Chapter 3. Exercises

1. Which of the following is *not* a solution $y(x)$ of the differential equation $y''(x) + k^2 y(x) = 0$ (k = constant): (i) $\sin(kx)$ (ii) $\cos(kx)$ (iii) e^{ikx} (iv) e^{-kx} (v) $\sin(kx + \alpha)$ (α = constant).

2. For a particle in a 1-dimensional box, calculate the probability that the particle will be found in the middle third of the box: $L/3 \le x \le 2L/3$. From the general formula for arbitrary n, find the limiting value as $n \to \infty$.

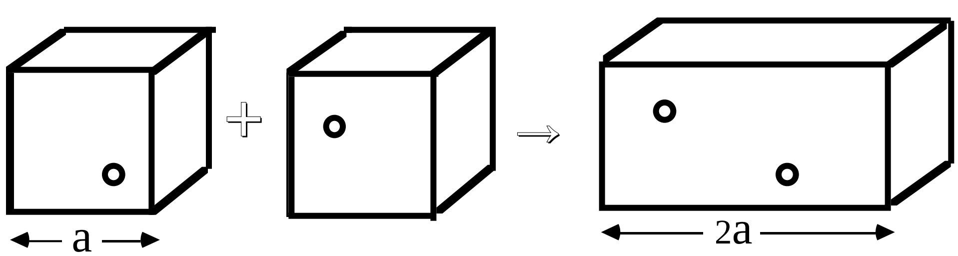
3. Predict the wavelength (in nm) of the lowest-energy electronic transition in the following polymethine ion:

$$(CH_3)_2N^+ = CH - CH = CH - CH = CH - N(CH_3)_2$$

Assume that all the C–C and C–N bonds lengths equal 1.40 Å. Note that N^+ and N contribute 1 and 2 π-electrons, respectively.

4. In this calculation you will determine the order of magnitude of nuclear energies. Assume that a nucleus can be represented as a cubic box of side 10^{-14} m. The particles in this box are the nucleons (protons and neutrons). Calculate the lowest allowed energy of a nucleon. Express your result in MeV (1 MeV = 10^6eV = 1.602 $\times 10^{-13}$ J).

5. Consider the hypothetical reaction of two "cube-atoms" to form a "moly-box":



Each cube-atom contains one electron. The interaction between electrons can be neglected. Determine the energy change in the above reaction.

6. Consider the two-dimensional particle-in-a-box—a particle free to move on a square plate of side a. Solve the Schrödinger equation to obtain the eigenvalues and eigenfunctions. You should be able to do this entirely by analogy with solutions we have already obtained. Discuss the degeneracies of the lowest few energy levels.

7. As a variant on the free-electron model applied to benzene, assume that the six π electrons are delocalized within a square plate of side a. Calculate the value of a that would account for the 268 nm ultraviolet absorption in benzene.

Answers to Exercises

1. $y = e^{-kx}$ is a solution of the differential equation $y''(x) - k^2 y(x) = 0$. (Note the minus sign.)

2.
$$P(L/3 \leq x \leq 2L/3) = \int_{L/3}^{2L/3} |\psi_n(x)|^2 \, dx$$
$$= \frac{2}{L} \int_{L/3}^{2L/3} \sin^2\left(\frac{n\pi x}{L}\right) dx = \frac{2}{L} \frac{L}{n\pi} \left[\frac{\theta}{2} - \frac{\sin 2\theta}{4}\right]_{n\pi/3}^{2n\pi/3}$$

Note

$$\sin(4n\pi/3) = \sin(4n\pi/3 - 2n\pi) = \sin(-2n\pi/3) = -\sin(2n\pi/3)$$

Thus
$$P = \frac{1}{3} + \frac{1}{n\pi} \sin\left(\frac{2n\pi}{3}\right)$$

As $n \to \infty$, this approaches 1/3.

3. Polymethine ion: N^+=C–C=C–C=C–N, 8 electrons (1 from each C, 1 from N^+, 2 from N), $L \approx 7 \times 1.40$Å.

$$\frac{hc}{\lambda} = \frac{h^2}{8mL^2}(5^2 - 4^2)$$

giving $\lambda = 352$ nm.

4. For particle of mass $M = 1.67 \times 10^{-27}$ kg in cubic box with $a = 10^{-14}$ m, ground-state energy is

$$E_{111} = \frac{h^2}{8Ma^2}\left(1^2 + 1^2 + 1^2\right) \approx 6.15\,\mathrm{MeV}$$

5. Energy of 2 electrons in molybox minus that of 2 electrons in cube-atoms:

$$\Delta E = 2 \times \frac{h^2}{8m}\left(\frac{1^2}{(2a)^2} + \frac{1^2}{a^2} + \frac{1^2}{a^2}\right) - 2 \times \frac{h^2}{8ma^2}\left(1^2 + 1^2 + 1^2\right) = -\frac{3}{16}\frac{h^2}{ma^2}$$

Note that the molybox is more stable (has lower energy). One of the factors promoting formation of molecules from atoms is the increased volume available to valence electrons.

6. By analogy with 3-dimensional particle-in-a-box

$$\psi_{n_1 n_2} = \frac{2}{a}\sin\left(\frac{n_1 \pi x}{a}\right)\sin\left(\frac{n_2 \pi y}{a}\right)$$

$$E_{n_1 n_2} = \frac{h^2}{8ma^2}\left(n_1^2 + n_2^2\right) \qquad n_1,\, n_2 = 1,\, 2 \ldots$$

Ground state $E_{11} = h^2/4ma^2$ is nondegenerate. First excited level, with $E_{21} = E_{21} = 5h^2/8ma^2$, is 2-fold degenerate.

7. Six π-electrons occupy E_{11}, E_{12} and E_{21}. Lowest-energy transition is from E_{12} or E_{21} to E_{22}:

$$\frac{hc}{\lambda} = E_{22} - E_{21} = \frac{h^2}{8ma^2}(8 - 5)$$

$\lambda = 268$ nm when $a = 4.94$Å.