.05}{10}\right) - \sin\left(2\pi\frac{4.95}{10}\right)\right\} \cong 0.02\end{aligned}$$

The particle has therefore a probability of approx. 2% of being found between 4.95 and 5.05 nm.

Exercise 3.2

The total energy of the particle in the box can be calculated as

$$E_{tot} = E_{kin} + E_{pot},$$

where the kinetic energy is given by

$$E_{kin} = \frac{1}{2}mv^2.$$

Write down an expression for the total energy of the particle in the box, using the de Broglie relationship ($p = mv = \frac{h}{\lambda}$) and the fact that the wavelength must satisfy $\lambda = \frac{2L}{n}$. What is the main implication of this equation?

Following the expression for the total energy and substituting, we get:

$$E_{tot} = \frac{1}{2}mv^2 + 0,$$

since $E_{pot} = 0$ inside the box.

Finally substituting the momentum, we obtain:

$$E_{tot} = \frac{1}{2}\frac{(mv)^2}{m}$$

$$E_{tot} = \frac{1}{2m}p^2 = \frac{1}{2m}\frac{h^2}{\lambda^2} = \frac{1}{2m}\frac{h^2n^2}{(2L)^2} = \frac{n^2h^2}{8mL^2}.$$

Exercise 3.3

Using the particle-in-a-box model for the hydrogen atom and treating the atom as an electron in a one-dimensional box of length 150 pm, predict the wavelength of radiation emitted when the electron falls from the level with $n = 5$ to that with $n = 4$.

Repeat the calculation for the transition from $n = 4$ to $n = 3$.

Using the formula obtained for the total energy from the previous exercise, we obtain for the energy difference, between an initial start n_i and a final state n_f, the following equation:

$$\Delta E(n_i, n_f) = (n_f^2 - n_i^2)\frac{h^2}{8mL^2}.$$

Finally, to convert into a wavelength we use:

$$E = h\nu = \frac{hc}{\lambda} \Leftrightarrow \lambda = \frac{hc}{E}$$

For the H-atom, we use:

$$m_e = 9.1 * 10^{-31}\ [\text{kg}]$$

$$L = 150\ [\text{pm}].$$

Plugging the appropriate values for n_i and n_f we obtain:

for $n_i = 5$ and $n_f = 4$, $\Delta E = \frac{(25-16)(6.626*10^{-34})^2}{8*9.1*10^{-31}*(150*10^{-12})^2} = 2.41 * 10^{-17}$ [J]

$$\lambda_{5,4} = \frac{1.626*10^{-34}*3*10^{8}}{\Delta E} = 8.24\ [\text{nm}],$$

and,

for $n_i = 4$ and $n_f = 3$, $\Delta E = \frac{(16-9)(6.626*10^{-34})^2}{8*9.1*10^{-31}*(150*10^{-12})^2} = 1.88 * 10^{-17}$ [J]

$$\lambda_{4,3} = 10.59\ [\text{nm}].$$

Exercise 3.4

The energy levels of a particle of mass m in a two-dimensional square box of size L are given by $\frac{(n_1^2+n_2^2)h^2}{8mL^2}$.

Do any of these levels have the same energy?

If so, find the values of the quantum number n_1 et n_2 for the first three cases.

Since levels are now defined by two independent principal quantum numbers n_1 and n_2, to obtain levels of the same energy we need to enforce:

$$(n_1^2 + n_2^2)\frac{h^2}{8mL^2} = E = (n_1'^2 + n_2'^2)\frac{h^2}{8mL^2}$$
$$\Leftrightarrow \quad (n_1^2 + n_2^2) = (n_1'^2 + n_2'^2).$$

Intuitively, it is clear the only obtain to satisfy this equation is to permute principal numbers so preserve the sum of the squares, since n_1 *and* $n_2 > 0$.

Mathematically, this can be solved by uncoupling the equation and creating a system of linear equation, like so:

$$(n_1^2 + n_2^2) = (n_1'^2 + n_2'^2) \Leftrightarrow \begin{cases} n_1^2 = n_2'^2 \\ n_2^2 = n_1'^2 \end{cases} \Leftrightarrow \begin{cases} n_1 & = n_2' \\ n_2 & = n_1' \end{cases},$$

with $n_1, n_2, n_1', n_2' \in N^+$.

Therefore, the three first cases are:

$$E_1 = E(1,2) = E(2,1)$$
$$E_2 = E(1,3) = E(3,1)$$
$$E_3 = E(2,3) = E(3,2)$$

Exercise 3.5

Refer to the previous exercise. If one side of the box is twice as long as the other, the energy levels are given by:

$$\left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2}\right) \cdot \frac{h^2}{8m},$$

with $L_2 = 2L_1$.

Do any of these levels have the same energy?

If so, find the values of the quantum numbers n_1 and n_2 for the two lowest levels having identical energies.

Using the information given above, we find for the following expression for the total energy:

$$E(n_1, n_2) = \left(\frac{{n_1}^2}{{L_1}^2} + \frac{{n_2}^2}{(2L_1)^2}\right)\frac{h^2}{8m} = \frac{4{n_1}^2 + {n_2}^2}{4{L_1}^2}\frac{h^2}{8m}$$
$$= (4{n_1}^2 + {n_2}^2)\frac{h^2}{32 \cdot m \cdot {L_1}^2}.$$

Using the same methodology as the previous exercise, we can decouple the equation into a corresponding set of linearly dependent equations, like so:

$$E(n_1, n_2) = E(n'_1, n'_2)$$
$$\Leftrightarrow \; 4{n_1}^2 + {n_2}^2 = 4{n'_1}^2 + {n'_2}^2$$

$$\Leftrightarrow \begin{cases} 4n_1^2 = {n_2'}^2 \\ n_2^2 = 4{n_1'}^2 \end{cases} \Leftrightarrow \begin{cases} 2n_1 & = n_2' \\ n_2 & = 2n_1' \end{cases},$$

with $n_1, n_2, n'_1, n'_2 \in N^+$.

The first lowest levels with identical energies are therefore:

$$E(1{,}4) = E(2{,}2)$$
$$E(1{,}6) = E(3{,}2).$$