Experimental Objective
The purpose of this experiment is to obtain the visible spectra of several cyanine dyes and then interpret them in terms of two simple models for conjugated \( \pi \)-electron systems: the Particle in a Box and the Modified Particle in a Box models. In addition, the Spartan molecular modeling software package will be introduced and a more sophisticated molecular orbital model of the cyanine dyes will be investigated.

SECTION 1: INTRODUCTION AND THEORETICAL BACKGROUND

In this experiment, you will study two sets of related conjugated cyanine dyes, shown in Figures 1 and 2. Note the conjugated chain of atoms between the two nitrogens. This conjugated chain is the focus of our studies because it is assumed that the motion of the electrons involved gives rise to the bands observed in the experimental visible absorption spectrum.

Notice that, in the dyes shown in Figures 1 and 2, the conjugated region is terminated at both ends by nitrogen atoms. The lone pair of electrons shown on the left-most nitrogen atom is part of the conjugated system, so for example in Dyes I and IB there are 6 \( \pi \)-electrons in the conjugated chain, while in Dyes II/IIB, III/IIB, and IVB there are 8, 10, and 12 \( \pi \)-electrons in the conjugated chains, respectively.
The models that will be utilized to interpret the absorption spectra assume that the electronic spectra of the conjugated dyes can be explained in terms of transitions involving only the $\pi$-electrons of the conjugated chain. Resonance structures for the conjugated chains are shown below. In these resonance structures, $R_1$ and $R_2$ refer to the remaining portions of the dye molecules.

\[
R_1\text{-N-}C(=C\text{-})N\text{-}R_2 \\
\text{and} \\
R_1\text{-}N=C(\text{-}C=\text{C})\text{-}N\text{-}R_2
\]

As you can see from the resonance structures above, the $\pi$-electrons of the cyanine dyes can be delocalized over the entire length of the chain moving from one nitrogen to the other.

The energy of an individual $\pi$-electron in the conjugated chain consists of its kinetic energy, its potential energy of interaction with the carbon and nitrogen nuclei, and its potential energy of interaction with the other sigma and $\pi$-valence electrons in the molecule. If all of these contributions are taken into account, the Hamiltonian operator is very complex and the Schrödinger equation is difficult to solve for the organic molecules considered here. Therefore, you will consider more simplified models that focus only on the $\pi$-electrons in the conjugated chain.

The two models to be studied, the Particle in a Box and the Modified Particle in a Box models, employ drastic assumptions to simplify the calculation of the $\pi$-electron energy levels. Surprisingly, these rather naive models compare reasonably well with the experimental spectra.

**The Particle in a Box Model**

In the Particle in a Box model, all potential energy interactions are assumed to be zero (constant) along the polymethine chain except at ends of the chain where the potential energy abruptly goes to $+\infty$. This means that every $\pi$-electron is considered to be a particle moving freely along the length of the conjugated chain, and it is constrained to be therein. The Schrödinger equation for an individual $\pi$-electron using this model is

\[
-(\frac{\hbar^2}{8\pi^2m}) \frac{d^2\Psi(x)}{dx^2} = E \Psi(x). \tag{1}
\]

The solutions of this equation (see your physical chemistry textbook) yields the following energy levels

\[
E_n = \frac{n^2h^2}{8mL^2} \quad n = 1, 2, 3 \ldots , \tag{2}
\]

where $n$ is an integer positive quantum number, $\hbar$ is Planck’s constant, $m$ is the mass of the particle and $L$ is the length of the box. Pauli and Aufbau principles tell us that only two $\pi$-electrons can be placed in each level beginning with the lowest energy level. Therefore, the highest occupied level (HOL) will have a quantum number $n = N/2$, where $N$ is the number of $\pi$-electrons in the conjugated system. The level above that is the lowest unoccupied level (LUL) corresponds to a quantum number $n + 1$ or $N/2 + 1$.

If we assume that the most intense band in the experimentally observed spectrum can be interpreted as absorption of electromagnetic radiation by an electron as it is promoted from the HOL to the LUL, we can derive the following expression for the energy absorption $\Delta E$,

\[
\Delta E = \frac{h^2[ (\lfloor N/2 \rfloor + 1)^2 - (N/2)^2 ]}{8mL^2}
\]

\[
\text{or} \quad \Delta E = \frac{h^2(N+1)}{(8mL^2)} \tag{3}
\]

Expressing the electronic transition in terms of wavelength, $\lambda = \frac{hc}{\Delta E}$, the absorption wavelength for the HOMO $\rightarrow$ LUMO transition is given by

\[
\lambda = \frac{8mcL^2}{h(N+1)}. \tag{4}
\]

Therefore, the Particle in a Box model predicts that the wavelength of the absorption maximum is a function of chain length ($L$) and number of $\pi$-electrons ($N$).
**The Modified Particle in a Box Model**

In reality the π-electrons are not really totally free to roam over the entire conjugated chain. There is, for example, a greater probability that they will be found in the bonding regions between the nuclei. We can incorporate this effect into the model by employing a suitably chosen sine function as a potential energy term. This model then becomes the Modified Particle in a Box model. For example, for Dye I/IB we might introduce the potential illustrated in Figure 3.

![Figure 3. A modified particle in a box model](image)

Notice that in Figure 3 the potential energy is higher in locations where there is a nucleus and lower in between the nuclei. Since the electrons tend to move into regions of lower potential energy, a potential function like the one above will lead to increased electron density in the bonding regions between the nuclei.

The Schrödinger equation for the potential energy function shown above cannot be solved analytically. However, using numerical techniques, the equation can be solved to yield the energies and wavefunctions. See Appendix 1 entitled *Description of Integration Algorithm* for details regarding the numerical solution of the Schrödinger equation for the Modified Particle in a Box model.

**SECTION 2: EXPERIMENTAL PROCEDURE**

**A. DETERMINATION OF EXPERIMENTAL ABSORPTION SPECTRA**

1. **Dye Solutions I-III**

   **IMPORTANT:** SEE THE INSTRUCTOR/TA FOR APPROVAL BEFORE YOU RUN THE FIRST SPECTRUM.

- You will find a stock solution of each dye dissolved in methanol. For ease, the dyes are subsequently referred to as I, II, and III, respectively, as designated in the previous section.
- Refer to appendix 2 for instructions on operating the diode array spectrophotometer. Use methanol as the reference (blank) liquid in one cuvette and each solution in turn in another cuvette and obtain the absorption spectra of the first series of dye solutions (I-III). Expand the spectra over the wavelength 400-800 nm range. You may adjust this range such that three overlapping bands with different intensities are displayed.
- The most intense absorption band for each dye corresponds to the HOL → LUL transition, the two additional smaller absorption bands, which appear as shoulders correspond to the HOL → LUL + 1 and HOMO → LUL + 2 transitions.
- Record the wavelengths at maximum absorbance (\(\lambda_{\text{max}}\)) for each band. The instructor/TA will indicate how to do use the cursor to locate these.
2. Dye Solutions IB-IVB

- Stock solutions of dyes IB-IVB also are available dissolved in methanol. You should once again use methanol as the reference liquid in one cuvette and each solution in turn in another cuvette. Use a procedure similar to that employed for dye solutions I-III to obtain UV-Vis absorption spectra of dye solutions IB-IVB. Use your own judgment about the scan range to use for each dye.

B. COMPUTER MODELING

1. Particle in a Box Model

- Assume a value of 1.40 Å as an average for the C–C, C=C, and C–N bond lengths and determine the total length of the conjugated system for Dye I/IB (note that our models should give identical results for both series of dyes even though the experimental absorption spectra are not the same). To get the box length L to use in the model, add to the previous total an additional three-quarters of a bond length (i.e. 1.05 Å) at each end of the chain to account for the lone pairs of electrons. Finally, the box length must be converted from units of Å to atomic units or bohr (for the definition, see Appendix 3).

- Once the box length L is calculated, run the chem363 program on the designated computer to determine the energy levels for the π-electrons of Dye I/IB using the Particle in a Box model. Your instructor or TA will assist you in running the computer program for the first time. You will need to determine the energy levels starting from the \( n = 1 \) level and going all the way up to the LUL+2 level in order be able to calculate transition wavelengths for the three absorption peaks found in each experimental absorption spectrum. This means that since Dye I has 6 π-electrons, the HOL corresponds to the \( n = 3 \) level, the LUL corresponds to the \( n = 4 \) level, the LUL+1 corresponds to the \( n = 5 \) level, and the LUL+2 corresponds to the \( n = 6 \) level. So, for Dye I, you need to determine the energies of the \( n = 1 \) to \( n = 6 \) levels using the computer program.

- Extend this approach to the other dyes by making the appropriate changes to the box length. To determine the absorption wavelengths for Dye II/IIB you will have to find seven energy levels because it has eight π-electrons. For Dye III/IIB you will have to determine eight energy levels because it has ten π-electrons, and for Dye IVB you will have to determine nine energy levels because it has twelve π-electrons.

2. Modified Particle in a Box Model

- Repeat the calculations of the energy levels for each dye with the Modified Particle in a Box model using the chem363 computer program. The same box lengths that were used in the Particle in a Box model should be used for the Modified Particle in a Box model. Beware, however, that you must enter the number of bonds (including the lone pairs) and that the program will calculate the length automatically. Since it is more difficult to determine some of the higher energy levels for the Modified Particle in a Box model because of instabilities in the computer algorithm, you should determine enough energy levels in each case to go to the LUL+1 level only (i.e., it is not necessary to get the LUL+2 levels).

3. Visualization of Cyanine Dye Molecular Structure and Orbitals

In order to get an idea of the true three-dimensional shapes of the dye molecules and how that affects the interpretation of the particle-in-a-box models, you will use the Spartan molecular modeling software package to build the structure of a representative dye molecule. Spartan performs a more advanced calculation based on molecular orbital theory. It also provides a model view of the equilibrium molecular geometry and display 3D views of the molecular orbitals for each of the dye molecules. Recall that an orbital surface is the square of the wavefunction, with that in mind try to correlate the surfaces obtained in Spartan with the results obtained using the particle in a box model.

a. Introduction to the Spartan Molecular Modeling Software Package

- To begin, go to SLB 260 and log on to one of the Linux workstations (username: chem363, password: quantum). Once you are logged on you should first briefly read through Chapter 2 of the manual entitled Spartan '02 Tutorial and User Guide, which can be found on the tables near the Linux workstations. Do not remove this manual from the lab. The Spartan program is started by typing "spartan" in the window on the screen and hitting the "Enter" or "Return" key.

- When you are reading Chapter 2 of the tutorial, pay special attention to the section on use of the menus and the section on use of the mouse for rotating, translating, and zooming molecules. To test the use of the mouse for manipulating molecules, select "Open" from the "File" menu at the top of the Spartan window, and then select "benzene" from the dialog box. A benzene molecule should appear on the screen, which you can use to practice mouse movements. You may also complete parts of Chapters 3 and 5 in the user’s guide, which will show you
how to build simple molecules and perform different types of calculations using the Spartan program. In Chapter 3, you may perform the calculations on acetonitrile only through step 12. In addition, you may do the first part of Chapter 5 in order to learn how to use the Expert Builder. You only need to complete the exercise on sulfur tetrafluoride, steps 1-7. Once you have read Chapter 2 and completed the specified portions of Chapters 3 and 5, you are ready to begin modeling the cyanine dye molecules. You will be required to build and perform a molecular orbital calculation on Dye I. In the interest of time, similar calculations have already been performed on the other dye molecules. You will be able to access the output from these calculations in order to analyze results and observe trends.

b. Building and Performing a Molecular Orbital Calculation on Cyanine Dye I

- Now that you have completed the suggested portions of the Spartan tutorial, you are ready to build Dye I, which is shown in Figure 1. Follow the instructions that you learned in the tutorial to create a new molecule.
- When building the dye molecule, it is easiest to begin with one of the naphthalene-like rings. To obtain a naphthalene ring, click on "Rings" in the Builder, select "Naphthalene" from the pull-down menu, and click in the builder window to position the naphthalene. To change one of the atoms in the naphthalene ring from carbon to nitrogen, switch to the Expert Builder, click on the nitrogen atom in the periodic table, and then double click on the atom in the builder window that you wish to change.
- At this point, you can continue to build the dye molecule in any order that you wish, either by adding the ethyl group onto the naphthalene-like ring or by adding the sp²-hybridized carbon bridge along with the second naphthalene-like ring structure. It is not necessary to include the lone pairs or the positive charge that are shown in Figure 1, nor is it necessary to include the iodide counter ion. The lone pairs are automatically accounted for in the calculation and the positive charge will be included when the calculation is set up. Once you have completed building the dye molecule, save it with a name such as "dye1-WXYZ," where WXYZ are you and your partner’s initials, and return to the main menu.
- To set up a calculation of the equilibrium structure of Dye I, select "Setup → Calculations". The task is "Equilibrium Geometry", the model is "Semi-Empirical AM1", and the Total Charge should be set to "Cation". Click "Save" and then, to run the calculation, select "Setup → Submit" from the main menu. If you get a message indicating that the calculation failed (ran out of cycles), submit it again. If you get any other sort of error message, consult your instructor for assistance.
- Once the equilibrium geometry calculation is complete, you must next run a calculation of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for the dye molecule. From the main menu, select "Setup → Surfaces". Then, select "HOMO" from the "Surfaces" pull-down menu and click "Add". (All the other default settings are fine.) Repeat for the LUMO. Click "Save" and then "Setup → Submit" from the main menu. The calculation of the HOMO and LUMO should complete in a few seconds.

c. Analysis and Molecular Orbital Visualization of Cyanine Dye Molecules

- To begin the analysis of the dye molecules, dye molecule 1 should still be displayed on your screen. You can rotate it using the middle mouse button. Note its shape. Is it planar as would be expected for a conjugated system? Why or why not?
- You can measure the nitrogen-nitrogen distance by selecting "Geometry → Measure Distance" from the Spartan main menu. Then, click on the two nitrogens to get the distance. Note that this distance is a straight line. Would electrons move along that line? Would they zig-zag through the bonds? What would this imply when modeling the system as a one-dimensional box?
- You can view the HOMO and LUMO by selecting "Display → Surfaces" from the Spartan menu. Click on the box next to HOMO to display it (red corresponds to a positive sign and blue a negative sign for the orbital). Look at both the HOMO and LUMO. Are they what you would expect for a planar conjugated molecule? If you are unsure, you might want to look at the HOMO and LUMO for the octatetraene molecule (available in the "dyes-spartan" folder). Do the HOMO and LUMO extend through parts of the molecule that are not in the nitrogen-nitrogen conjugated region?
- To view and analyze the rest of the dye molecules, close Dye I and then from the main Spartan menu, select "File → Open" and double click on the listing for the directory called "dyes-spartan". Then, select "dye2" and click on "Open". You should look at dye2 to view its shape, determine the nitrogen-nitrogen distance, and visualize the HOMO and LUMO. After you have analyzed dye2, repeat the same analysis for dye3. Note any trends that you observe in the shapes, distances, and orbitals.
- Finally, you should also look at the thiacarbocyanine dyes, IB-IVB. Make sure to note interesting structural or orbital differences between dye series I-III and dye series IB-IVB.
SECTION 3: CALCULATIONS

Particle in a Box Calculations
From the Particle in a Box computer simulations, for each of the dyes, calculate the three absorption wavelengths for the following π-electron transitions: HOL → LUL, HOL → LUL+1, and HOL → LUL+2. The wavelengths can be calculated from the energy level differences using the equation

\[ \lambda = \frac{hc}{\Delta E}. \] (5)

The energy units provided by the software are atomic units or hartrees. Make sure you convert this to SI units (joules) before using equation (5). From Eq. (3), you can also calculate the HOL → LUL absorption wavelength analytically. Do this for each of the dyes.

Modified Particle in a Box Calculations
From the Modified Particle in a Box computer simulations, for each of the dyes, calculate the absorption wavelengths for the following π-electron transitions: HOL → LUL and HOL → LUL+1.

SECTION 4: ITEMS TO INCLUDE IN THE LAB REPORT

Please note that the list of items to include in the lab report does not include everything that should go into the lab report. Since this is a formal report, you should refer to the handout on writing lab reports for a full description of the formal report style. The formal report must include an abstract, an introduction, and experimental procedures in addition to the items listed below. The items listed below are meant to give a selection of some of the key items that must be included.

Experimental Absorption Wavelength Data
Include a tabulation of the experimental absorption wavelengths for each of the dyes (obtained from the experimental absorption spectra).

Computer Simulation Data and Results
For each of the dyes, prepare a list of the energy levels that were obtained from the computer simulations of the Particle in a Box and Modified Particle in a Box models.

Prepare a tabulation of the calculated absorption wavelengths from the Particle in a Box (both from the computer simulation and analytic solution) and Modified Particle in a Box models for each dye.

Discussion
Compare the results for the experimental absorption wavelengths for each dye to the two computer simulation models. Compute percent differences between the experimental values and the models. Discuss any trends observed. Is the quantitative agreement good or do the models merely account for the trends in the absorption wavelengths for this series of dyes? Discuss how the agreement between the models and experimental spectra is different for dye series I-III compared to dye series IB-IVB. Discuss whether one of the models seems to provide better agreement with experiment than the other.

Compare the HOL → LUL absorption wavelengths for each dye obtained from the computer program for the Particle in a Box with those obtained analytically from Eq. (4). Do they agree? What does this tell you about using a numerical approximation (from the computer program) as opposed to using the analytical solution from Eq. (4)?
Compare the wavelengths of the HOL → LUL, HOL → LUL+1, and HOL → LUL+2 transitions for the Particle in a Box model. What happens to each of these transitions as the length of the box increases? What does this suggest in general based on the errors with respect to the experimental wavelengths about the box lengths that were used in the Particle in a Box calculations? That is, were the box lengths employed in the calculations too large or too small for dyes I-III? What about for dyes IB-IVB?

Discuss how the three-dimensional structures deviated from your expectations for conjugated systems in dyes I-III and 1B-IVB. Were the measured nitrogen-nitrogen distances in accord with what you employed in the computer simulations? Note that you may want to add in 1.5 bond lengths to the measured nitrogen-nitrogen distances to account for spill-over of electron density to be consistent with the simulation lengths.

From the analytical equation for the HOL → LUL transition wavelength, Eq. (5), substitution of the experimental transition wavelength for dye I and the number of π-electrons allows you to solve for the “experimental” box length. Repeat this process to get experimental box lengths for each of the dyes. Discuss how the experimental box lengths compare with the values used in the Particle in a Box models as well as with the measured nitrogen-nitrogen distances. Also, discuss how the experimental box lengths correlate with what you observed with respect to the extent of the HOMOs and LUMOs. Based on these observations, can you propose a more appropriate way to determine box lengths to use in the Particle in a Box simulations?

Finally, discuss one or two significant factors that are omitted in the Particle in a Box and Modified Particle in a Box models that could lead to deviations between the experimental and computer simulation results.

Treatment of Data
Show a sample calculation of the box length used in the Particle in a Box and Modified Particle in a Box simulations.

Provide sample calculations of the HOL → LUL, HOL → LUL+1, and HOL → LUL+2 wavelengths from the Particle in a Box energy levels and of the HOL → LUL and HOL → LUL+1 wavelengths from the Modified Particle in a Box energy levels.

Also, provide a sample calculation of the HOL → LUL absorption wavelength obtained from the analytic solutions to the Particle in a Box model, Eq. (3), and a sample calculation of the “experimental” box length obtained from the experimental wavelength assigned to the HOL → LUL transition and Eq. (5).

No uncertainty or propagation of error calculations are required.
APPENDIX 1: DESCRIPTION OF INTEGRATION ALGORITHM

For one-dimensional systems, the Schrödinger equation in atomic units is given by

\[ \Psi''(x) = 2m [V(x) - E] \Psi(x). \tag{1} \]

A simple finite-difference algorithm can be used to obtain solutions (wavefunctions and energy eigenvalues) to the Schrödinger equation. For small increments, \( \delta \), the following approximations for the first and second derivatives are valid:

\[ \Psi''(x) = \left[ \Psi(x + \delta/2) - \Psi(x - \delta/2) \right]/\delta \tag{2} \]
\[ \Psi'(x + \delta/2) = \left[ \Psi(x + \delta) - \Psi(x) \right]/\delta \tag{3} \]
\[ \Psi'(x - \delta/2) = \left[ \Psi(x) - \Psi(x - \delta) \right]/\delta. \tag{4} \]

Substitution of Eqs. (3) and (4) into Eq. (2), followed by the substitution of Eq. (2) into Eq. (1) yields after rearrangement,

\[ \Psi(x + \delta) = 2\Psi(x) - \Psi(x - \delta) + 2m [V(x) - E] \Psi(x) \delta^2. \tag{5} \]

The crux of the algorithm presented here is that if \( V(x), \Psi(x), \Psi(x - \delta), \) and \( E \) are known, then \( \Psi(x + \delta) \) can be calculated. Once the system is specified, \( V(x) \) is known and can be calculated. The left-hand boundary condition dictates the value of \( \Psi(x - \delta) \) and \( \Psi(x) \) can be given an arbitrary positive value, so only \( E \) has to be supplied in order for the iterative character of the algorithm to take over. Once \( \Psi(x + \delta) \) is calculated, it serves as \( \Psi(x) \) in the next iteration and \( \Psi(x) \) serves as \( \Psi(x - \delta) \).

If the guess used for \( E \) generates a wavefunction which satisfies the right-hand boundary condition, then \( E \) is an energy eigenvalue. If the right-hand boundary condition is not satisfied, then another guess for \( E \) must be made. It is quite easy to bracket the correct value of \( E \) because guesses for \( E \) which are too large yield wavefunctions that miss negatively at the right boundary, while \( E \) values which are too small yield wave functions that miss positively.
APPENDIX 2: INSTRUCTIONS FOR RUNNING THE HP 8453 UV-VIS SPECTROPHOTOMETER

1) Turn on the power to the instrument. The power button is located in the lower left corner of the UV-Vis spectrophotometer.

2) Start the instrument software in the computer. To do this, simply double click on the icon labeled Uv-vis (online) on the desktop or into the Start button, then All Programs, then ChemStation, then Instrument 1 (Online).

3) After a short time a dialog box will appear asking for the Operator Name and Password. Enter your name, then OK.

4) The next step is to make sure that the Deuterium and Tungsten lamps are on. In the lower left corner of the screen is a box with a diagram of the spectrophotometer. In this diagram there are two bulbs. If the lamp icons are ON, you can go on to step 5. Otherwise, move the mouse over one and the cursor should change from an arrow to a hand. Once the hand appears click on the left mouse button and a small dialog box should appear. Click on the Lamp ON option. After a couple of minutes, the lamp will either 'light up' or a box will appear stating that lamp ignition failed. If the box appears, click on retry until the lamp ignites. Repeat the above procedure for the other lamp.

5) Next, insert the cuvette with the blank in the spectrophotometer. In the lower left box, click on Blank button. When the scan is done, minimize (DO NOT CLOSE) the box with the blank spectrum.

6) Remove the blank and insert the dye. Click on the Sample button.

7) When the scan is done the Instructor or TA will show you how to obtain the wavelengths at maximum for all the bands.

8) Repeat steps 5 to 7 for the other dyes.

9) When you are all finished, turn the lamps off, close the program and shut off the spectrophotometer.
APPENDIX 3: ATOMIC UNITS

Because of their convenience in quantum mechanical calculations, atomic units are used in the computer simulations. Some conversion factors are provided below:

Length: \(1.0 \text{ bohr} = a_\text{o} = 52.9 \text{ pm} = 0.529 \text{ Å}\)

Energy: \(1.0 \text{ hartree} = 27.21140 \text{ eV} = 4.359748 \times 10^{-18} \text{ Joule} = 2.194746 \times 10^5 \text{ cm}^{-1}\)