4.4: Spectroscopy of the Particle-in-a-Box Model

The wavefunctions that describe electrons in atoms and molecules are called orbitals. An orbital is a wavefunction for a single electron. When we say an electron is in orbital n, we mean that it is described by a particular wavefunction Ψ_n and has energy E_n. All the properties of this electron can be calculated from Ψ_n as described in Chapter 3.

We will now use the particle-in-a-box model to explain the absorption spectra of the cyanine dyes. When an atom or molecule absorbs a photon, the atom or molecule goes from one energy level, designated by quantum number n_i, to a higher energy level, designated by n_f. We can also say that the molecule goes from one electronic state to another. This change is called a transition. Sometimes it is said that an electron goes from one orbital to another in a transition, but this statement is not general. It is valid for a particle-in-a-box, but not for real atoms and molecules, which are more complicated than the simple particle-in-a-box model.

The energy of the photon absorbed ($E_{photon} = h\nu$) matches the difference in the energy between the two states involved in the transition (ΔE_{states}). In general, the observed frequency or wavelength for a transition is calculated from the change in energy using the following equalities,

$$\Delta E_{states} = E_f - E_i = E_{photon} = h\nu = hc\bar{\nu} \tag{4.4.1}$$

Then, for the specific case of the particle-in-a-box,

$$E_{photon} = \Delta E_{states} = E_f - E_i = \frac{(n_f^2 - n_i^2)h^2}{8mL^2} \tag{4.4.2}$$

where n_f is the quantum number associated with the final state and n_i is the quantum number for the initial state. A negative value for E_{photon} means the photon is emitted as a result of the transition in states; a positive value means the photon is absorbed.

Generally the transition energy, E_{photon} or ΔE_{states}, is taken to correspond to the peak in the absorption spectrum. When high accuracy is needed for the electronic transition energy, the spectral line shape must be analyzed to account for rotational and vibrational motion as well as effects due to the solvent or environment. Contributions of rotational and vibrational motion to an absorption spectrum will be discussed in later chapters.

In a cyanine dye molecule that has three carbon atoms in the chain, there are six π-electrons. When light is absorbed, one of these electrons increases its energy by an amount $h\nu$ and jumps to a higher energy level. In order to use Equation 4.4.1, we need to know which energy levels are involved.

We assign the electrons to the lowest energy levels to create the ground-state lowest-energy electron configuration. We could put all six electrons in the $n = 1$ level, or we could put one electron in each of $n = 1$ through $n = 6$, or we could pair the electrons in $n = 1$ through $n = 3$, etc.

The Pauli Exclusion Principle says that each spatial wavefunction can describe, at most, two electrons, or in other words, that each energy level can have only two electrons assigned to it. Spatial refers to our 3-dimensional space, and a spatial wavefunction depends upon the spatial coordinates x, y, or z. We will discuss the Pauli Exclusion Principle more fully later, but you probably have encountered it in other courses.

Rather than appeal to the Pauli Exclusion Principle to assign the electrons to the energy levels, let's try an empirical approach and discover the Pauli Exclusion Principle as a result. Assign the electrons to the energy levels in different ways until you find an assignment that agrees with experiment.

When there is an even number of electrons, the lowest-energy transition is the energy difference between the highest occupied level (HOMO) and the lowest unoccupied level (LUMO). HOMO designates the highest-energy occupied molecular orbital, and LUMO designates the lowest-energy unoccupied molecular orbital. The term orbital refers to the wavefunction or energy level for one electron. All other transitions have a higher energy. For the case with all the electrons in the first energy level, the lowest-energy transition energy would be $h\nu = E_2 - E_1$. With one electron in each of the first six levels, $h\nu = E_7 - E_6$, and with the electrons paired, $h\nu = E_4 - E_3$.

Example 4.4.1

Draw energy level diagrams indicating the HOMO, the LUMO, the electrons and the lowest energy transition for each of the three cases mentioned in the preceding paragraph.

Example 4.4.2

For the three ways of assigning the 6 electrons to the energy levels in Exercise 4.4.17, calculate the peak absorption wavelength λ for a cyanine dye molecule with 3 carbon atoms in the chain using a value for L of 0.849 nm, which is obtained by estimating bond lengths. Which wavelength agrees most closely with the experimental value of 309 nm for this molecule?

It turns out that the assignment that gives a reasonable wavelength for the absorption of a cyanine dye with 6 π electrons is $h\nu = E_4 - E_3$ as you concluded from Exercise 4.4.2. In this way we have "discovered" the Pauli Exclusion Principle, electrons should be paired in the same energy level whenever possible, and we accept it for now because it agrees with the experimental observations of the cyanine dye spectra.

In molecules with an odd number of electrons, it is possible to have transitions between the doubly occupied molecular orbitals and the singly occupied molecular orbital as well as from the singly occupied orbital to an unoccupied orbital.