Chemistry 1410, Hour Exam 1, Solution Key

1) a) Appeal to the 1D Particle in the Box (PinB) model for the single electron energy levels of the pi electrons in hexatriene. Furthermore: respect the Pauli Exclusion Principle, putting no more than two (spin-paired) electrons in each single-electron spatial state. This leads to the diagram shown in *Fig. A1*, and thus the conclusion that the highest energy pi electron goes into the PinB level *n=3* when the system is in its electronic ground state configurations (electrons are packed into the lowest single-electron states possible without violating the Pauli Exclusion Principle).

b) The lowest energy transition possible would be for an electron occupying n=3 to make a transition into the (previously unoccupied) level *n=4*. Denoting E_n as the PinB energy eigenvalue corresponding to level *n*, then $\Delta E_{43} = E_4 - E_3$ is the increase in electronic energy incurred when an electron makes the transition from $n = 3 \rightarrow n = 4$. This energy has to supplied by the absorbed photon, i.e., $E_{ph} = \Delta E_{43}$.

Recall that for an electron moving in a 1D PinB, $E_n = \frac{h^2}{8m_e L^2}$, where m_e is the electron mass and L is the effective box length. Using the same arguments used for butadiene (cf. Fig. 1 on the exam) and octatetraene (see class notes), we arrive at the approximation for all-trans hexatriene (with *6* carbon atoms) that $L \cong 6R$, with R being the effective average C-C bond length: cf. Fig. A2. Now we can calculate:

$$E_{ph} = \Delta E_{43} = \frac{h^2}{8m_e(6R)^2}[4^2 - 3^2] = \frac{7}{36}\frac{h^2}{8m_e R^2}$$

Thus: $\alpha = 7/36 \cong 0.194$.

c) Since $\frac{h^2}{8m_e R^2}$ =1.6x10^{5}cm^{-1}, then the absorbed photon energy is $E_{ph} = \frac{7}{36} \cdot 1.6\times10^5\, cm^{-1} = 3.1\times10^4\, cm^{-1}$. This corresponds to a wavelength of $[3.1\times10^4]^{-1} cm = 3.23\times10^{-5} cm = 3,233$ Å.

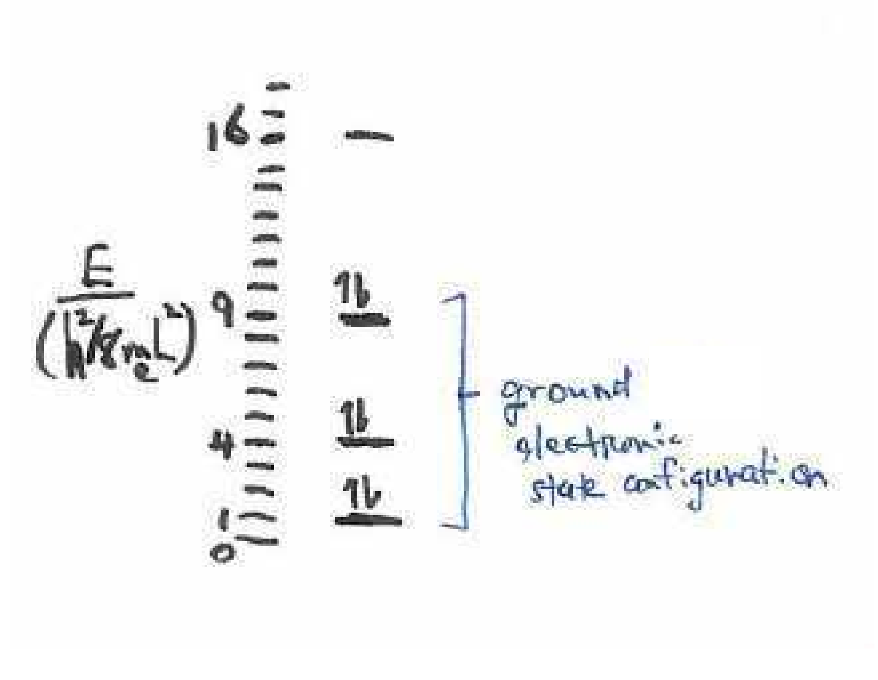


Fig. A1. Ground electronic state configuration for all-trans hexatriene, assuming a 1D Particle in a Box model for the single electron states.

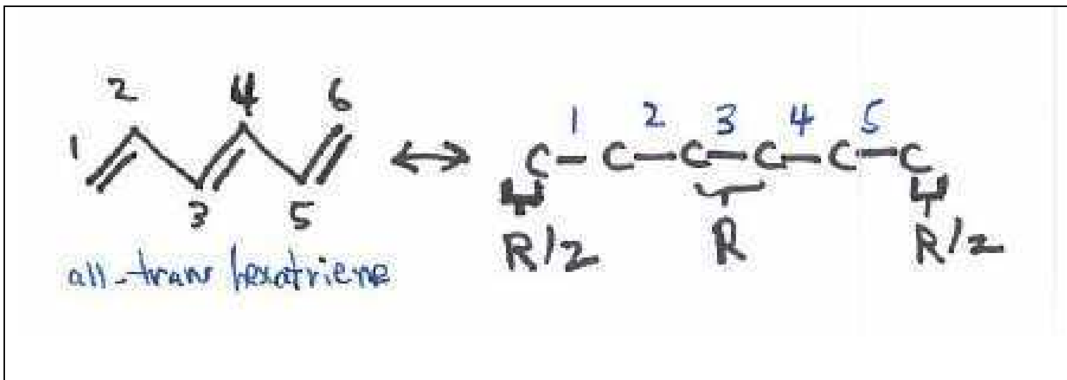
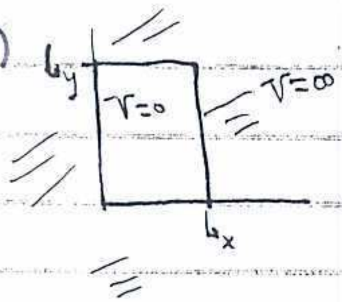


Fig. A2. Mapping the all-trans hexatriene molecule to a 1D Particle in a Box: determining the box length L=5R + 2(R/2) = 6R.

2)



Hamiltonian is: $\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)$

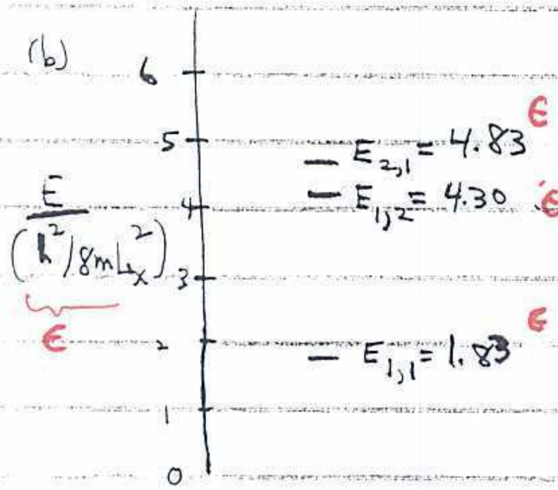
Boundary Conditions are: $\psi(x,y) = 0$ at box edges

So... (i) is an eigenfunction, corresponding to $E = \frac{h^2}{8m}\left[\frac{1}{L_x^2} + \frac{9}{L_y^2}\right]$

(ii) is not an eigenfunction, since ψ does not vanish along upper edge if $L_x \neq L_y$, as assumed.

(iii) is not " " , " " " " " at either left or right edge.

(b)



} NB: $E_{2,1} \neq E_{2,1}$; degeneracy is "lifted" by symmetry breakdown

[Generally: $E_{n_x,n_y} = \frac{h^2}{8mL_x^2}\left(\frac{n_x^2}{1^2} + \frac{n_y^2}{(1.1)^2}\right)$

$= (n_x^2 + 0.83\, n_y^2)\,\epsilon$]

3) a) For a generic 1D harmonic oscillator characterized by mass *m* and force constant *k*, the allowed energy eigenvalues are given by $E_n = (n + \frac{1}{2})\hbar\omega$, *n=0,1,2,...*, with $\omega \equiv \sqrt{k/m}$. The energy of the 2nd excited state thus corresponds to n=2, or $E_2 = \frac{5}{2}\hbar\omega$.

b) From the class notes (or Engel textbook), the energy eigenfunction corresponding to E_2 is

$$\psi_2(x) = \frac{1}{2\sqrt{2}}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4} H_2\left(\sqrt{\frac{m\omega}{\hbar}}x\right)\exp\left\{-\frac{m\omega}{2\hbar}x^2\right\}$$

with Hermite polynomial $H_2(y) \equiv 4y^2 - 2$.

A sketch is provided in Fig. A3. [Note the following properties: i) $\psi_2(x)$ is even about *x=0*; ii) $\psi_2(x) \to 0$ as $x \to \pm\infty$.]

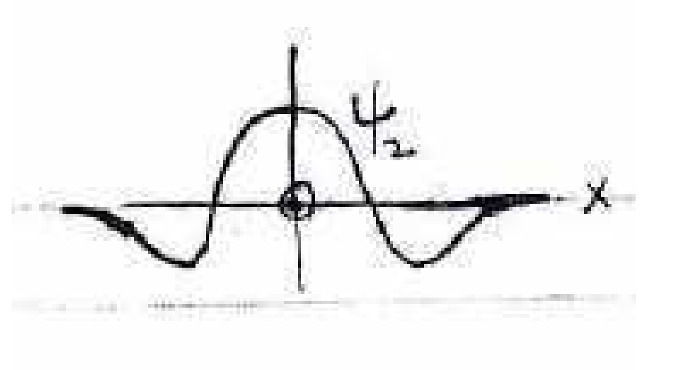


Fig. A3: sketch of $\psi_2(x)$.

c)

i) Let $a_0 = 0.775, a_1 = 0.5, a_2 = -0.387$. Then:

$$\int_{-\infty}^{\infty} dx\psi^*(x)\psi(x) = \int_{-\infty}^{\infty} dx\left(a_0\varphi_0 + a_1\varphi_1 + a_2\varphi_2\right)^*\left(a_0\varphi_0 + a_1\varphi_1 + a_2\varphi_2\right)$$

$$= \int_{-\infty}^{\infty} dx\left(a_0\varphi_0 + a_1\varphi_1 + a_2\varphi_2\right)\left(a_0\varphi_0 + a_1\varphi_1 + a_2\varphi_2\right) \quad , \quad \text{[A1]}$$

where the second line follows from the first because the coefficients a_j and the energy eigenfunctions $\varphi_j(x)$ are real-valued. Note next that $\int_{-\infty}^{\infty} dx\varphi_j(x)\varphi_k(x) = 0$ for $j \neq k$, because the energy eigenfunctions are orthogonal, and that $\int_{-\infty}^{\infty} dx\varphi_k(x)\varphi_k(x) = 1$ for $k = 0,1,2$, since these eigenfunctions are stated to be "normalized". Thus, all the integrals in Eq. (A1) can easily be performed, with the result that:

$$\int_{-\infty}^{\infty} dx\psi^*(x)\psi(x) = \sum_{j=0}^{2} a_j^{\;2} = .775^2 + .5^2 + .387^2 = 1$$

QED.

ii) The probability P_n that a measurement of energy yields E_n is given by a_n^2. In particular, $P_1 = 0.5^2 = 0.25$.

iii) $< E >= \sum_{n=0}^{2} a_n^{\;2} E_n = 1.05\hbar\omega$.