4.6: Selection Rules for the Particle-in-a-Box

This section explores the use of symmetry to determine selection rules. Here we derive an analytical expression for the transition dipole moment integral for the particle-in-a-box model. The result that the magnitude of this integral increases as the length of the box increases explains why the absorption coefficients of the longer cyanine dye molecules are larger. We use the transition moment integral and the trigonometric forms of the particle-in-a-box wavefunctions to get Equation 4.6.2 for an electron making a transition from orbital i to orbital f.

$$\mu_T = \frac{-2e}{L} \int_0^L \sin\left(\frac{f\pi x}{L}\right) x \sin\left(\frac{i\pi x}{L}\right) dx \tag{4.6.1}$$

$$= \frac{-2e}{L} \int_0^L x \sin\left(\frac{f\pi x}{L}\right) \sin\left(\frac{i\pi x}{L}\right) dx \tag{4.6.2}$$

> **Exercise 4.6.1**
>
> Why is there a factor $2/L$ in Equation 4.6.2? What are the units associated with the dipole moment and the transition dipole moment?

Simplify the integral in Equation 4.6.2 by substituting the product-to-sum trigonometric identity

$$\sin\psi \sin\theta = \frac{1}{2}[\cos(\psi - \theta) - \cos(\psi + \theta)] \tag{4.6.3}$$

and also redefine the sum and difference terms:

$$\Delta n = f - i$$

and

$$n_T = f + i$$

So Equation 4.6.2

$$\mu_T = \frac{-e}{L} \int_0^L x \left[\cos\left(\frac{\Delta n\pi x}{L}\right) - \cos\left(\frac{n_T\pi x}{L}\right)\right] dx \tag{4.6.4}$$

$$= \frac{-e}{L} \left[\int_0^L x \cos\left(\frac{\Delta n\pi x}{L}\right) dx - \int_0^L x \cos\left(\frac{n_T\pi x}{L}\right) dx\right] \tag{4.6.5}$$

These two definite integrals can be directly evaluated using this relationship

$$\int_0^L x \cos(ax) dx = \left[\frac{1}{a^2}\cos(ax) + \frac{x}{a}\sin(ax)\right]_0^L \tag{4.6.6}$$

where a is any nonzero constant. Using Equation 4.6.6 in Equation 4.6.5 produces

$$T = \frac{-e}{L}\left(\frac{L}{\pi}\right)^2 \left[\frac{1}{\Delta n^2}(\cos(\Delta n\pi) - 1) - \frac{1}{n_T^2}(\cos(n_T\pi) - 1) + \frac{1}{\Delta n}\sin(\Delta n\pi) - \frac{1}{n_T}\sin(n_T\pi)\right] \tag{4.6.7}$$

> **Exercise 4.6.2**
>
> Show that if Δn is an even integer, then n_T must be an even integer and $\mu_T = 0$.

Exercise 4.6.3

Show that if i and f are both even or both odd integers then Δn is an even integer and $\mu_T = 0$.

Exercise 4.6.4

Show that if Δn is an odd integer, then n_T must be an odd integer and μ_T is given by Equation 4.6.8.

$$\mu_T = \frac{-2eL}{\pi^2}\left(\frac{1}{n_T^2} - \frac{1}{\Delta n^2}\right) = \frac{8eL}{\pi^2}\left(\frac{f_i}{\left(f^2 - i^2\right)^2}\right) \tag{4.6.8}$$

Exercise 4.6.5

Show that the two expressions for the transition moment in Equation 4.6.8 are in fact equivalent.

Example 4.6.1

What is the value of the transition moment integral for transitions $1 \to 3$ and $2 \to 4$?

Solution

For these two transitions, either n and f are both odd or they are both even integers. In either case, Δn and n_T are even integers. The cosine of an even integer multiple of π is +1 so the cosine terms in Equation 4.6.7 become (1-1) = 0. The sine terms are zero because the sine of an even integer multiple of π is zero. Therefore, $\mu_T = 0$ for these transitions and they are forbidden. The same reasoning applies to any transitions that have both i and f as even or as odd integers.

Exercise 4.6.1

What is the value of the transition moment for the n = 8 to f = 10 transition?

Example 4.6.2

What is the value of the transition moment integral for transitions $1 \to 2$ and $2 \to 3$?

Solution

For these two transitions $\Delta n = 1$ and nT = 3 and 5, respectively, all odd integers. The cosine of an odd-integer multiple of π is -1 so the cosine terms in Equation 4.6.7 become (-1-1) = -2. The sine terms in Equation 4.6.7 are zero because the sine of an odd integer multiple of π is zero. Therefore, μ_T has some finite value given by Equation 4.6.8. The same reasoning is used to evaluate the transition moment integral for any transitions that have Δn and nT as odd integers, e.g. $2 \to 7$ and $3 \to 8$. In these cases $\Delta n = 5$ and nT = 9 and 11, respectively. Again the transition moment integral for each of these transitions is finite.

Exercise 4.6.2

Explain why one of the following transitions occurs with excitation by light and the other does not: $i = 1$ to $f = 7$ and $i = 3$ to $f = 6$.

From Examples 4.6.1 and 4.6.2, we can formulate the selection rules for the particle-in-a-box model: Transitions are forbidden if $\Delta n = f - i$ is an even integer. Transitions are allowed if $\Delta n = f - i$ is an odd integer. In the next section we will see that these selection rules can be understood in terms of the symmetry of the wavefunctions.

Through the evaluation of the transition moment integral, we can understand why the spectra of cyanine dyes are very simple. The spectrum for each dye consists only of a single peak because other transitions have very much smaller transition dipole moments. We also see that the longer molecules have the larger absorption coefficients because the transition dipole moment increases with the length of the molecule.

Exercise 4.6.6

The lowest energy transition is from the HOMO to the LUMO, which were defined previously. Compute the value of the transition moment integral for the HOMO to LUMO transition $E_3 \rightarrow E_4$ for a cyanine dye with 3 carbon atoms in the conjugated chain. What is the next lowest energy transition for a particle-in-a-box? Compute the value of the transition moment integral for the next lowest energy transition that is allowed for this dye. What are the quantum numbers for the energy levels associated with this transition? How does the probability of this transition compare in magnitude with that for $3 \rightarrow 4$?