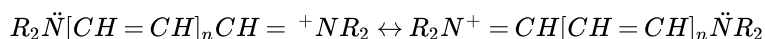


4.3: Cyanine Dyes as Two-State Electronic Systems

Using the particle-in-a-box (PIB) approximation or Hückel molecular orbital theory (HMOT) to model the π -electrons of various dyes is a standard lecture/lab exercise in the traditional undergraduate physical chemistry curriculum (1-8). In Volume III of his celebrated *The Feynman Lectures on Physics*, Richard Feynman offers a different approach by considering such dyes as examples of two-state electronic systems (9). Other examples of two-state systems that Feynman presents are photon polarization, the ammonia inversion, bonding in the hydrogen molecular ion and the hydrogen molecule, spin $\frac{1}{2}$ systems, the strong nuclear force, and other more esoteric nuclear phenomena.

The PIB and HMOT models provide a manifold of quantized π -electron energy levels which are then populated with electrons. A HOMO-LUMO electronic transition provides the mechanism for the absorption of a photon of light and the origin of the dye color. These models each have one parameter: box length for PIB and the resonance integral, β , for HMOT.

Both models also start with Lewis structures, as does the Feynman approach. Two equivalent resonance structures can be written for the symmetric cyanine dyes, the subject of this tutorial.



The resonance structures are used to determine the box length for the PIB model and to construct the energy matrix for the HMOT calculation.

Feynman, however, considers the resonance structures as base states in a simple quantum mechanical analysis.

$$|1\rangle = |R_2\ddot{N}[CH=CH]_nCH = {}^+NR_2\rangle \quad |2\rangle = |R_2N^+ = CH[CH=CH]_n\ddot{N}R_2\rangle$$

The energy matrix for these base states is shown below. The presence of off-diagonal elements indicates that these base states are not stationary states of the energy operator.

$$\begin{bmatrix} E^0 & A \\ A & E^0 \end{bmatrix}$$

Here E^0 and A are negative quantities, which are generally approximated by an appeal to experimental data.

$$\langle 1|\hat{H}|1\rangle = \langle 2|\hat{H}|2\rangle = E^0 \quad \langle 1|\hat{H}|2\rangle = \langle 2|\hat{H}|1\rangle = A$$

The following quantum mechanical superpositions of the base states diagonalize the energy matrix and are, therefore, stationary states.

$$|\Psi_{elec}^{\pm}\rangle = \frac{1}{\sqrt{2}} \left[|R_2\ddot{N}[CH=CH]_nCH = {}^+NR_2\rangle \pm |R_2N^+ = CH[CH=CH]_n\ddot{N}R_2\rangle \right] = \frac{1}{\sqrt{2}} [|1\rangle \pm |2\rangle]$$

$$\begin{bmatrix} E^0 + A & 0 \\ 0 & E^0 - A \end{bmatrix}$$

$$\langle \Psi_{elec}^+ | \hat{H} | \Psi_{elec}^+ \rangle = E^0 + A \quad \langle \Psi_{elec}^- | \hat{H} | \Psi_{elec}^- \rangle = E^0 - A \quad \langle \Psi_{elec}^- | \hat{H} | \Psi_{elec}^+ \rangle = \langle \Psi_{elec}^+ | \hat{H} | \Psi_{elec}^- \rangle = 0$$

The in-phase superposition represents the ground electric state, while the anti-symmetric superposition represents the excited electronic state.

It must be stressed that a superposition is not a mixture. The dye is not a 50-50 mixture of two equivalent structures, nor is it rapidly oscillating back and forth between two equivalent structures. According to quantum mechanics the dye is simultaneously in both electronic base states.

To proceed to the issue of experimental validation, we need to recognize that the values of the matrix elements will depend on n , the length of the dye chromophore. This can be accomplished by adding subscripts in the energy matrix shown above.

$$\begin{bmatrix} E_n^0 + A_n & 0 \\ 0 & E_n^0 - A_n \end{bmatrix}$$

This leads to the following picture of the absorption of visible light by the dyes.

$$\begin{array}{c}
 |\Psi_{elec}^{-}\rangle_n - - - - E_n^0 - A_n \\
 \uparrow \\
 |\Psi_{elec}^{+}\rangle_n - - - - E_n^0 + A_n
 \end{array}$$

The wavelength of the photon required for this electronic excitation is,

$$\lambda_n = -\frac{hc}{2A_n}$$

It is clear from this result that two experimental photon wavelengths are required to calibrate the model. These can be used to calculate the photon wavelength of a third dye. In general this would be formulated as follows.

$$\frac{\lambda_{n+1}}{\lambda_n} = \frac{A_n}{A_{n+1}} \xrightarrow[\text{implies}]{\text{constant ratio}} \lambda_{n+2} = \lambda_{n+1} \left(\frac{\lambda_{n+1}}{\lambda_n} \right)$$

Due to rotational and vibrational fine structure, and other complications, the visible spectra of dyes exhibit broad electronic absorption bands. The theoretically calculated wavelength is therefore compared to the longest wavelength absorption maximum, λ_{\max} , in the UV-VIS spectrum. The table below compares calculated photon wavelengths with experimental λ_{\max} values for a series of symmetric cyanine dyes (8), and shows that Feynman's two-state model gives modest agreement with experimental results. This generally is also the level of success achieved by the PIB and HMOT models.

	Symmetric Cyanine Dye Results			
n	1	2	3	4
Experimental λ_{\max}/nm	313	416	519	625
Theoretical Prediction			553	647

The interaction of the dye chromophores with electromagnetic radiation is a complicated process, so simple models such as PIB, HMOT and Feynman's two-state approach which isolate the electronic event from other degrees of freedom can only be expected to give "ball park" quantitative agreement with experimental results. However, conceptually we believe that these simple models capture the essence of the photon absorption process. From a pedagogical perspective it is valuable to have three complementary models for the same physical phenomenon.

Literature cited:

1. Gerkin, R. E. *J. Chem. Educ.* **1965**, 42, 490-491.
2. Farrell, J. J. *J. Chem. Educ.* **1985**, 62, 351-352.
3. Shoemaker, D. P.; Garland, C. W.; Nibler, J. W. *Experiments in Physical Chemistry*, 5th ed.; McGraw-Hill: New York, 1989, pp 440-445.
4. Sime, R. J. *Physical Chemistry: Methods, Techniques, and Experiments*; Saunders: Philadelphia, 1990; pp 687-694.
5. Moog, R. S. *J. Chem. Educ.* **1991**, 68, 506-508.
6. Bahnick, D. A. *J. Chem. Educ.* **1994**, 71, 171-173.
7. Anderson, B. D. *J. Chem. Educ.* **1997**, 74, 985.
8. Autschbach, J. *J. Chem. Educ.* **2007**, 84, 1840-1845.
9. Feynman, R. P.; Leighton, R. B.; Sands, M. *The Feynman Lectures on Physics*; Addison-Wesley Publishing Co.: Reading MA, 1965; p. 10-12.

This page titled [4.3: Cyanine Dyes as Two-State Electronic Systems](#) is shared under a [CC BY 4.0](#) license and was authored, remixed, and/or curated by [Frank Rioux](#) via [source content](#) that was edited to the style and standards of the LibreTexts platform.