

LAB 5 ABSORPTION SPECTRA OF CONJUGATED DYES

Introduction

- Particle in a box*
- Computational Chemistry*
- HOMO/LUMO of conjugated dyes*
- TDDFT*

5.1 Quantum Theory Background

5.1.1 Particle in a Box

The quantum mechanical problem of describing the motion of a particle confined in a one-dimensional box is the first problem encountered as we begin to wade into modern atomic and molecular theory in the first semester of Physical Chemistry. Mathematically, the problem of the particle-in-a-box illustrates the key features of quantum theory with respect to translational motion such as eigenfunctions and eigenvalues, operators, and the non-classical concept of a zero-point energy. Consider a particle confined to move in the x -dimension in a box of length L . Inside the box, the potential, $V(x)$, is zero while outside the box, $V(x)$ is infinite (see Figure 5.1a).

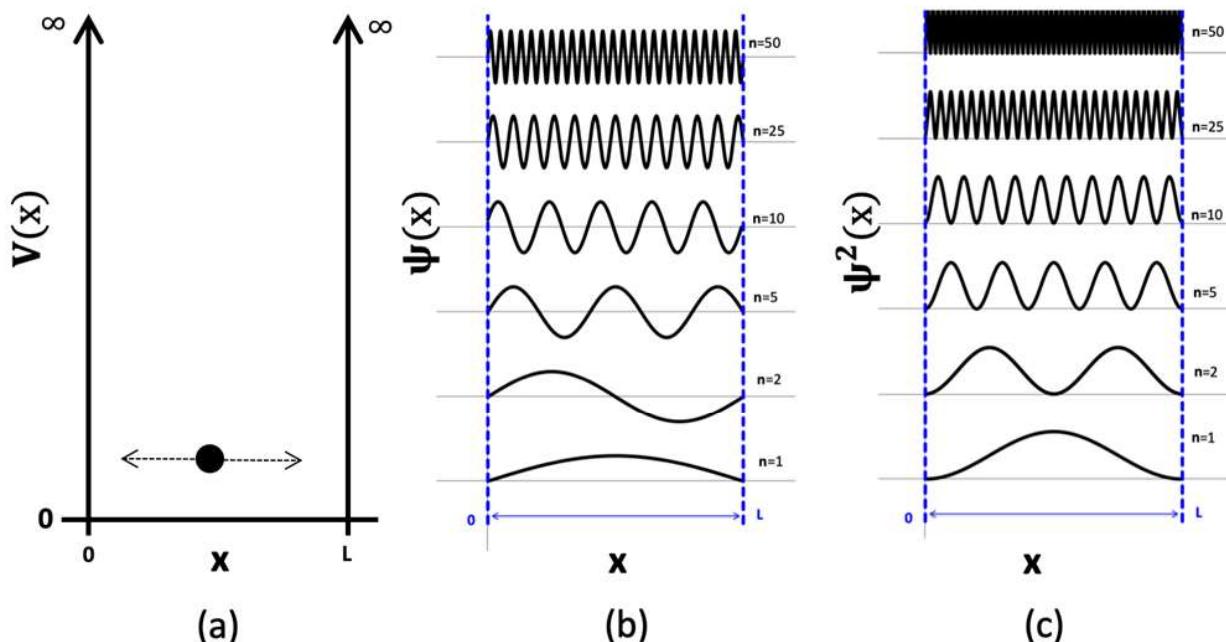


Figure 5.1: $V(x)$, $\Psi(x)$ and $\Psi^2(x)$ for the particle in the box solutions.

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Schrödinger's equation for a particle confined to move one-dimensionally (in x) is given by Equation 5.1.

$$-\frac{\hbar^2}{2m_e} \frac{d^2}{dx^2} \Psi(x) + V(x) = E\Psi(x) \quad (5.1)$$

Confining the particle inside a one-dimensional box ($0 \leq x \leq L$) leads to a quantization of allowed energies. Outside the box ($x \leq 0$ and $x \geq L$) $V(x)$ is infinite and thus $\Psi(x)$ is zero. In quantum mechanical terms, that $\Psi^2(x)$ is zero outside the box means there is zero-probability of finding the particle outside the box. Inside the box ($0 \leq x \leq L$), $V(x) = V$ (constant). Schrödinger's equation becomes

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi_i(x) = (E_i - V)\Psi_i(x) \quad (5.2)$$

which is solvable with elementary differential equations giving the following eigenfunctions, $\Psi(x)$ and eigenvalues, E .

$$\Psi_i(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n_i\pi x}{L}\right) \quad (5.3)$$

$$E_i - V = \frac{\hbar^2 n_i^2}{8mL^2} \quad (5.4)$$

For a finite well when $V < V_0$, Equation 5.4 becomes

$$E_i - V = \frac{\hbar^2 n_i^2}{8mL^2} \quad (5.5)$$

Far from being only a pedagogical and mathematical exercise, confining a particle to move in one dimension in a bounded region has application in predicting properties of molecules that can be measured. The energy levels predicted by solutions to the one-dimensional particle-in-the-box problem may be used to predict the maximum absorption wavelength, λ_{MAX} , for some chemical compounds that absorb light in the visible spectrum. Such compounds generally have delocalized electrons, such as the odd electron in a free radical species or the π electrons in a conjugated organic molecule. In this experiment λ_{MAX} will be determined for several conjugated dye molecules (having the general form shown in Figure 5.2) which absorb in the visible part of the spectrum. The measurements will be compared to predictions of λ_{MAX} by Equation 5.4 as manipulated below. This approach is referred to in the literature as the “free-electron model.”¹

The λ_{MAX} of the visible spectrum may be approximated as transitions of the π electrons between the **HOMO** (Highest Occupied Molecular Orbital) and the **LUMO** (Lowest Unoccupied Molecular Orbital) as defined in Equation 5.4. Referring to Figure 5.3, each carbon atom in the π -electron backbone contributes one (1) electron, the nitrogen at the left boundary contributes two electrons (sp^3), and the nitrogen on the right boundary (ionized) contributes one more. Thus, the total number of electrons (M) populating the π -molecular orbitals is given by Equation 5.6 where

¹W. Jensen, O. Schmidt, J. Platt. “The Free-Electron Model,” ACS Symposium Series; American Chemical Society (2013): 117-137.

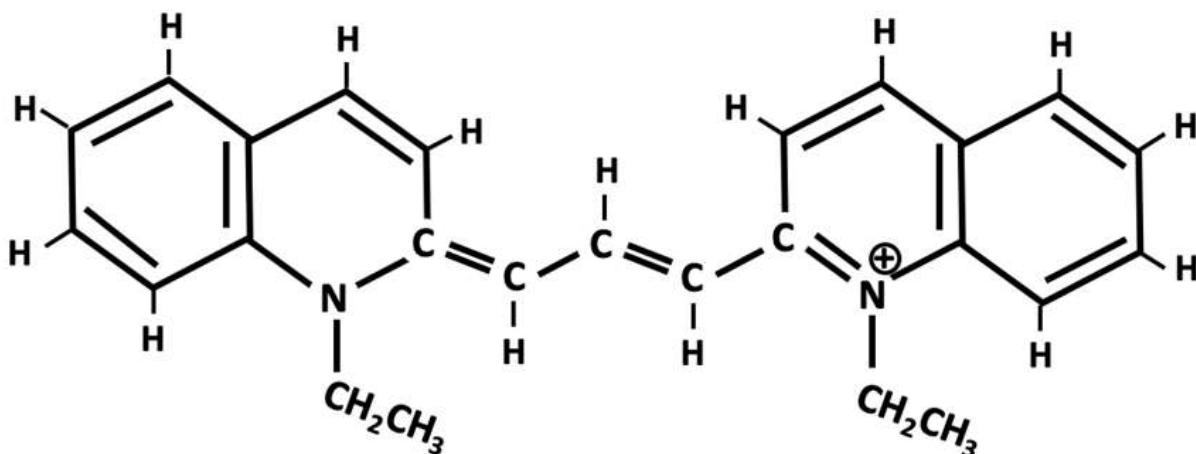


Figure 5.2: A conjugated dye compound with five carbons in the forming the π -electron backbone

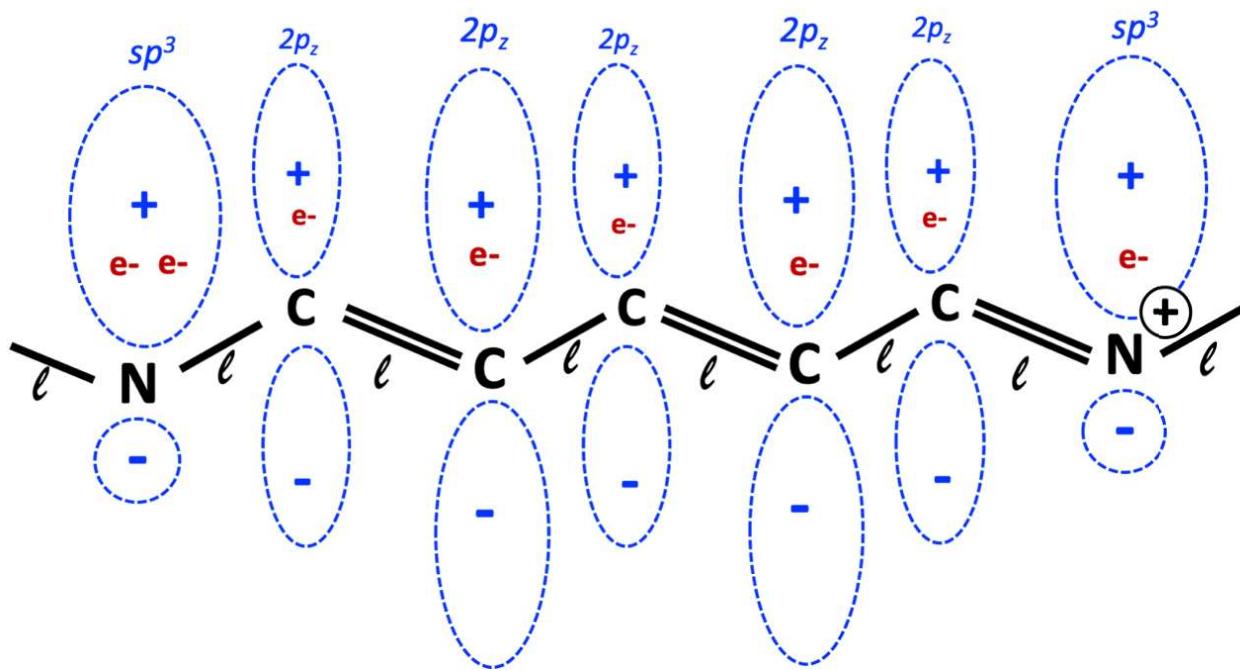


Figure 5.3: The atomic orbitals forming the π -electron backbone in a conjugated dye compound with five (5) carbons.

p is the number of carbon atoms in the π -electron backbone.

$$M = p + 3 \quad (5.6)$$

For a molecule with M electrons in the conjugated system, using the standard building-up (Aufbau) principle, the $M/2$ lowest energy levels will be filled in the ground state (see Figure 6.4). The absorption of light is associated with the transition from the HOMO ($n_1 = M/2$) to the LUMO

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$(n_2 = M/2 + 1)$ is ΔE defined in Equations 5.7-5.9.

$$E_2 - V - (E_1 - V) = \Delta E = \frac{h^2}{8m_e L^2} \times (n_2^2 - n_1^2) \quad (5.7)$$

$$(n_2^2 - n_1^2) = \left(\frac{M}{2} + 1\right)^2 - \left(\frac{M}{2}\right)^2 = \frac{M^2}{4} + M + 1 - \frac{M^2}{4} = M + 1 \quad (5.8)$$

$$\Delta E = \frac{h^2}{8m_e L^2} \times (M + 1) \quad (5.9)$$

n=6 —————

n=5 ————— LUMO: $n_2 = \frac{M}{2} + 1 \quad (M = 8, n_2 = 5)$

$$\Delta E = \frac{hc}{\lambda_{MAX}}$$

n=4 ↑↓ ————— HOMO: $n_1 = \frac{M}{2} \quad (M = 8, n_1 = 4)$

n=3 ↑↓ —————

n=2 ↑↓ —————

n=1 ↑↓ —————

Figure 5.4: The "building up" of the molecular energy levels for a conjugated dye compound with five (5) carbons and therefore $M=8$ electrons.

It is assumed that the potential energy, $V(x)$, is constant along the π -electron backbone, and that it rises sharply to the infinity at the ends. To determine the length, L of the approximated one-dimensional "box," refer again to Figure 5.3. As a simplifying assumption, the average C-C and C-N bond distance is designated l . For a conjugated dye compound with p carbon atoms, there are $p - 1$ C-C bonds, two C-N bonds, and an additional length of one bond length on either side of the nitrogen atoms.²

$$L = (p - 1 + 2 + 2)l = (p + 3)l \quad (5.10)$$

Substituting Equations 5.10 and 5.6 into Equation 5.9, we have the working equations for ΔE and λ_{MAX} in terms of known constants and p , the number of carbons in the π -electron conjugated

²Hans Kuhn, "A Quantum-Mechanical Theory of Light Absorption of Organic Dyes and Similar Compounds", *J. Chem. Phys.*, **1949**, 17, 12, 1198

backbone. The literature value the average bond distance, l , is 1.39 Å.³

$$\Delta E = \frac{h^2(p+4)}{8m_e l^2(p+3)^2} \quad (5.11)$$

$$\lambda_{\text{MAX}} = \frac{8m_e cl^2(p+3)^2}{h(p+4)} \quad (5.12)$$

5.1.2 Computational Chemistry

Computational chemistry emerged as a field of chemistry in conjunction with the digital age. However, the seminal work of chemists, mathematicians, and physicists such as Erwin Schrödinger and Douglas R. Hartree, as well as Chemistry Nobel Laureates John Pople and Walter Kohn, throughout the 20th century constructed the foundation of computational chemistry long before the digital age began. Computational chemistry has become so important because it can provide valuable insight into chemical processes and properties that are difficult to measure experimentally and rationale for mechanistic features within known chemical reactions. There are many sub-fields of computational chemistry, which can be categorized based upon their theoretical foundation such as *ab initio* methods, density functional theory (DFT), semiempirical methods, and molecular dynamics. These approaches are used to investigate the vast numbers of chemical systems ranging from atoms to proteins and semiconductor materials like graphene and TiO₂. Among the more rigorous of these methods are *ab initio* approaches, or methods based on first principles, which focus on modeling the electronic structure of atoms and molecules but often at a high computational cost (memory, disk space, CPU time) relative to DFT.

Computational chemistry experiments consist of combining a method, e.g., most commonly *ab initio* or DFT, with a basis set, which is a set of mathematical functions used to describe the electronic wavefunction. Gaussian-type functions ($\phi(\zeta, r) = Ne^{-\zeta r^2}$) were chosen for the construction of basis sets since the product of two Gaussians is another Gaussian, which greatly simplifies the most computationally expensive steps in computing the electronic energy. As far as method choice, DFT is among the more popular computational methods due to their ability to yield results comparable to more rigorous and computationally demanding methods at a reduced computational cost. DFT originates from the Hohenberg-Kohn theorems in 1964, an existence proof that proved that the charge density ($\rho[r]$) completely determines the electronic properties of the ground state including energy. The implementation of DFT is the development of numerous functionals that approximate the relationship between electron exchange and correlation and comes in numerous flavors, which makes picking a functional to use like darts on a dartboard—hoping to hit a bulls-eye for accuracy to experiment.

³David P. Shoemaker, Carl W. Garland, and Joseph W. Nibler, Experiments in Physical Chemistry, 5th ed. (New York: McGraw-Hill, 1989), 442.

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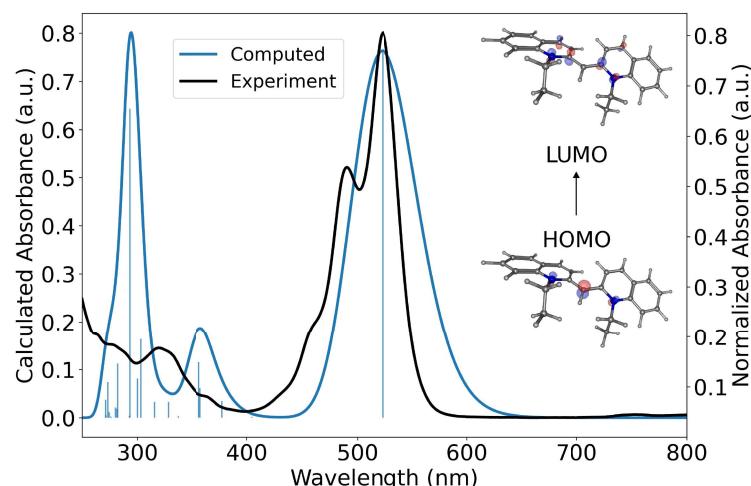
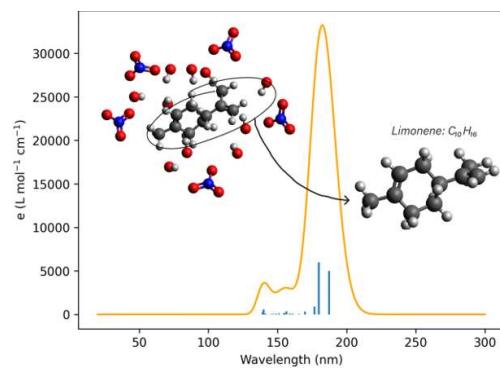


Figure 5.5: A combined experimental and computational spectra with the exact transition energies as vertical lines. The computed spectra is linearly shifted by +81.8 nm to overlap with the experimental spectra. The molecular orbital picture showcases where the electrons are located at the transition corresponding to λ_{MAX} .

correct description of the chemistry of the transitions. To correct this underestimation, linear shifts (shifting absorption energies by the mean absolute error) and linear transformations (shifting the absorption energies via the best fit line between computed and experimental absorption energies) are techniques employed to show how TDDFT correctly predicted the lineshape of the spectra (Figure 5.5).⁴ Range separated hybrid density functionals, such as CAM-B3LYP and ω B97X-D3, are constructed to deal with long range interactions between electrons, which makes these types of functionals suitable for modeling absorption spectroscopy.

A use case for computed UV-Vis spectra is the prediction of the structure, spectroscopy, and formation mechanisms of aerosols. Coordination spheres consisting of solvent or other atmospheric gas phase particles present in the atmosphere at night can be used to simulate more realistic conditions. This example consisted of O₃ and NO₃ radicals coordinated to monoterpenes. The figure on the right was contributed by Bianca Aridjis-Olivos (B.S. Chemistry '23).

To model absorption spectra, as needed for this experiment, computational methods that target excited state electronic configurations must be utilized. Within the scope of DFT, time-dependent density functional theory (TDDFT) has been shown to be useful for modeling UV-Vis absorption as well as X-ray absorption, which follows the same principles of absorption by exciting core electrons rather than valence electrons to the unoccupied orbitals. It is also well-established that TDDFT severely underestimates X-ray absorption energies by around 30-100 eV depending on the choice of functional but get the



⁴Patel, P. et al., Integrated Experimental and Computational K-edge XANES Analysis of Vanadium Catalysts. *J. Phys. Chem. C*. 2022, 126, 11949-11962. <https://doi.org/10.1021/acs.jpcc.2c02049>.

5.1.3 Particle in a Finite Well

In terms of model complexity, the finite well is one step above the particle in an infinite well problem. The inclusion of a finite potential at V_0 allows for particles to tunnel through the potential. This is denoted with exponential functions. Figure 5.6 shows the general solutions to the wavefunctions within each region (I, II, and III).

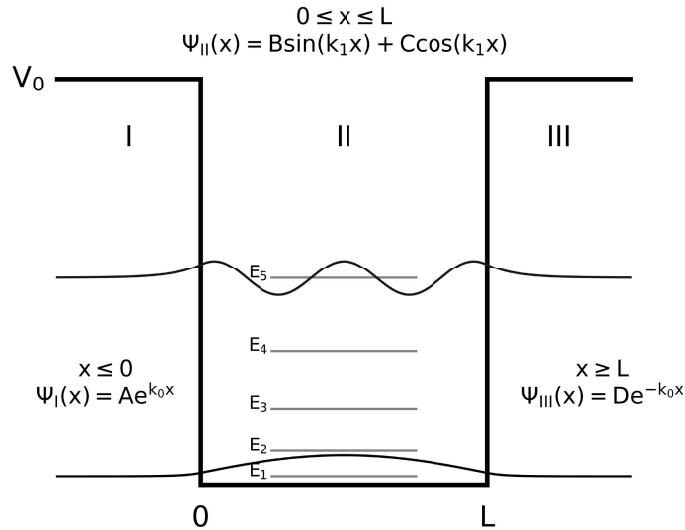


Figure 5.6: Schematic and Wavefunction for the particle in a finite well model.

Consider a particle in a finite well model where

$$k_0 = \sqrt{\frac{2m_e}{\hbar^2}(V_0 - E)} \quad (5.13)$$

$$k_1 = \sqrt{\frac{2m_e E}{\hbar^2}} \quad (5.14)$$

To determine the energy eigenvalues from the wavefunction, we begin the derivation where $\Psi_I(x)$ and $\Psi_{II}(x)$ must follow the boundary conditions at $x=0$, i.e., $\Psi_I(0) = \Psi_{II}(0)$ and $\Psi'_I(0) = \Psi'_{II}(0)$.

$$Ae^{k_0(0)} = B\sin(k_1 * 0) + C\cos(k_1 * 0) \quad (5.15)$$

$$Ak_0e^{k_0(0)} = Bk_1\cos(k_1 * 0) - Ck_1\sin(k_1 * 0) \quad (5.16)$$

By solving the system of Equations 5.15 and 5.16,

$$C = A \quad (5.17)$$

$$B = A\frac{k_0}{k_1} \quad (5.18)$$

At $x=L$, the system of equations containing $\Psi(L)$ and $\Psi'(L)$ is

$$De^{-k_0L} = B\sin(k_1L) + C\cos(k_1L) \quad (5.19)$$

$$De^{-k_0L} = Bk_1\cos(k_1L) - Ck_1\sin(k_1L) \quad (5.20)$$

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By multiplying Equation 5.19 by k_0 and using Equations 5.17 and 5.18,

$$Dk_0e^{-k_0L} = A \frac{k_0^2}{k_1} \sin(k_1 L) + Ak_0 \cos(k_1 L) \quad (5.21)$$

$$Dk_0e^{-k_0L} = -A \frac{k_0}{k_1} k_1 \cos(k_1 L) + Ak_1 \sin(k_1 L) \quad (5.22)$$

By equality, Equations 5.21 and 5.22 may be solved for the quantity $Dk_0e^{-k_0L}$

$$\begin{aligned} \frac{k_0^2}{k_1} \sin(k_1 L) + k_0 \cos(k_1 L) &= -k_0 \cos(k_1 L) + k_1 \sin(k_1 L) \\ k_0^2 \sin(k_1 L) + k_1 k_0 \cos(k_1 L) &= -k_1 k_0 \cos(k_1 L) + k_1^2 \sin(k_1 L) \\ 2k_1 k_0 \cos(k_1 L) &= (k_1^2 - k_0^2) \sin(k_1 L) \\ 2k_1 k_0 &= (k_1^2 - k_0^2) \tan(k_1 L) \end{aligned} \quad (5.23)$$

By substituting k_0 and k_1 into Equation 5.23,

$$2 \left(\frac{2m_e E}{\hbar^2} \right) \sqrt{E(V_0 - E)} = \left(\frac{2m_e E}{\hbar^2} - \frac{2m_e (V_0 - E)}{\hbar^2} \right) \tan \left(\sqrt{\frac{2m_e E L^2}{\hbar^2}} \right) \quad (5.24)$$

$$\frac{2\sqrt{E(V_0 - E)}}{2E - V_0} = \tan \left(\sqrt{\frac{2m_e E L^2}{\hbar^2}} \right) \quad (5.25)$$

The values of E where the two quantities in Equation 5.25 are equal correspond to the energy levels of the finite well. These functions can be plotted in Python to solve for all values of E within the well.

5.2 Procedure

5.2.1 Computational

You do not need your safety goggles for the computational portion of the experiment.

STEP 1. Build the molecules

For 1,1'-diethyl-2,2'-cyanine iodide, 1,1'-diethyl-2,2'-carbocyanine chloride, and 1,1'-diethyl-2,2'-dicarbocyanine iodide, build a three-dimensional representation in Avogadro or Chemcraft and optimize the structure using the AutoOptimization tool or a symmetry feature, respectively. Set the force field to UFF if it is not there by default. Once the optimization is complete, save the file in the xyz format. This will be the 3D structure that will be used in the calculations. Normally, we would use a more sophisticated method to get the optimized 3D geometry of the molecule, but due to time, this structure optimized with UFF will suffice as the major structural parameters of the current structure is close enough to a 3D geometry optimized with DFT.

STEP 2. Build the input files

Use the ORCA file template below to insert the xyz coordinates into the file using a notepad editor. Do not copy the first two lines that include the number of atoms and the title generated.

Note 5.1

```
# Arbitrary Title
! RIJCOSX CAM-B3LYP def2-SVP def2-SVP/C TightSCF LargePrint PrintBasis
%pal nprocs 12 end
%MaxCore 2000

%output Print [P_MOs] 1 end

%tddft
NRoots 20
MaxDim 5
TPrint 0.1
end

%cpcm smd true
smdsolvent "methanol"
end

*xyz 1 1
# XYZ coordinates go here
C 0.000 0.000 0.000 # (Example of what goes here – do not actually use this line)
...
*
```



Make sure the file extension is set to .inp.

STEP 3. Submitting jobs on the PC

Note 5.2

Underscores and dashes are a better tool than spaces for naming files and directories in Unix.



Make sure all the input files are on one of the workstation computers. Copy the three bash scripts to the folder with the input files (dye.inp). These scripts are **mkdir.sh**, **submit.sh**, and **spectra.sh**.

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Transfer your files to the Linux workstation. Open the terminal window in your respective folder.

Note 5.3

You can use the tab key to autocomplete typing in a terminal window.



Once completed, run the scripts on the local PC by typing by typing in the following

`./mkdir.sh`

`./submit.sh`

These jobs will take approximately 30-45 minutes to complete. In the meantime, collect the experimental UV-Vis spectra.

Note 5.4

**YOU MUST WEAR SAFETY GOGGLES TO EXECUTE THIS
PROCEDURE**



5.2.2 Experimental

The Perkin-Elmer Lambda 35 UV-VIS spectrophotometer will be used to take the spectra from each of three dyes in this laboratory. 10^{-3} M solutions of **1,1'-diethyl-2,2'-cyanine iodide**, **1,1'-diethyl-2,2'-carbocyanine chloride**, and **1,1'-diethyl-2,2'- dicarbocyanine iodide** dyes will be provided.

STEP 4. Set up the UV-Vis

For each of the of the three dyes, scan the visible spectrum in the region 300-800 nm to find the wavelength of maximum absorption, λ_{MAX} .

STEP 5. Collect the absorption spectra

Dilute the initial solution with methanol until the peak absorbency is about 1.0 or slightly less (≤ 1 absorption will cause a saturated signal and large errors in determining λ_{MAX}). Use only a few drops of the dye from a disposable pipette and then dilute with methanol. Record the λ_{MAX} for each scan. If the scan is not at a sufficient resolution, use an interpolation function to create a spectra with more curvature. Export the data files as csv (Comma separated values) files so you can plot the data in Excel/Python for inclusion in the formal lab report. Estimate $\Delta_{95\%}\lambda$.

5.2.3 Analyze the Computational Data

STEP 6. Generate Data Files

Once your job is finished, you should see a file with a *.out* extension and a *.cis* extension. Output (*.out*) and CIS (*.cis*) files contain **A LOT** of information, which requires one to know what information they need. Use the pre-made extraction script (**spectra.sh**) to extract the relevant information from the TDDFT calculation by typing the following in the terminal window:

```
./spectra.sh
```

This will create a *.csv* file with the information you need to plot the spectra in Python using Equation 5.27. This will count as the raw data for the computed spectra, therefore, you need to either provide a printout, or create a table (below) in your notebook. There will be 20 rows since there are 20 states that you calculated.

λ (nm)	f (a.u.)

Transfer all contents of the folder to your flash drive preferably to wherever you are storing your data for this lab.

Note 5.5

$\Delta_{95\%}$ calculations are not common for computational results as the same structure with the same parameters in the same program will yield the same results up to numerical precision. When converting from the default unit (E_h) to a more common energy unit (kJ/mol, kcal/mol, eV, etc.), the changes are negligible when the energy converges to $\sim 10^{-10} E_h$, and thus uncertainty is not typically reported for a single measurement.



STEP 7. Analyze Data

Analyze the output files by opening the output file (*.out) in Chemcraft. Right-click and open the same output file with Notepad++. On the Notepad++ window, scroll to the bottom of the output file. Then start scrolling up until you hit a section called TRANSITIONS. For STATE 1, find the line where it says XXa \rightarrow YYa. The coefficient shown on the right represents the ϵ^2 coefficient we have seen in class, indicating the highest weighted transition, i.e., the dominant contribution.

In ChemCraft, open the Tools \rightarrow Orbitals \rightarrow Render molecular orbitals tool. With your identified orbital numbers, click the orbital numbers that correspond to the MOs identified in the text file. Note that ORCA starts counting at 0 while ChemCraft starts at 1.

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Save images (File → Save as → Save image) of the molecular orbitals. Play around with the isovalue/contour value (0.03 to 0.1) and the color. **What happens to the size of the molecular orbitals as you increase/decrease the isovalue?** Feel free to rotate the molecule to adjust the zoom and isovalue to get the right angle. These will be used as part of a figure and as part of the discussion.

The extracted results from the ORCA calculations contain information about the excitation wavelength (λ) and the oscillator strength (f). You will need to broaden each transition using Equation 5.26

$$\varepsilon_i(\lambda) = 1.306\,297\,4 \times 10^8 \frac{f_i}{\sigma} \exp\left[-\left(\frac{1/\lambda - 1/\lambda_i}{\sigma}\right)^2\right] \quad (5.26)$$

where i represents the i^{th} electronic excitation, λ is the excitation wavelength in nm, f_i is the oscillator strength (a.u.), and σ is the parameter for peak broadening. Setting $\sigma = 0.2 \text{ eV} = 1/6199.2 \text{ nm}^{-1} = 10^7/6199.2 \text{ cm}^{-1}$ will result in the following reduction

$$\varepsilon_i(\lambda) = 1.306\,297\,4 \times 10^8 \frac{f_i}{10^7/6199.2} \exp\left[-\left(\frac{1/\lambda - 1/\lambda_i}{1/6199.2}\right)^2\right] \quad (5.27)$$

Equation 5.27 covers how to broaden a singular excitation. The overall spectrum will come from the sum of all the individual excitations.

$$\varepsilon(\lambda) = \sum_{i=1}^n \varepsilon_i(\lambda) = \sum_{i=1}^n \left(1.306\,297\,4 \times 10^8 \frac{f_i}{10^7/6199.2} \exp\left[-\left(\frac{1/\lambda - 1/\lambda_i}{1/6199.2}\right)^2\right] \right) \quad (5.28)$$

where n is the number of states you calculated (in this case, NStates=20). You will need to use Equation 5.28 to generate a computed spectra. In Equation 5.28, your wavelengths (λ) are the x-values and λ_i is the computed wavelength corresponding to the transition with oscillator strength f_i . Some molecular visualization programs like GaussView and Avogadro can plot the UV-Vis absorption spectra; however, you will need to combine the experimental and computational spectra into a single plot for your analysis. These programs will generate a separate image for the spectra but not the data points needed in order to combine the plots together. This is where using data analysis tools within Python could be more efficient than Excel. Plotting the results in the same figure can better show the overlaps between computed and experimental spectra, leading to insights about the chemistry occurring at an excitation wavelength. Since this formula yields the molar absorptivity coefficients (ε) in units of $\text{L mol}^{-1} \text{ cm}^{-1}$, multiply the results of Equation 5.27 by the concentration (M) of the sample. If the length l of the cuvette in cm is known, multiply by the length l of the cuvette, otherwise, assume a length of 1 cm (you would multiply the ε by 1). This will give you a calculated absorbance that you can more readily compare to the experimental spectra.

You can plot these on a two-axis plot (two separate y-axes plotted against a singular x-axis) with **Calculated Absorbance (a.u.)** on the first axis and **Normalized Absorbance (a.u.)** on the second axis (Figures 5.5 and 5.7). The extracted text file with the results gives a set of ordered pairs (λ, f) that are also represented as vertical lines on a computed spectra. You don't want the transitions to overshadow the peaks, so scale the oscillator strengths f based on the maximum calculated absorbance and include these as part of the computed spectra. Make sure the top of the vertical line appears below the maximum calculated absorbance. Using vertical lines indicate the exact calculated wavelength of the excitation. Theoretically, if line broadening was not an issue, all spectra would be a series of vertical lines. Here is the tutorial going into more detail on Equations 5.26-5.28: [How to plot UV-Vis spectra from Gaussian](#)

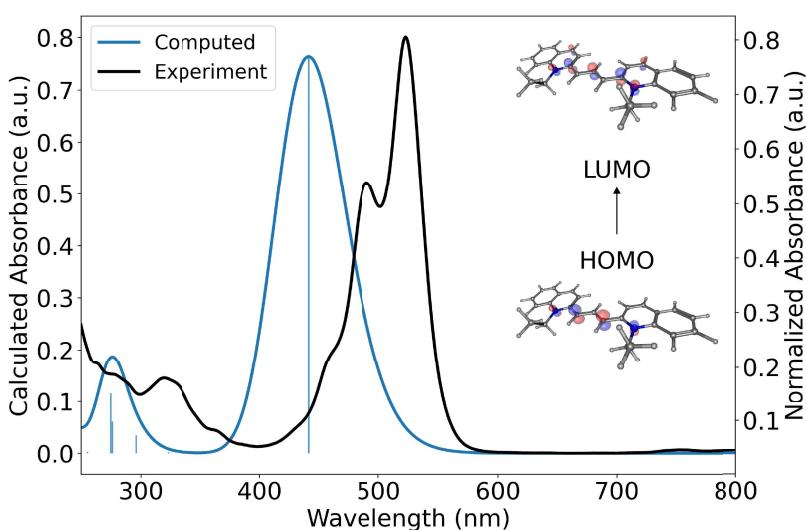


Figure 5.7: A sample figure combining an experimental and computed spectra with the exact transition energies (blue vertical lines scaled by $0.95 \cdot ABS_{MAX,computed}$) and a MO picture showcasing the location of electrons at the transition corresponding to λ_{MAX} . The code used to generate this figure is on page 86.

Examples 5.1 and 5.2 show the Python code used to make Figure 5.7. This uses a two-axis plot to compare the experimental spectra to the theoretical/computed spectra. The `vlines` function creates vertical lines. This is useful to identify the transitions obtained via theoretical spectra, as these are the centers for broadening, which can shift the peak location based on the density of states. Scaling of these lines is arbitrary as it is more for a visual aid and qualitative assessment of the ratios between transition energies rather than a quantitative analysis.

Example 5.1

```
import matplotlib.lines as mlines # Create lines for custom legends
from matplotlib.lines import Line2D

fig, ax1 = plt.subplots(figsize=(12,8))
ax2 = ax1.twinx() # Create a dual-axis plot

# Plot the computed spectra (data) and the vertical lines (transitions)
ax1.vlines(data[0], np.zeros(len(data[1])), np.array(data[1])/max(data[1])*0.95*max(spec),
color='C0', alpha=0.75)
ax1.plot(X, spec, lw=3) # spec is generated using Example 5.2.

# Plot the experimental UV-Vis data
ax2.plot(expdata[0], expdata[1], color='k', lw=3)
ax1.set_xlim(250, 800)
ymin2, ymax2 = ax2.get_ylim()

# Create a custom legend
custom_lines = [Line2D([0], [0], color='C0', lw=3), Line2D([0], [0], color='k', lw=3)]
ax1.legend(custom_lines, ['Computed', 'Experiment'], fontsize=20)

plt.tight_layout()
```

**Example 5.2**

```
# Define the function for Equation 5.26
def e(X,h,f,sigma=1/3099.6/1.5):
    f2=1e7*sigma
    A=1.3062974e8
    e1=1/h-1/X
    return A*(f/f2)*np.exp(-(e1/sigma)**2)

# Define the broadened UV-Vis spectra (spec)
X=np.linspace(100, 800, 1000)
spec=np.zeros(len(X))

# Create the computed broadened UV-Vis spectra (spec)
```

YOU WILL CODE THIS (pre-lab)



5.2.4 Theoretical

STEP 8. Use the finite well model

Equation 5.25 has been coded into Python for you to identify the energy eigenvalues. You will need to specify the box length and the value for the potential V_0 . The box length will be the calculated distance from the theoretical "free-electron" model. The potential V_0 will be calculated using the orbital energy eigenvalues. The orbital energy eigenvalues are computed by diagonalizing the Slater Determinant. Open the output file in a text editor and find the "ORBITAL ENERGIES" section. Identify the orbitals that correspond to the lowest energy conjugated π orbitals on the region within the well. Grab the energy of this orbital and the LUMO. This will represent the well depth. Since both values are negative, you will add these values together and then take the absolute value to compute V_0 . You will be responsible for reading and interpreting how this code operates while using the output of the code to compute the wavelength of the corresponding transition λ_{MAX} . A discussion of this numerical process will need to be included in the formal report.

5.3 Required Elements for the Lab Report

This is a group lab report. Every group member will need to be involved in constructing the figures and answering discussion questions.

Tables and Calculations

1. Include a table for the required dilutions for each dye to obtain a well-scaled spectrum. **(Procedure)**
2. Report how you determined or estimated $\Delta_{95\%}\lambda$. No propagation of errors is required in this lab because the λ_{MAX} is not used in a calculation, but it still needs to have a quantified precision. **(Results and Discussion)**
3. Include a table in it with the name, chemical formula, p , M , *theoretical* λ_{MAX} (Infinite Well), *theoretical* λ_{MAX} (Finite Well), *computed* λ_{MAX} , and *experimental* $\lambda_{MAX} \pm \Delta_{95\%}\lambda$. You already have prepared most of this table in your pre-lab assignment. **(Results and Discussion)**

Figures

1. You should have a total of six spectra: for each of three dyes there will be one experimental spectrum (400-750 nm) and one broadened computed spectra. Properly label the figures for reference in the text. Each group member should be responsible for creating the figures for the dye that they constructed. **(Appendix)**
2. A schematic with the energy levels of the finite well model for each dye using the box length you calculated and the V_0 obtained from the MO analysis **(Appendix)**. A representative schematic for one dye can be placed in the **Results and Discussion** section.
3. Create an overlap graph between computed and experimental spectra on a two-axis plot. **(Results and Discussion)**
 - (a). This can be a three-part one-column figure where each dye is a separate plot (a 3 row, 1 column subplot). Each group member should contribute to making this figure.
 - (b). Include the transition energies (λ, f) as vertical lines.
 - (c). Include an inset figure that showcases the orbitals involved in the transition corresponding to λ_{MAX} .
 - (d). Your figure should emulate either Figure 5.5 or 5.7 with the appropriate ranges depending on which spectra you use (coarse or precision). Whichever you choose, make sure to justify your reasoning.
 - (e). While it is possible to create the figure in a single program, you may use separate programs to create the plot and inset figure, e.g., Excel/Python and PowerPoint, based on what you think is the best use of your time and how you want to construct the figure.

Discussion Questions

1. Based on your experimental results, make a general statement about the accuracy of the free-electron model. Include a table containing the theoretical λ_{MAX} from the free-electron model, the theoretical λ_{MAX} from the finite well, the computed λ_{MAX} from TDDFT, and the experimental λ_{MAX} . Include the $\Delta_{95\%}\lambda$ and %-error calculated by Equation 5.29.

$$\% \text{ error} = \left| \frac{\text{theoretical } \lambda_{MAX} - \text{experimental } \lambda_{MAX}}{\text{theoretical } \lambda_{MAX}} \right| \times 100 \quad (5.29)$$

2. Discuss sources of systematic error that might give rise to the % error in λ_{MAX} that you observe. Use the resources provided in Brightspace (and footnoted herein) for this discussion. Proper citation is required.
3. As discussed in class, the finite well model is the next step in complexity from the PIB model. How does the finite well PIB model correspond to the conjugated dyes? What is the effect of well depth on the calculated absorbance wavelengths? Did using the finite well model improve your results from the theoretical λ_{MAX} calculated from the infinite well?
 - (a). How did the Python code used for the finite well model work? What did the code do? These two questions can go into the **Procedure** section if the text flows better there.
4. Based on your spectra, account for the observed colors of the dyes.
5. Which orbitals were responsible for the transition that corresponds to λ_{MAX} ?
6. Are there other features in your experimental spectra that the TDDFT results can identify? If so, how would you go about identifying those?
7. What causes peak broadening in spectroscopy? Why do computed spectra return vertical lines rather than a broad spectra? *Hint: Consider Heisenberg's Uncertainty Principle and the chapters on spectroscopy (covered in CHE 3332).*

5.4 Pre-lab Quiz (5 pts)

Close out Lab 4 in your notebook and enter the page numbers in the table of contents. Make a clear beginning in the notebook for Lab 5. Use this space to work through equations 5.7 through 5.12 to make sure you have a firm grasp on how λ_{MAX} is estimated from the framework of the energies predicted by the solutions to particle-in-a-box problem. Answer these questions on the Pre-lab worksheet and add to your notebook.

1. Determine p and M for each dye listed in the Procedure section. Obtain chemical formulae and chemical structure for each and enter them into your notebook. A useful source for information on the dyes is [Sigma Aldrich](#).
2. Use Equation 5.12 to calculate the theoretical λ_{MAX} from the free-electron model. Your notebook should have a table in it with the name, chemical formula, p , M , and *theoretical* λ_{MAX} . Keep a blank column in reserve for your *experimental* λ_{MAX} .
3. Find the references for CAM-B3LYP, def2-SVP, SMD solvation model, and ORCA 5. List them in ACS format in your notebook. *Hint: These are highly cited articles.*
4. Use Equation 5.28 and Example 5.2 to create a computationally broadened spectra for a 2×10^{-5} M solution of a dye-like molecule with the information provided below. Include the vertical lines that will correspond to these transitions.

λ (nm)	f
560.12	2.5769
500.17	0.0035
450.74	0.4934
345.56	0.0657
323.45	0.0063

5.5 Lab Notebook Grading Rubric (20 pts)

1. **(8 pts)** Laboratory notebook set-up
 - (a). Notebook labeling (2 pts)
 - (b). Closure of the previous lab, clear beginning of Lab 6 (2 pts)
 - (c). Page numbering (2 pts)
 - (d). Use of ink (2 pts)
2. **(8 pts)** Laboratory work
 - (a). Neat and organized.
 - (b). All data collected in the lab contained in the notebook.
 - (c). Key graphs
 - (d). Each page signed and dated.
3. **(4 pts)** Clear, *data-based*, scientific conclusion for the laboratory work.

5.6 Formal Report Grading Rubric

Submission Instructions: Submit to **Brightspace** as a PDF. Only one group member needs to do this.

NAME: _____

Date submitted:

Formal report * 0.75	75	
Lab notebook	20	
Pre-Lab Quiz	5	
Total	100	

Section	Key Points	Points	Grade
ALL	Formatting	10	
ALL	Spelling and Grammar	5	
Abstract	Clarity and Completeness	5	
Introduction	<ul style="list-style-type: none">Purpose, MethodStart with $E_n = \frac{h^2 n^2}{8m_e L^2}$ (don't derive this) and discuss its relevance to absorption spectra of these conjugated systems. Also include finite wells.How computational chemistry, i.e., TDDFT, can be used to model UV-Vis absorption spectra.	10	
Experimental Procedure	<ul style="list-style-type: none">Equipment and procedure (computational as well)Flow (step-by-step)Table of amounts and types of each dye with dilutionsHow to determine λ_{MAX}	15	
Results and Discussion	<ul style="list-style-type: none">Table of data (λ_{MAX} for each dye and method) (see instructions above)A figure in the main text like either Figure 5.5 or 5.7.	10	
	<ul style="list-style-type: none">What is the end goal?Include clear understanding of how ΔE and λ_{MAX} are related to the number of carbons in the chain.	20	
	<ul style="list-style-type: none">Discuss each of the discussion questions on page 89Table of λ_{MAX} (theory, exp, computed), $\Delta_{95\%}\lambda$, and %error calculated by Equation 5.29.	20	
Conclusion	Summary, next steps, suggestions	5	
Total		100	