



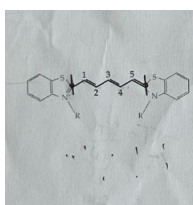
PHY208 – TD2: How Long

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1 Introduction to the problem

Cyanines are a type of molecule with the particularity of having a chain of carbon atoms connecting two symmetric carbon rings. Some electrons of the chain are completely delocalized. This means they are not bound to the atoms and can wiggle around the carbon chain. This molecule can absorb and emit light at precise wavelengths which depend on the length of this chain. The molecule and the emission wavelengths are presented here below.



Name	Emission wavelength	C in the chain
Kuhn V	425	3
Kuhn VI	555	5
Kuhn VII	650	7
Kuhn VIII	760	9
Kuhn IX	870	11
Kuhn X	995	13

Figure 1: Table of emission wavelength for different lengths of the carbon chain

The goal is to estimate the distance between two carbon atoms in the chain.

2 Problem-solving

2.1 General Thought



Looking at the picture of the molecule, two types of bonds in the carbon chain can be identified: single and double. In single bonds, electrons shared by the two carbon atoms involved are bound to the atoms, hence they are localized. Double bonds can move along the atom as pictured in figure 2. Hence, the electrons involved in them are delocalized.

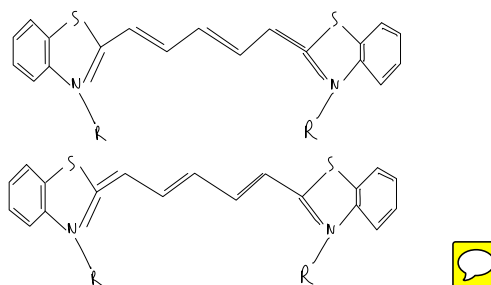



Figure 2: Two possible ways of sketching the skeletal formula of the same cyanine molecule. These two differ in the location of the double bonds

Moreover, we know that delocalized electrons are constrained by the bounds of the chain. We use this to connect this problem to an infinite potential well. The bottom of this well can be assumed to be flat because delocalized electrons are free to move along the chain. If the bottom was not flat, some states might not allow electrons to do so. Hence our problem is analog to finding the width of an infinite flat potential well, pictured in figure 3. 

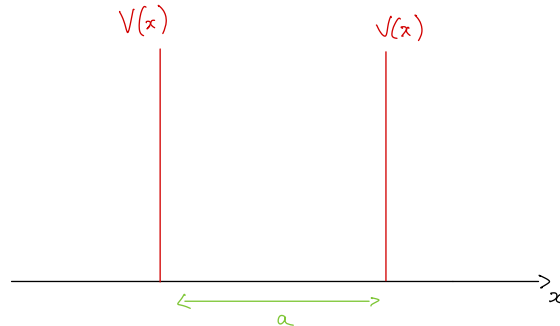


Figure 3: Diagram of a flat infinite potential well

The horizontal bottom of the well, a is the distance that we are trying to find.

From then on, the plan goes as follows :

1. We estimate the number of delocalized electrons, N_e
2. If their energy eigenstates E_n , so the energy states they can occupy, contains the distance a and the level n ; and if the energy difference ΔE between two states can be expressed as a function of λ the emission frequency, then we relate a to λ and n .
3. We find what energy states are typically occupied by electrons and from that we estimate what is the most probable transition, i.e the most probable values for ΔE and for the levels n associated to it.
4. We plug this value as ΔE and we can express a in terms of known values.

We will detail steps 1 and 3 below. As for the formulas and computations of steps 2 and 4, they will be given in part 2.2

Each carbon atom in the chain has 6 electrons in its cloud. 2 of these are bound to the nucleus and are not involved in any bond. Among the other four, 3 make single bonds with two carbon atoms and one hydrogen atoms and 1 is involved in a double bond. Recalling that electrons involved in double bonds are the delocalized ones, we conclude that there are as many delocalized electrons N_e as carbon atoms N .

By Pauli's exclusion principle, we know only two electrons can fit into an energy state (one of each spin). Since a cyanine carbon chain always contains an odd number of carbon atoms N^1 , N_e is odd and therefore, there is always a state which is occupied by a single electron as pictured in figure 4. Since the most probable states to be occupied are the ones with the lowest energy, this state is the highest energy one and it has level n_f . Moreover, the excitation that will be the most stable and probable will be for an electron on the n_{f-1} energy level to jump up because that is the excitation for which ΔE is the smallest.

2.2 Equations and Numerical Applications

We recall that the energy eigenstates for an electron in an infinite flat potential well are

$$E_n = \frac{\pi^2 \hbar^2 n^2}{2ma^2} \quad (1) \quad \text{$$

¹otherwise, the double bonds cannot move along the chain which implies there are no delocalized electrons

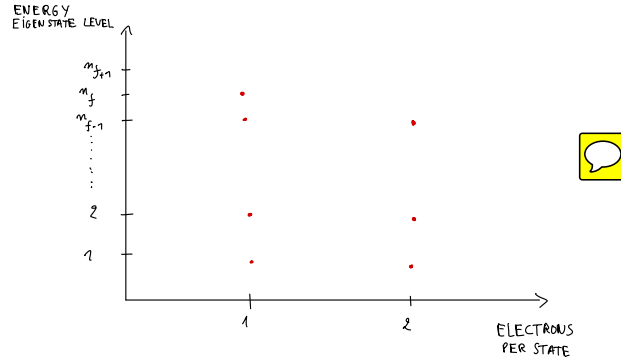


Figure 4: Allocation of the N electrons on the eigenstates

where n is the energy level and a is the width of the potential well.

Moreover, the energy difference for some arbitrary levels k and $k + 1$ writes $\Delta E = E_{k+1} - E_k = \frac{hc}{\lambda}$. Recalling that we have N electrons, the difference between the levels of the most probable transition is

$$n_f - n_{f-1} = \frac{N+1}{2} - \frac{N-1}{2} \quad (2)$$

From this, we write

$$\Delta E = \frac{hc}{\lambda} = E_{n_f} - E_{n_{f-1}} = \frac{\pi^2 \hbar^2 n_f^2}{2ma^2} - \frac{\pi^2 \hbar^2 n_{f-1}^2}{2ma^2} = \frac{\pi^2 \hbar^2}{2ma^2} \frac{N}{N+1} \quad (3)$$

We can then find the value of $a = \sqrt{\frac{h\lambda N}{c(N+1)8m}}$. The next table presents the different values of a depending on the number of atoms in the chain.

N	a (in m)
3	3.1×10^{-10}
5	3.7×10^{-10}
7	4.2×10^{-10}
9	4.6×10^{-10}
11	4.9×10^{-10}
13	5.3×10^{-10}

Although it seems natural to compute the average of these results to reach a final conclusion, the weights of each result seem unknown and we have no methods to have a further result. Therefore, we can only conclude that the distance between two carbon atoms is of the order of 1 Angstrom (10^{-10} m).

