4.E: Electronic Spectroscopy of Cyanine Dyes (Exercises)

Q4.1

Write the Schrödinger equation for a particle in a two dimensional box with infinite potential barriers and adjacent sides of unequal length (a rectangle). Solve the equation by separating variables with a product function X(x)Y(y) to obtain the wavefunctions X(x) and Y(y) and energy eigenvalues. How many different sets of quantum numbers are needed for this case? Sketch an energy level diagram to illustrate the energy level structure. What happens to the energy levels when the box is a square? When two or more states have the same energy, the states and the energy level are said to be degenerate. What is the zero point energy for an electron in a square box of length 0.05 nm?

Q4.2

A materials scientist is trying to fabricate a novel electronic device by constructing a two dimensional array of small squares of silver atoms. She thinks she has managed to produce an array with each square consisting of a monolayer of 25 atoms. You are an optical spectroscopist and want to test this conclusion. Use the particle-in-a-box model to predict the wavelength of the lowest energy electronic transition for these quantum dots. Which electrons do you want to describe by the particle-in-a-box model, or do you think you can apply this model to all the electrons in silver and get a reasonable prediction? In which spectral region does this transition lie? What instrumentation would you need to observe this transition?

Q4.3

Model the pi electrons of benzene by adapting the electron in a box model. Consider benzene to be a ring of radius r and circumference 2πr. You can find r by using the bond length of benzene (0.139 nm) and some trigonometry. Show how the electron on a ring is analogous to the electron in a linear box. Derive this analogy by thinking, not by copying from some book. What is the boundary condition for the case of the particle on a ring? Find mathematical expressions for the energy and the wavefunctions. Draw an energy level diagram. What is the physical reason that the energy levels are degenerate for this situation? Predict the wavelength of the lowest energy electronic transition for benzene. Compare your prediction with the experimental value (256 nm). What insight do you gain from this comparison?

Q4.4

Explain how and why the following two sets of selection rules for the particle-in-a-box are related to each other: (1) If Δn is even, the transition is forbidden; if Δn is odd, the transition is allowed. (2) If the transition is g to g or u to u, it is forbidden; if the transition is g to u or u to g, it is allowed.

Q4.5

The factor $fi/(f^2 - i^2)^2$ in Equation (4-32) determines the relative intensity of transitions in the particle-in-a-box model. Make plots of $[fi/(f^2 - i^2)^2]$ vs f for several values of i with f starting at i+1 and increasing. What conclusions can you make about particle-in-a-box spectra from your plots?

Q4.6

Starting with the mathematical definition of uncertainty as the standard or root mean square deviation σ from the average, show by evaluating the appropriate expectation value integrals that

$$\sigma_x = \frac{L}{2\pi n}\left(\frac{\pi^2 n^2}{3} - 2\right) \text{and} \sigma_p = \frac{n\pi\hbar}{L} \tag{4.E.1}$$

for a particle in a one-dimensional box of length L as given in the chapter. Then show that the product $\sigma_x \sigma_p \geq \frac{\hbar}{2}$.

Q4.7

Use the symbolic processor in Mathcad to help you carry out the steps leading from Equation (4-27) to Equation (4-31). See Activity 4.3 for an introduction to the symbolic processor.

Q4.8

An electron is confined to a one-dimensional space with infinite potential barriers at x = 0 and x = L and a constant potential energy between 0 and L. The electron is described by the wavefunction $\psi(x) = N(Lx - x^2)$

In responding to the following questions (a through g), do not leave your answers in the form of integrals, i.e. do the integrals. Note:

$$\text{Note}: \int x^n dx = \frac{1}{n+1} x^{n+1} + C \text{for} x \neq 0 \tag{4.E.2}$$

1. Explain why this wavefunction must be normalized, and find an expression for N that normalizes the wavefunction.
2. Define what is meant by the expectation value, and find the expectation value for the position of the electron and the momentum of the electron.
3. Find the expectation value for the energy of the electron.
4. Is your energy expectation value consistent with your momentum expectation value? Explain.
5. What is the energy of the n = 1 state for the one-dimensional particle-in-a-box model? How does the energy obtained in (c) compare with this value? Explain why these two energies must have such a relationship to each other.
6. Does the wavefunction, $\psi(x) = N(Lx - x^2)$, for this electron represent a stationary state of the electron?
7. What is the probability that the electron will be located at x = L/3 in an interval of length L/100? Explain why you expect this probability to be time dependent or time independent.

Q4.9

How does choosing the potential energy inside the box to be –100 eV rather than 0 modify the description of the particle-in-a-box?

David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")