Modeling electronic excitation in conjugated dyes as a particle-in-a-box

Introduction

Although the particle-in-a-box (PIB) model is among the simplest quantum models, it can be used to estimate the size of a conjugated chain in an organic molecule.[1] In this lab, we will measure the absorption spectra of a variety of different conjugated organic dyes,[2] and correlate the peak in absorption to the length of the conjugated system.

In the quantum treatment of chemical systems, we solve the Schrödinger equation

$$\hat{H}\psi_n = E_n\psi_n \tag{1}$$

to determine the wavefunctions (ψ) and their respective eigenvalues (E), which give the energy levels accessible to the system. In Eq. 1, $\hat{H}$ is the Hamiltonian operator, which is composed of two terms, a kinetic energy term (in terms of $\hbar$ and the mass of the particle, m) and a potential energy term ($V(x)$) which varies depending on the model used:

$$\hat{H} = \frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \tag{2}$$

Thus, the potential energy term contains all of the information which is system specific. In the simplest case, the free particle, $V(x) = 0$.[3] In this case, energy levels are not quantized in any experimentally observable way. The PIB model has a slightly more complicated form for the potential:
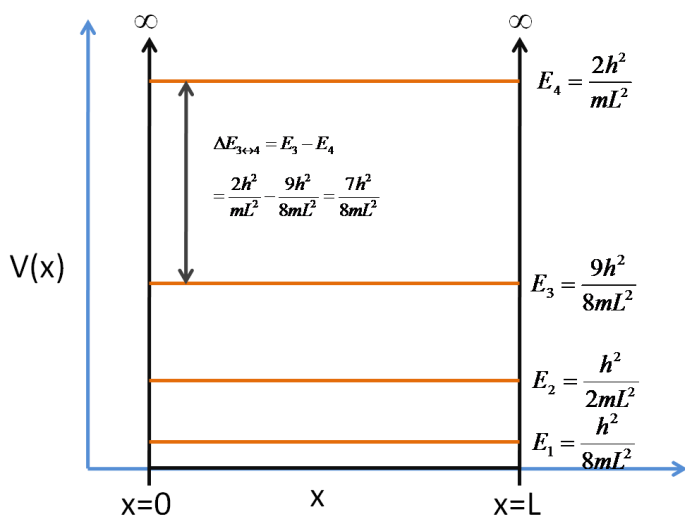

Figure 1. The particle-in-a-box potential, showing the four lowest energy levels. To determine the spectrum predicted by this model, the energy differences must be calculated, as shown in the example. This energy difference must match the photon energy, given by $E = hc/\lambda$.

$$V(x) = 0, \text{ for } L > x > 0$$
$$V(x) = \infty, \text{ for } x \geq L, x \geq 0 \tag{3}$$

Thus, a particle at a position (x) between 0 and L is "trapped" in the box, and, for small sizes of L, the length of the box, we expect quantum mechanical behavior. The eigenvalues (E_n) for the particle in the box are determined as a function of L, m, and a quantum number n

$$E_n = \frac{h^2 n^2}{8mL^2} \tag{4}$$

for $n = 1, 2, 3\ldots$ Because of the square dependence of E_n on n, the energy levels become further and further apart with increasing n. For a system in the ground state, $n = 1$, the lowest energy excitation is the difference between E_1

and E_2. This is the lowest energy (longest wavelength) transition that would be expected to be seen in the spectrum for the system.

In a conjugated system, an electron is "delocalized" over many nuclei because of the overlap of π-orbitals. This delocalization means that the electron's energy levels are well modeled by a one-dimensional PIB.[1] Thus, the UV-visible spectrum of such systems will depend on the length of the conjugated system. By the Pauli principle, each orbital can support up to two electrons. We use the total number of π electrons (N), where the level of the highest electron goes from $n_1 = N/2$ to the lowest unoccupied orbital, $n_2 = (N/2) + 1$, so that

$$\Delta E = \frac{h^2}{8mL^2}\left(n_2^2 - n_1^2\right) = \frac{h^2}{8mL^2}\left(N + 1\right) \tag{5}.$$

The dyes we will use are shown in the appendix. We will determine the total length of the box (L), as well as the average bond length, and compare it to determinations using other methods.

Experimental Procedures

For each of the dyes shown in the appendix, a solution is already present in the lab. You will measure the absorbance of each of these solutions as a function of wavelength using the UV-visible spectrometer. Save the data as an ASCII file so that you can read it later when you need to. Each group should blank the spectrometer with methanol before measuring the spectrum of the dye solutions. Only one group may use the spectrometer at a time, so when your group is not on the spectrometer, you should work on the calculations of the box length, which will allow you to predict the wavelengths you expect to see.

Computational Procedures

Our objective in the computational portion of this laboratory is to use electronic structure calculations to calculate the length of the box. This will provide a "calculated" value for L, which we can compare with the "experimental" value based on the UV-vis spectrometer and the "literature" value based on average bond lengths. We will optimize the geometries of the different dye molecules using the Gaussian '09 package. The first step is to use GaussView, which is a graphical interface that allows you to set up molecular coordinates and produce the input file for Gaussian. We will then upload the input file to the WKU High Performance Computing Center (HPCC), which is the server on which Gaussian jobs will be run. A small amount of editing will be required, but we will cover all of this in class as we learn how to perform such electronic structure calculations.

1. Open Gaussview. Begin constructing the dye molecule you are assigned to model. Be careful about adding nitrogens and carbons in the right place, having the correct number of hydrogen atoms on each, and the single/double bond structure. You may find it useful to periodically perform "clean structure" on your work. Once you have a working structure, save it as a Gaussian input file (*.gjf), where the filename is your last name (we will all log into the server with the same user name, so all our files will be in one place), then use Putty's FTP interface to transfer the file to the server.

2. Use the text editor of your choice (not MS Word!) to edit your input file. You will need to edit the check files and slashes as indicated in the Gaussian quickstart guide. You will need to select the following parameters:

Method: B3LYP
Basis Set: 3-21G
Job Type: Geometry Optimization (no frequency analysis!)

Don't forget that you should check the charge and multiplicity of your compound. The dyes are not neutral, so you will need to change from the default value for charge. Assume that the multiplicity is 1 for this case. This means that all electron spins are paired.

3. Log into the HPCC using the protocols described in class. You can now give commands to the HPCC, which allows you to get things done. This is the text-based equivalent of running programs in an environment like windows or OSX.

4. Submit your job to the server using the command given in the quickstart guide. You should expect your job to require several minutes to complete. Once the job is completed, transfer your output file (should be of type *.log) back to your computer. Save it for yourself on your flash drive or cloud, even though you may not be able to open that file on your computer. That way, if you need to go back and look at something again, you can (see Dr. Nee for help).

5. Use GaussView to look at your result. You should see a molecule that looks approximately like you expect. Use GaussView's features to measure the bond lengths that you need for your writeup.

Data Analysis and Lab Reports: Formal Lab Report

This is a formal lab report. As such, you need to have an introduction/experimental section that summarizes the background theory and equations you will use as well as the experimental details of what you did, including the computation method you used. Explain what instrumentation you used, what the resolution was, and any sample details. You do not need to give every computational detail (such as transferring files between servers, etc.), but you do need to explain what you had Gaussian do. A reference to Gaussian09 is necessary. See your output file for the full reference to use. It is long.

Your data section will have several spectra, which you should label, caption, and refer to and describe in the text of your report. You should address the uncertainty in the wavelength of your spectra, noting that this is the uncertainty you will use to propagate your errors in your calculations. In your discussion, you should guide the reader through your thought process as you go from spectrum to calculating L (and comparing to literature and calculated values). The calculations you will need to do are outlined below. Be sure to address all questions in your discussion in narrative form.

1. For each of your UV-visible spectra, you will see multiple peaks. Given that there is only one compound present in your spectrum, why are there multiple peaks?

2. Determine the value of the wavelength corresponding to the maximum of absorption for the peak with the longest wavelength, λ_{max}. From this, calculate ΔE, the energy corresponding to that wavelength. Why is this the peak of interest?

3. Use your ΔE value and the number of π-electrons to calculate the length of the box, L. Divide this by the number of bonds in the chain to calculate the average bond length. For these calculations, a

reasonable guess might be that the chain runs from nitrogen to nitrogen, but does not include anything in the cyclic π system or the ethyl amine group. Is that consistent with what you find here? If not, propose a different "chain" that would be more consistent with the experimental result.

4. Evaluate the experimental uncertainty in average bond length based on the resolution of the spectrometer. Compare it to the difference between your experimental value for bond length and a literature value for this or similar conjugated chain. Are your results within experimental error of the literature value?

5. Use your Gaussview data to calculate L as another form of comparison. How do the calculated values compare (always give percent difference when asked to "compare") with the average bond lengths? What does this tell you about the way that we have chosen to draw alternating single and double bonds?

In your conclusions, summarize the numerical results (with final errors) for the box length, and the comparisons with literature and calculations. Address the extent to which the particle-in-a-box model is appropriate for predicting the spectra of conjugated chains. For what molecular structures might the model be more successful? How can you account for any discrepancies between your data and the model predictions?

References

1. Shoemaker, D. P., Garland, C. W., and Nibler, J. W. *Experiments in Physical Chemistry*, 6ed.; WCB McGraw-Hill: New York, 1996; pp. 378-383.
2. Anderson, B. "Alternative Compounds for the Particle in a Box Experiment," *J. Chem. Educ.* **74**, 985 (1997).
3. Engel, T., and Reid, P. *Physical Chemistry*, 2ed.; Pearson Education: Upper Saddle River, NJ, 2006; pp. 345-348.
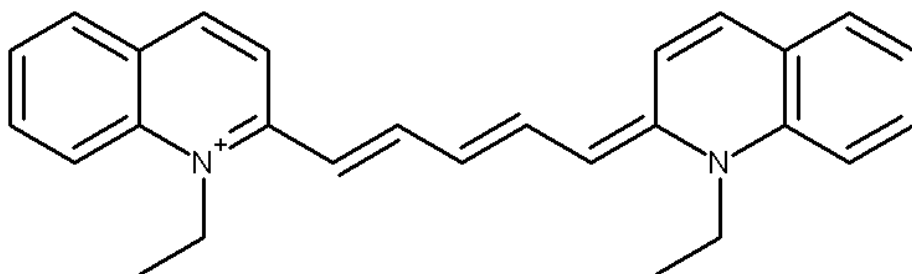
Appendix:

The dyes used are listed below, with a structure for each. To determine the number of π electrons, count the number of π-bonds in the conjugated chain (nitrogen to nitrogen) and multiply by 2 (two electrons in each p-orbital).
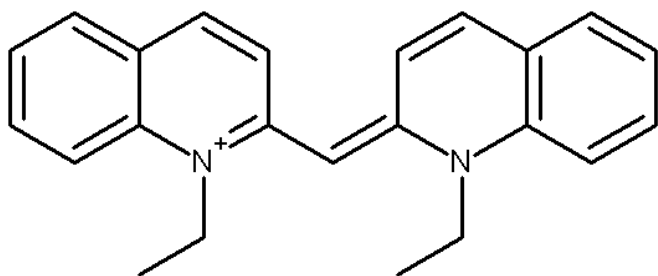
1,1'-diethyl-2,2'-cyanine iodide
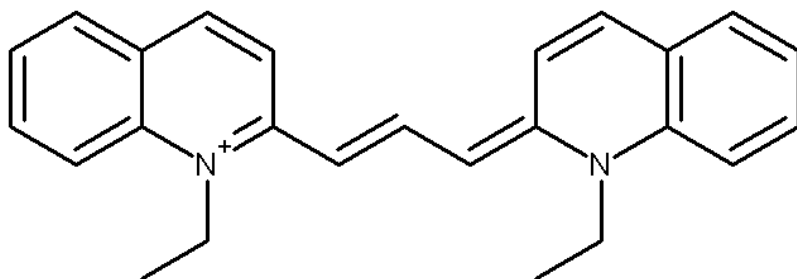
1,1'-diethyl-2,2'-carbocyanine iodide

1,1'-diethyl-2,2'-dicarbocyanine iodide