

# Quantum Mechanics of Hydrocarbon Chains

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We study a simple model of hydrocarbon chains which gives a reliable quantitative picture of their absorption spectra. The model relies on the simplest bound-state quantum system (the infinite potential well) and uses perturbation theory to compute the corrections to the spectra due to a nitrogen atom at the center of the chain.

## I. INTRODUCTION

Some pigments consists solely of hydrocarbons chains through which electrons can move freely. These pigments absorb and reflect specific wavelengths of light thus making them ideal coloring agents. Here we will examine pigments composed of hydrocarbon molecular ions in an attempt to explain their absorption spectra. We will consider molecular ions of the form  $(C_nH_{n+2})^-$  which come from removing a CH group from polyethylene molecules. Ions of this type form a linear structure of the form



We are considering the case of an odd number of  $n$  equally spaced carbon atoms. We will consider the  $n+1$  electrons of the original double bonds as moving independently of one another. This problem comes from chapter 22 of [1].

## II. PURE HYDROCARBON IONS

We model our hydrocarbon chain as a one dimensional infinite potential well

$$V(x) = 0 \quad \text{for } 0 \leq x \leq L_n \\ = \infty \quad \text{for otherwise} \quad (1)$$

where  $L_n = (n-1)d + 2b$  with

$$n \equiv \text{number of carbons atoms} \quad (2)$$

$$d \equiv \text{average spacing between carbons} \simeq 1.4 \text{ \AA} \quad (3)$$

$$b \equiv \text{edge length.} \quad (4)$$

For simplicity we will take  $b = d/2$  so that  $L_n = d/2$ . Experimentally this is an appropriate approximation. The energy levels for this potential are well known. They are defined by

$$\epsilon_k = \frac{\hbar^2 k^2}{2m(nd)^2}. \quad (5)$$

If we have  $n+1$  electrons the ground state energy of the hydrocarbon is

$$E_0 = \frac{\hbar^2 \pi^2}{24m(nd)^2} (n^3 + 3n^2 + 5n + 3). \quad (6)$$

$\lambda_n$	Experimental $\lambda_n$	Theoretical
$\lambda_9$	$\sim 4700 \text{ \AA}$	$= 4759 \text{ \AA}$
$\lambda_{11}$	$\sim 6000 \text{ \AA}$	$= 6015 \text{ \AA}$
$\lambda_{13}$	$\sim 7200 \text{ \AA}$	$= 7282 \text{ \AA}$

TABLE I: Experimental and Theoretical of absorbed wavelengths of light

The energy of the first excited state, computed by projecting an electron from the fermi level to the next excited state is

$$E_1 = \frac{\hbar^2 \pi^2}{24m(nd)^2} (n^3 + 3n^2 + 17n + 27). \quad (7)$$

With  $E_1$  and  $E_0$  determined we can compute the wavelength of light absorbed in a ground state-to-first excited state transition. Using  $\Delta E = hc/\lambda_n$  we find

$$\lambda_n = \frac{8d^2}{\lambda_c} \frac{n^2}{n+2} \quad (8)$$

We experimentally observe that molecular ions with different numbers of carbon atoms absorb different wavelengths of light. Table 1 lists the rough experimental values and the calculated theoretical values of the wavelength of absorption for certain values of  $n$ . We see that our simplistic model of the hydrocarbon does well to reproduce the experimental results. We note that  $\lambda_7 = 350 \text{ nm}$  and  $\lambda_{15} = 850 \text{ nm}$  so the hydrocarbons with  $n \geq 15$  or  $n \leq 7$  do not absorb colored light.

## III. NITROGENOUS IONS

In this section we study how the spectrum of absorbed light changes if we replace our central hydrocarbon with a single nitrogen atom. We model this modification by adding an attractive potential at the center of our infinite potential well:

$$\delta V(x) = -V_0 \quad \text{for } \frac{L_n - \alpha}{2} \leq x \leq \frac{L_n + \alpha}{2} \\ 0 \quad \text{for otherwise} \quad (9)$$

The first order corrections to the energy eigenvalues with  $\alpha/d \leq 1$  are then

$$\delta\epsilon_k^{(1)} = \frac{\alpha V_0}{nd} [(-1)^k - 1]. \quad (10)$$

To compute the first order corrections to  $E_0$  and  $E_1$  we must carefully treat the cases of I:  $(n+1)/2$  even and II:  $(n+1)/2$  odd separately. We must separate these cases because of the  $(-1)^k$  term in (10). However, it turns out that the correction to the ground state energy is the same in both cases:

$$E_0^{(1)} = -\frac{\alpha V_0}{d} \frac{n+1}{n}. \quad (11)$$

For the first excited state we find the corrections

$$\text{Case I: } E_1^{(1)} = -\frac{\alpha V_0}{d} \frac{n+3}{n} \quad (12)$$

$$\text{Case II: } E_1^{(1)} = -\frac{\alpha V_0}{d} \frac{n-1}{n}. \quad (13)$$

With these results we can compute the energy separation between the first excited state and the ground state to first order in  $\alpha$ .

$$\text{Case I: } \Delta E = \frac{\hbar^2 \pi^2}{2md} \frac{n+2}{n^2} - \frac{2\alpha V_0}{nd} \quad (14)$$

$$\text{Case II: } \Delta E = \frac{\hbar^2 \pi^2}{2md} \frac{n+2}{n^2} - \frac{2\alpha V_0}{nd} \quad (15)$$

$$(16)$$

or, more compactly,

$$\Delta E = \frac{\hbar^2 \pi^2}{2md} \frac{n+2}{n^2} \left[ 1 + (-1)^{\frac{n+3}{2}} \gamma \frac{n}{n+2} \right]. \quad (17)$$

where  $\gamma \equiv 4m\alpha V_0 d / \hbar^2 \pi^2$ . The wavelength for absorbed light for the nitrogenous hydrocarbon is therefore

$$\lambda_n^N = \frac{\lambda_n^0}{1 + (-1)^{\frac{n+3}{2}} \gamma \frac{n}{n+2}}. \quad (18)$$

From this result we see that if  $(n+1)/2$  is odd then the wavelength of  $\lambda^N$  is blue shifted from the  $\lambda^0$  and if  $(n+1)/2$  is even then  $\lambda^N$  is red shifted.

#### IV. CONCLUSION

We were able to reproduce the absorption spectra of few carbon hydrocarbons with a very simple model. We found that when nitrogen is included in the center of the hydrocarbon spectra is red or blue shifted contingent on whether  $(n+1)/2$  (where  $n+1$  is the number of electrons) is even or odd, respectively. However, some of our assumptions could be contested. For example, we assumed that the bond length was the constant throughout the hydrocarbon and treated double bonds on the same

footing as single bonds. Double bonds are experimentally known to draw molecules closer to one another. Also, we assumed that the electrons were completely free. A better model would be one which is similar to a dirac comb in which there is a small periodic potential. Further extensions should include these criticisms.

#### APPENDIX A

In this section we provide explicit computation of our results in the above sections. The zeroth order ground state  $E_0$  was computed via  $\sum_{k=1}^n k^2 = n(n+1)(2n+1)/6$ . Specifically

$$\begin{aligned} E_0 &= 2 \sum_{k=1}^{\frac{n+1}{2}} \frac{\hbar^2 \pi^2}{2m(nd)^2} k^2 - \frac{\hbar^2 \pi^2}{2m(nd)^2} \left( \frac{n+1}{2} \right)^2 \\ &= \frac{\hbar^2 \pi^2}{24m(nd)^2} (n^3 + 6n^2 + 11n + 6) \\ &\quad - \frac{\hbar^2 \pi^2}{8m(nd)^2} (n^2 + 2n + 1) \\ &= \frac{\hbar^2 \pi^2}{24m(nd)^2} (n^3 + 3n^2 + 5n + 3) \end{aligned} \quad (A1)$$

where the second term in the first line comes from the fact that we have an odd number of electrons and hence the highest energy state is only half filled; the factor of 2 and the end number  $(n+1)/2$  in the first line come from the spin degeneracy of electrons. The first excited state energy is computed similarly except that our end limit in the sum is  $(n+1)/2 - 1 = (n-1)/2$  and we must add (instead of subtract) the energy of the next highest energy state.

$$\begin{aligned} E_1 &= 2 \sum_{k=1}^{\frac{n-1}{2}} \frac{\hbar^2 \pi^2}{2m(nd)^2} k^2 + \frac{\hbar^2 \pi^2}{2m(nd)^2} \left( \frac{n+3}{2} \right)^2 \\ &= \frac{\hbar^2 \pi^2}{24m(nd)^2} (n^3 - n) \\ &\quad - \frac{\hbar^2 \pi^2}{8m(nd)^2} (n^2 + 6n + 9) \\ &= \frac{\hbar^2 \pi^2}{24m(nd)^2} (n^3 + 3n^2 + 17n + 27). \end{aligned} \quad (A2)$$

Subtracting ((A1)) from ((A2)) gives us

$$\begin{aligned} E_1 - E_0 &= \frac{\hbar^2 \pi^2}{24m(nd)^2} (12n + 24) \\ &= \frac{\hbar^2 \pi^2}{2m(nd)^2} \frac{n+2}{n^2}. \end{aligned} \quad (A3)$$

from which we found ((8)). To compute the first order corrections to the energy eigenvalues we used time

independent perturbation theory

$$\begin{aligned}
\epsilon_k^{(1)} &= -\frac{2V_0\alpha}{nd} \int_{\frac{L_{n-\alpha}}{2}}^{\frac{L_{n+\alpha}}{2}} dx \sin^2\left(\frac{k\pi x}{nd}\right) \\
&= -\frac{V_0}{nd} \left[ \alpha - \frac{nd}{2k\pi} \sin\left(k\pi + \frac{k\pi\alpha}{nd}\right) \right. \\
&\quad \left. - \frac{nd}{2k\pi} \sin\left(k\pi - \frac{k\pi\alpha}{nd}\right) \right] \\
&= -\frac{V_0}{nd} \left[ \alpha - \frac{nd}{k\pi} \sin\left(\frac{k\pi\alpha}{nd}\right) \cos(k\pi) \right] \\
&\simeq -\frac{\alpha V_0}{nd} [(-1)^k - 1]
\end{aligned} \tag{A4}$$

Computing the corrections to the ground state energy in Case I ( $\frac{n+1}{2}$  even) we have

$$\begin{aligned}
\text{Case I : } E_0^{(1)} &= 2 \sum_{k=1}^{\frac{n+1}{2}} \epsilon_k^{(1)} - \epsilon_{\frac{n+1}{2}}^{(1)} \\
&= 2 \left( \frac{n+1}{2} \right) \frac{1}{2} \frac{\alpha V_0}{nd} (-2) - 0 \\
&= -\frac{\alpha V_0}{d} \frac{n+1}{n}.
\end{aligned} \tag{A5}$$

for Case II ( $\frac{n+1}{2}$  odd) we have

$$\begin{aligned}
\text{Case I : } E_0^{(1)} &= 2 \sum_{k=1}^{\frac{n+1}{2}} \epsilon_k^{(1)} - \epsilon_{\frac{n+1}{2}}^{(1)} \\
&= 2 \left( \frac{n+3}{2} \right) \frac{1}{2} \frac{\alpha V_0}{nd} (-2) - \frac{\alpha V_0}{nd} (-2) \\
&= -\frac{\alpha V_0}{d} \frac{n+1}{n}.
\end{aligned} \tag{A6}$$

We note that, as stated in the text, the ground state correction for Case I is identical to that for Case II. For the first excited state of Case 1, we have

$$\begin{aligned}
\text{Case I : } E_1^{(1)} &= 2 \sum_{k=1}^{\frac{n-1}{2}} \epsilon_k^{(1)} + \epsilon_{\frac{n+3}{2}}^{(1)} \\
&= 2 \left( \frac{n+1}{2} \right) \frac{1}{2} \frac{\alpha V_0}{nd} (-2) + \frac{\alpha V_0}{nd} (-2) \\
&= -\frac{\alpha V_0}{d} \frac{n+3}{n}.
\end{aligned} \tag{A7}$$

For Case II we have

$$\begin{aligned}
\text{Case II : } E_1^{(1)} &= 2 \sum_{k=1}^{\frac{n-1}{2}} \epsilon_k^{(1)} + \epsilon_{\frac{n+3}{2}}^{(1)} \\
&= 2 \left( \frac{n-1}{2} \right) \frac{1}{2} \frac{\alpha V_0}{nd} (-2) + 0 \\
&= -\frac{\alpha V_0}{d} \frac{n-1}{n}.
\end{aligned} \tag{A8}$$

The difference in energy at first order for Case I and II is

$$\begin{aligned}
\text{Case I : } \Delta E^{(1)} &= -\frac{\alpha V_0}{d} \left( \frac{n+3}{n} - n + 1n \right) \\
&= \frac{2\alpha V_0}{nd}
\end{aligned} \tag{A9}$$

$$\begin{aligned}
\text{Case II : } \Delta E^{(1)} &= -\frac{\alpha V_0}{d} \left( \frac{n-1}{n} - n + 1n \right) \\
&= -\frac{2\alpha V_0}{nd}
\end{aligned} \tag{A10}$$

$$\tag{A11}$$

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[1] J. Basdevant et al. , *The Quantum Mechanics Solver: How to Apply Quantum Mechanics to Modern Physics*, 2nd Ed.

(Springer-Verlag, Berlin Heidelberg 2006) *Phys. Rev.* pg. 231-35.