Quantum mechanics in the lab: Particle-in-a-box experiment

Introduction

In classical mechanics, a given particle's location and its momentum can be readily determined with exactness; however, these calculations apply only to relatively large objects. When we start to investigate particles with sizes on the atomic level, like electrons, classical mechanics no longer fully explains their behavior. To better understand these systems, we must view them through a quantum mechanical lens, where the answers to these questions are more probabilistic than strictly known.

For example, the 1-dimensional particle-in-a-box model is a simplified quantum mechanical system describing the behavior of a particle, typically an electron, in an infinite potential well of length L. By using the Schrödinger equation (Eqn. 1),

$$E\phi(x) = -\frac{\hbar^2}{2m_e}\frac{d^2\phi(x)}{dx^2} + V(x)\phi(x)$$

Equation 1.

where *E* is energy, *V(x)* is the positional potential energy, m_e is the mass of an electron, $\hbar$ is the reduced Planck's constant, and $\phi(x)$ is the time-independent wavefunction and *x* is the position in the box, a potential solution to *E*, as well as $\phi(x)$, can be derived.[1]

$$E_n = \frac{h^2 n^2}{8m_e L^2}$$

Equation 2.

Equation 2 outlines the solution for *E* using the 1-dimensional particle-in-a-box model using the boundary conditions that *V(x)* is infinite at the "walls" of the box.[1,2] From this equation, the energy is shown to be discrete (n = 1, 2, 3, 4, …) and inversely proportional to the length of the theoretical box. Consequently, a box of a smaller size will have a higher associated energy for each n-level (Fig. 1).

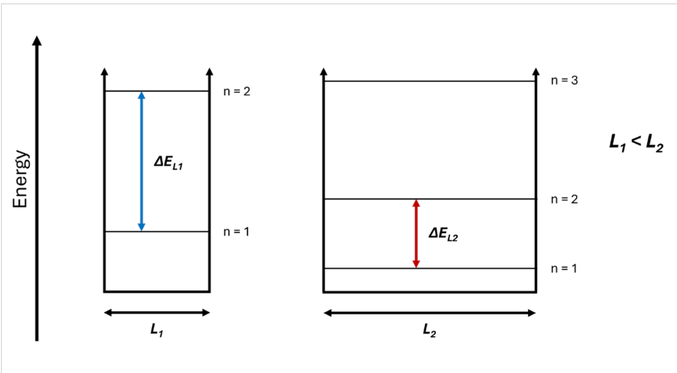


Figure 1. Comparison of energy spacing for 1-dimensional potential wells of varying length (L).

Using Equation 2, the difference in energy between each level can be determined, as shown in Equation 3,

$$\Delta E = \frac{h^2 (n_f^2 - n_i^2)}{8m_e L^2}$$

Equation 3.

where n_f is n for the final (higher) energy level and n_i is n for the initial (lower) energy level.[2] As is shown in Figure 1, the energy difference is expected to be larger for smaller box sizes. Using this equation from the model system, we can interrogate this dependence on box length with the energy difference between levels by applying UV-Visible absorption spectroscopy.

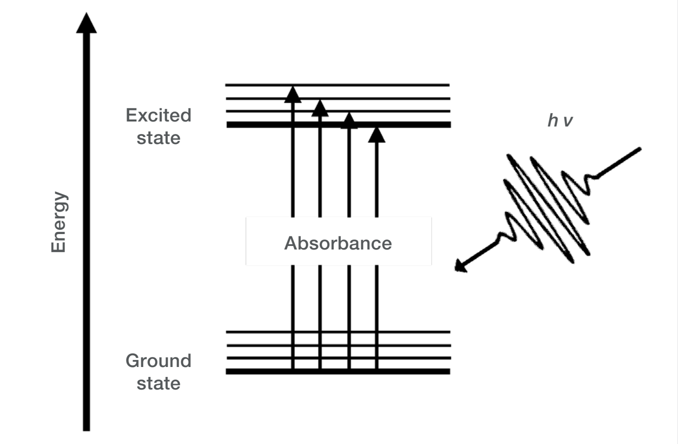


Figure 2. General depiction transition of electron from the ground state to the excited state through absorption of light. Thin lines denote vibrational levels while thick lines depict the lowest vibrational levels for the ground and excited states.

UV-Visible absorption spectroscopy uses the interaction of ultraviolet or visible light (typically 200–800 nm) with a substance to learn more about the electronic transitions within the material. Because the energy of a photon is inversely proportional to wavelength, as shown in equation 4,

$$E = hv = \frac{hc}{\lambda}$$

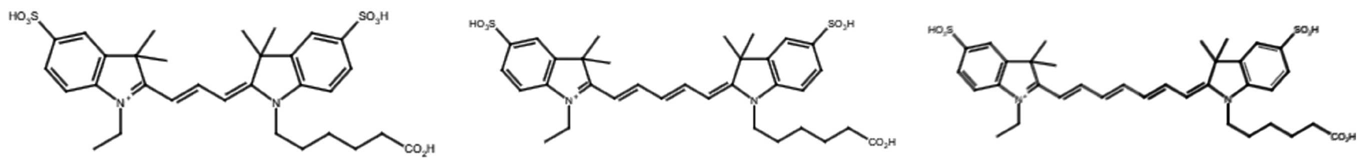
Equation 4.

the wavelength of light absorbed by a compound correlates to the energy difference between the ground and excited states. These electronic energy levels are discrete, like the energy levels from the particle-in-a-box model; therefore, only photons with sufficient energy are capable of being absorbed by a molecule. This results in a UV-Visible absorption spectrum which is specific to the substance analyzed.

In this lab, you will be measuring the UV-Visible absorption spectrum of three cyanine dyes. As shown in Figure 3, these dyes contain similar structural motifs with a different number of carbon-carbon double bonds between two aromatic subunits. By applying the particle-in-a-box model, the length of these molecules can be estimated and compared to the expected dye length.

References

1. Engel, T.; Reid, P., Physical Chemistry; Pearson, 2013.
2. Anderson, B. D., Alternative compounds for the particle in a box experiment, *J. Chem. Ed.*, **1997**, 74, 985.
3. Autschbach, J., Why the Particle-in-a-Box Model Works Well for Cyanine Dyes but Not for Conjugated Polyenes, *J. Chem. Ed.*, **2007**, 84, 1840 - 1845.



Cy3 Cy5 Cy7

Figure 3. Structure of cyanine dyes.

Experimental

Materials

- Thermo Scientific™ GENESYS™ G5 Visible or UV-Vis Spectrophotometer
- 1.0 cm plastic disposable cuvettes
- Lint-free lab wipes
- Deionized (DI) water
- 3.3 µM Cyanine 3 mono acid (Cy3)
- 3.8 µM Cyanine 5 mono acid (Cy5)
- 4.5 µM Cyanine 7 mono acid (Cy7)
- USB or USB-C

Safety

Eye protection and gloves should be worn at all times when handling reagents used in this experiment. Ensure students and any individual preparing or handling the chemicals described herein are using the correct personal protective equipment and are instructed in the proper waste disposal procedures. For more details, please refer to the Safety Data Sheet (SDS) for each material prior to handling.

Instructions*

1. Turn on the spectrophotometer.
2. Select the "Scan" application. Set the instrument to the following settings (Fig. 4):
    a. Y-axis: Abs
    b. Range: 400–900 nm
    c. Speed: Medium
    d. Interval: 1 nm
3. Select "Start Run." Collect the blank/background using a 1.0 cm cuvette filled with DI water.
4. Fill the 1.0 cm cuvette with Cy3. Use the lint-free lab wipe to remove any dust or fingerprints from the sides of the cuvette before measuring. (This wipe-down step will be done prior to each time a cuvette is placed in the spectrophotometer.)
5. Collect the UV-Visible spectra of the Cy3 solution.
6. Repeat steps 4 and 5 for Cy5 and Cy7 dyes.
7. Click the arrow in the top right-hand side of the display screen to end the experiment.
8. Export the data to a USB or USB-C. This data will be needed for the report.

* This procedure is based on the procedure outlined by Autschbach.[3]

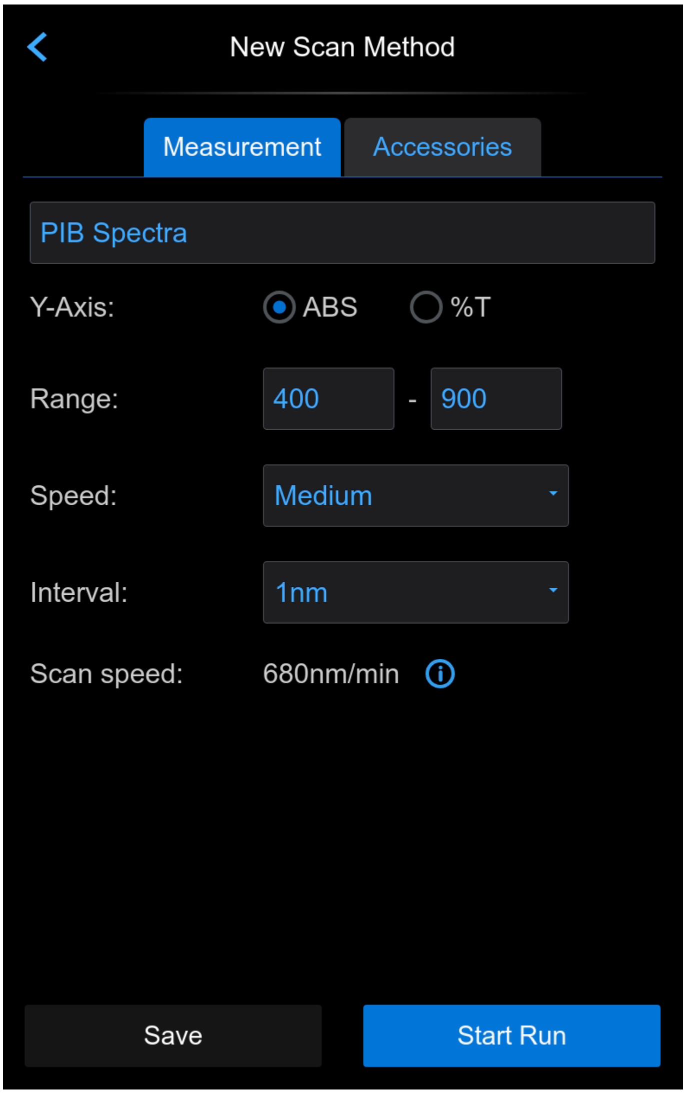


Figure 4. Scan application settings.

Lab report

Ensure that you have saved your experimental data and results where you can access them. Your results should be included in the final laboratory report, along with the following:

1. Derive Equation 2 using Equation 1 for the 1-dimensional particle-in-a-box system described in the introduction.
2. Include the spectra for each cyanine dye measured.
3. Calculate box length (L) for each dye using the λ_{max} and compare against the estimated dye length.
4. Explain why we can apply the particle-in-a-box model to these molecules.
5. Comment on real-world applications of the particle-in-box concept.