
# HOW LONG (HAS THIS BEEN GOING ON)

## PHY204

April 2023

Shanya MISHRA, Magdalena, Jankowska, Antonia-Alma GHITA, Naman BANSAL, Emile DUREL

ÉCOLE POLYTECHNIQUE

IP PARIS

# 1 Problem statement

Cyanines are a family of molecules with a central chain of carbon atoms. Electrons are completely delocalized along the chain, where they are confined by end of the molecules. Cyanines are widely used as organic dyes, because they can absorb and emit light at precise wavelengths, which depend on the length of this central chain.

**Question:** Estimate the distance between two carbon atoms in the chain.

# 2 Variables

## 2.1 Known data and constants

From the problem statement we can extract the following data:

- $N$ - number of carbon atoms in the central chain
- $\lambda_N$ - emission wavelength for n carbon atoms in the central chain

We can sum up all of the known data in Table 1.

| $n$ | 3 | 5 | 7 | 9 | 11 | 13 |
|---|---|---|---|---|---|---|
| $\lambda_N[nm]$ | 425 | 555 | 650 | 760 | 870 | 995 |

Table 1: Emitted wavelength $\lambda_n$ depending on the number of carbon atoms $N$ in the central chain

The constants used in this problem are:

- $m_e$ - mass of the electron taken to be $9.109 \times 10^{-31}$ kg
- $c$ - speed of light taken to be $2.998 \times 10^{8}$ ms$^{-2}$
- $h$ - Planck constant taken to be $6.626 \times 10^{-34}$ m$^2$kg

## 2.2 Intermediate variables

The intermediate variable used while solving the problem are:

- $E_n$ - the $n^{th}$ energy level
- $\Delta E_{n,m}$ - difference in energy between energy state n and m
- $L$ - total length of the central chain of carbon atoms

## 2.3 Sought after variable

The variable we are looking for is:

- $a$ - distance between two carbon atoms in the central chain

## 3 Model

We choose to apply the semi-quantum model to this problem since the electrons are confined between the end of the molecules, we model this by the fact that each electron moves in a potential well. Since the electrons belonging to the double bonds are completely delocalized, we can assume this potential to have the shape of an infinite square well. We also use some results from quantum mechanics about an infinite potential well.

The energy levels in the infinite square well of size $L$ have the following expression:

$$E_n = \frac{n^2 h^2}{8mL^2} \tag{1}$$

The wavelength $\lambda$ corresponding to the emission of light associated to a transition between energy levels with an energy difference of $\Delta E$ is:

$$\Delta E = \frac{hc}{\lambda} \tag{2}$$

We assume that the only transition that causes emission takes place between the n$^{th}$ energy level which is the highest doubly occupied energy level and n+1$^{th}$ energy level which is the lowest singly occupied energy level in the ground state (We only perform this analysis for an odd number of electrons because the data we are given is only for an odd number of C-atoms and we make the assumption that each C-atom in the chain contributes exactly 1 electron). The difference between energies of level $n+1$ and $n$ is:

$$\Delta E_{n,n+1} = E_{n+1} - E_n = \frac{h^2}{8mL^2}(2n+1) \tag{3}$$

We also assume that the length of the chain scales with the number of carbon atoms and the distance $a$ between them as $L = (N+1)a$. This will allow us to obtain the wavelengths of the transitions as:

$$\lambda = \frac{8ma^2c}{h(2n+1)}(N+1)^2 \tag{4}$$

An important quantum mechanical aspect is that electrons are fermions so they obey the Pauli exclusion principle: there cannot be more than one electron in the same state. Since each electron can have either spin up or down without changing the energy (in a first approximation), we will have at most two electrons on each energy level. We notice that we only have an odd number of Carbon atoms in all cases and thus we will have $N+1$ number of electrons which are free (only those corresponding to double bonds are free). The last doubly occupied energy level in ground state $n$ is given by $n = \frac{N-1}{2}$ due to Pauli's exclusion principle. This means that $\lambda$ asymptotically scales linearly with $N+1$, with a slope of $\frac{8ma^2c}{h}$.

$$\lambda = \frac{8ma^2c}{h}\frac{(N+1)^2}{N} \tag{5}$$

This slope can then be used to calculate the value of $a$. Figure 1 summarizes all the important ideas needed to solve the problem. It shows the electrons in an infinite potential well and not more than two electrons in each energy level due to Pauli's exclusion principle. The only transition responsible for emission is between $n$ and $n+1$, not between $n+1$ and $n+2$ because $\Delta E_{n,n+1} < \Delta E_{n+2,n+1}$. The length of the Carbon chain is proportional to the C-C bond length.

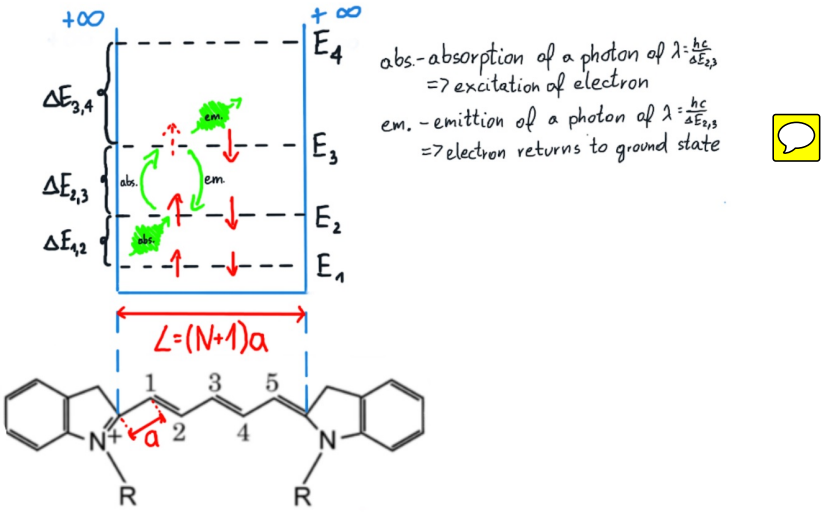


Figure 1: Schematic of energy levels in cyanine

Performing a linear fit (constraining the intercepts to 0) of the data we obtain a slope of $A = 69.3\,\text{nm}$ which gives us the following value for the bond length:

$$a = 1.45 \cdot 10^{-10}\text{m} \tag{6}$$

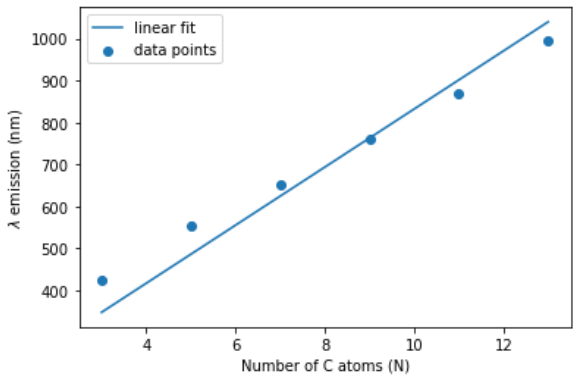


Figure 2: linear fit of data

Since the scaling is only asymptotically linear not perfectly linear, the value of $a$ will be closer to the real value of $a$ if we consider longer carbon chains.

This result is close to the real value of a C-C (Carbon-Carbon) bond length of $1.54\mathring{A}$ with a less than 6% deviation from the real value. Another way to check this result without comparing it with a known value is to compare it with the diameter of the Hydrogen atom which is known to be around $0.53\mathring{A}$. We would estimate the C-C bond to be more than two atomic Hydrogen radii because Carbon atoms are larger, but also not too large since a bond involves overlapping of the orbitals of the Carbon atoms.