Subject: Chemistry (Hons.)
Semester: 4
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Topic: Particle in a box (Quantum Mechanics)

[Based on the class-lectures, here is the 3rd installment of home-assignments. The students must go through all the assignments. The students are advised to remain in contact for any type of academic discussion.]

1. The wavefunction corresponding to the 'particle in 1-dimensional box' can be represented as: $\psi = N . \sin(kx)$ where N and k are independent of x. Show that k can have only quantized values. Also, deduce an expression of N in terms of the length (L) of the box.

Hints:

At $x = L, \psi = 0 \quad \Rightarrow k = n\frac{\pi}{L}$ where n = 1, 2, 3, ...(any positive integer)

$$\int_{x=0}^{L} \psi^* \psi \, dx = 1 \quad \Rightarrow N = \sqrt{\frac{2}{L}}$$

2. Using the operator corresponding to the kinetic energy of a particle, find out the energy expression of the particle moving in '1-dimensional box'.

Hints: The operator corresponding to the kinetic energy of a particle: $\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$

$$E_n = \frac{n^2 h^2}{8mL^2} \quad .$$

3. While the energy of a freely moving particle can have any possible value, the same for a 'particle in 1-dimensional box' is quantized – Comment.

4. In case of 'particle in 1-dimensional box' the particle cannot move with fixed linear momentum – Justify or criticize.

5. Show that the wavefunctions ψ_1 and ψ_2 of 'particle in 1-dimensional box' are orthogonal to each other.

6. Plot ' ψ_n *vs* x ' and ' ψ_n^2 *vs* x ' for 'particle in 1-dimensional box' for n = 1, 2, 3.

Hints: Keep special attention at $x \to 0$.

7. Probability of finding the particle is zero around $x=\frac{L}{2}$ for ψ_2 of 'particle in 1-dimensional box' – Justify or criticize.

8. In case of 'particle in 1-dimensional box' find out the following expectation values: $\langle x\rangle, \langle p_x\rangle, \langle x^2\rangle, \langle p_x^2\rangle$. Also, show that $\Delta p_x . \Delta x=\frac{\hbar}{2}\sqrt{1+\frac{n^2\pi^2-3^2}{3}}$, where Δp_x and Δx are standard deviations (root-mean-square deviations) from the respective expectation values.

9. The kinetic energy of an electron (mass = m) trapped in a cubical box of edge-length L is given as:
E = $14h^2/8mL^2$. How many degenerate states do you expect?

Hints: Energy expression of a 'particle in 3-dimensional (rectangular cuboid) box' is:
$$E_{3d}=\frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}+\frac{n_z^2}{L_z^2}\right)$$

10. Calculate the wavelength of radiation that will be absorbed in promoting an electron from the HOMO to the LUMO in butadiene. Approximate the butadiene molecule to 1-dimensional box of length 578 pm.
Given:
h = 6.626×10^{-34} J s
m_e = 9.109×10^{-31} kg
c = 2.998×10^{8} m s^{-1}

Hints:
$$E_3-E_2=\frac{(3^2-2^2)h^2}{8mL^2}$$
$$\lambda=\frac{hc}{E}$$